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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS WITH MORE THAN FOUR RINGS IN CRUDE OILS ON A RP-18 COLUMN

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SUMMARY

The hydrocarbon fraction in crude oils has been separated from Asphaltenes on a RP-18 column. The hydrocarbons were subsequently fractionated on an aluminium oxide micro-column, yielding an homogeneous fraction of polycyclic aromatic hydrocarbons with more than four rings. The method was applied to crude oils from different geographical areas. The limits of application of the method, related to the percentage of Asphaltenes in crude oils, are discussed.

INTRODUCTION

The identification and determination of primary pollutants are the main aims in the analysis of complex organic matrices, such as crude oils, fuel oils, etc. Polycyclic aromatic hydrocarbons (PAHs) with more than four rings are an important part of this group[1-5].

In the analysis of such compounds it is necessary to use pre-separation procedures to obtain homogeneous hydrocarbon fractions separated from non-hydrocarbon compounds, which such as Asphaltenes[6]. The presence of Asphaltenes may cause problems, such as saturation of the stationary phase of the chromatographic column, changing its physical properties. In this way, absorption problems and/or non-reproducibility of the results may occur, as well as contamination of the hydrocarbon fraction.

This separation is quite difficult, because Asphaltenes are not a homogeneous class, but are identified by their insolubility in aliphatic solvents and their solubility in aromatic ones. Their chemical composition is very complex, as they contain organic compounds with condensed rings[7,8], short aliphatic chains[9-11], heteroatoms[12-16] and metals[17,18]. There are several methods for the elimination of Asphaltenes, such as extraction with organic solvents (ASTM D893,BS 200 part. 143/85, IP 143/84) and chromatographic techniques (API-60, SARA)[12,19-21]. All of these procedures have some disadvantages[21]: the amount of solvents used, lengthy analysis time and difficulties in obtaining reproducible fractions for the subsequent separation into homogeneous classes[12,21-23].

In this work we studied the possibility of separating hydrocarbons from Asphaltenes in crude oils, and of obtaining an homogeneous fraction of PAHs having more than four rings, by using a RP-18 micro-column.

EXPERIMENTAL

Reagents and materials
        Crude oils from the Middle East, Africa, Russia and South America were used: Arabian Light (LA) (Saudi Arabia), Dubay (DU) (Dubay), Qatar Marine off-shore (QM) (Qatar), Emeraude (EM) (Zaire), Mandji (MA) (Gabon), Es Sider Oasis (LI) (Libya), Ural (RU) (Russia), Tia Juana (TJ) (Venezuela). The samples were stored in the dark at 5°C.
        The stationary phases for column chromatography were LiChroprep RP-18 (Merck) and aluminium oxide Type E (activity I) (Merck). The latter was maintained at 130°C for 12 h before use. These supports were dry-packed in glass columns.
        n-Pentane (spectroscopy), *n*-hexane (pesticide), toluene (Lichrosolv), carbon tetrachloride (analysis), all purchased from Merck, and dichloromethane (Chromasolv, Riedel) were used.

Fractionation of crude oils on RP-18 micro-column
        A 0.1-ml volume of a solution containing 500 mg of crude oil per millilitre of carbon tetrachloride was fractionated on an RP-18 micro-column (9 cm × 0.6 cm) filled with 1.3 g of stationary phase after treatment of the with 20 ml of *n*-hexane. The elution was carried out with 3.5 ml of *n*-hexane and then with 10 ml of toluene, after drying the column under nitrogen.

Fractionation of standard hydrocarbons on RP-18 micro-column
        The RP-18 column employed was the same as described above. The standard hydrocarbons were dissolved in carbon tetrachloride (concentration 1 mg/ml) and the solutions stored in the dark. Part of the solution (30 μl) was placed onto the column which was then eluted with *n*-hexane, 100-μl fractions being collected for gas chromatographic (GC) analysis.

Isolation of PAHs with more than four rings
        The same RP-18 micro-column and an aluminium oxide one (11 cm × 0.6 cm) treated with 20 ml of *n*-pentane were used for a two-step fractionation. The elution scheme is shown in Fig. 1. Eluents: (a) 2.5 ml of *n*-hexane; (b) 2.5 ml of *n*-hexane; (c) 7 ml of *n*-pentane–dichloromethane (6:4, v/v); (d) 3 ml of dichloromethane. The PAH fraction was evaporated to 0.1 ml under nitrogen[24].

Extraction
        A 500-mg sample was directly weighed in a flask and refluxed with 100 ml of *n*-hexane for 1 h. After cooling, the suspension was filtered on Millipore 0.45-μm filters, and the residue dried in a vacuum. The solution was then analyzed by UV spectrophotometry and the dry residue weighed. The residue was then dissolved in 100 ml of toluene and the solution analyzed by UV spectrophotometry.
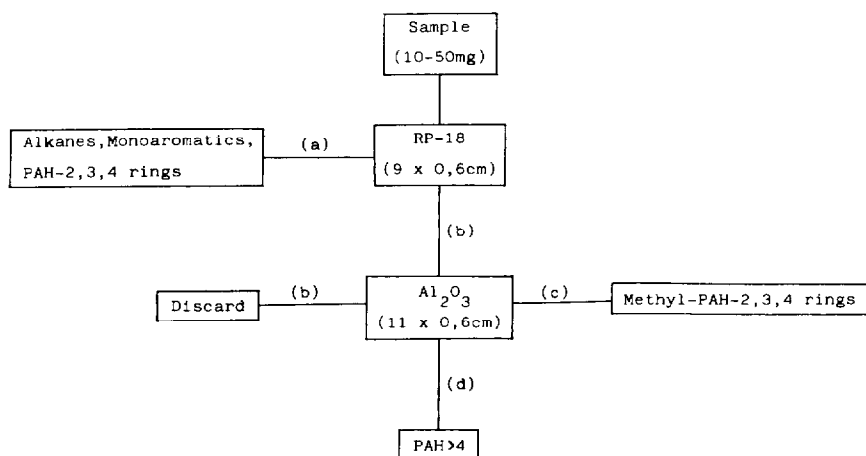
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                              ┌──────────────┐
                              │   Sample     │
                              │  (10-50mg)   │
                              └──────┬───────┘
                                     │
┌─────────────────────────┐  (a)  ┌──┴───────┐
│ Alkanes,Monoaromatics,  ├───────┤  RP-18   │
│ PAH-2,3,4 rings         │       │(9 x 0,6cm)│
└─────────────────────────┘       └──┬───────┘
                                     │ (b)
                                     │
┌──────────┐  (b)  ┌─────────┐  (c)  ┌─────────────────────┐
│ Discard  ├───────┤  Al₂O₃  ├───────┤ Methyl-PAH-2,3,4 rings │
└──────────┘       │(11 x 0,6cm)│    └─────────────────────┘
                   └────┬────┘
                        │ (d)
                   ┌────┴────┐
                   │ PAH >4  │
                   └─────────┘
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Fig. 1. Separation scheme. Eluents: (a) 2.5 ml of *n*-hexane; (b) 2.5 ml of *n*-hexane; (c) 7 ml of *n*-pentane–dichloromethane (6:4); (d) 9 ml of dichloromethane.

Apparatus

A UV–VIS spectrometer Model 552 S (Perkin-Elmer) was used. The spectra were registered in the 200–400 nm region.

An HRGC-5160 Mega series gas chromatograph (Carlo Erba) with flame ionization detection (FID) was used, together with a computer system Mega-2 (Shimadzu). Standards were determined with the "on-column" technique, by using a glass capillary column with a "retention gap" (25 m × 0.32 mm I.D., film thickness 0.15 μm) (Mega-Carlo Erba). Chromatographic conditions: 50°C for 1 min, linear increase of 8°C/min to 300°C; carrier gas hydrogen. Crude oil fractions were analyzed by the "splitless" technique, with a 20 ml/min head flow and silica capillary column SPB-5 (30 m × 0.25 mm I.D. film thickness 0.25 μm) (Supelco). Chromatographic conditions: injector temperature 270°C; initial temperature 50°C, then increase at 5°C/min to 300°C; carrier gas, hydrogen.

Gas chromatographic–mass spectrometric (GC–MS) analyses were performed with a spectrometer Model VG 7070 EQ (VG Analytical), under the following conditions: acceleration voltage 6 kV; source current 100 μA; ionizing voltage 70 eV.

RESULTS AND DISCUSSION

Isolation and fractionation of hydrocarbons in crude oils on RP-18 micro-column

Crude oils from different geographical (see Experimental) areas were examined to determine the reliability of results for different samples. Small amounts of crude oil (50 mg) were applied to a RP-18 micro-column to obtain a fast and reproducible fractionation with small volumes of eluents. For the elution of the hydrocarbon fraction 3.5 ml of *n*-hexane were used. Tests on a standard hydrocarbon mixture on the same micro-column showed that all hydrocarbons examined (*n*-paraffins, alkyl-benzenes, PAHs) are eluted with this solvent volume (see Fig. 2). PAHs were eluted differently on the basis of their aromatic rings; those with the highest number of rings having the highest retention volumes. In particular, it was possible to obtain an
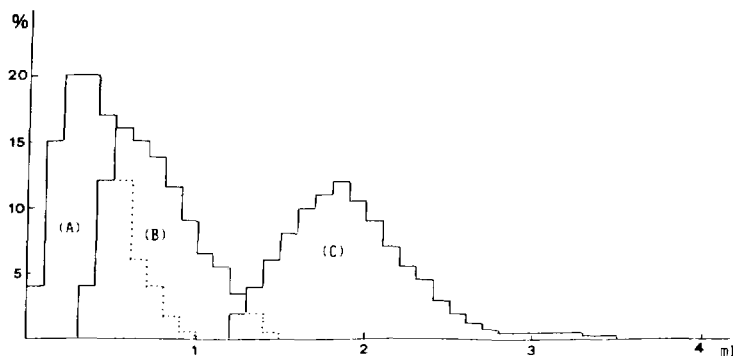
Fig. 2. Fractionation of a hydrocarbon standard mixture with 3.5 ml of *n*-hexane. Column: 9 cm × 0.6 cm I.D. packed with 1.3 g of LiChroprep RP-18. Abscissa: elution volumes of *n*-hexane from the RP-18 micro-column. Ordinate: percentage of elution for (A) *n*-paraffins, alkylbenzenes, PAH with two rings; (B) PAHs with three or four rings; (C) PAHs with greater then four rings.

homogeneous fraction of PAHs having greater than four rings without *n*-paraffins, monoaromatic and other polycyclic hydrocarbons, which constitute the main part of the hydrocarbon fraction of crude oils, and which are eluted in the first millilitre of solvent. Such a separation, in a short time (5 min) and in small volumes of solvent, was difficult to obtain on silica[25]. The recovery for all hydrocarbons was practically quantitative, as shown in Table I, where the percentage recovery and the standard deviation relative to five measurements are reported.

It is important to note that the elution profile of Fig. 2 was maintained in crude oil fractionation. The only difference concerned the composition of fraction C, which contained some residual methylnaphthalenes, methyl-substituted chrysenes and yellow-brown compounds (resins) strongly retained on silica and aluminium oxide columns[26]. Fraction C did not contain aliphatic, monoaromatic compounds and the greater part of polycyclic compounds with two to four rings. Furthermore, *n*-hexane-insoluble compounds remained on the column.

As regards the retention mechanism on this column, it is important to note the increase in retention volumes from *n*-decylbenzenes to toluene, as shown in Table I, where alkylbenzenes are reported in their order of elution. Xylenes are the most strongly retained compounds, owing to their higher electron density. Analogous behaviour has been reported for the same compounds on silica columns[27], and shows that, under the present experimental conditions, RP-18 behaves as a polar stationary phase. The retention of hydrocarbons is therefore due to the free silanol groups on the surface of the silanized silica[28–30].

Isolation of PAHs with more than four rings

This hydrocarbon fraction, which has already been used in "fingerprinting" of crude oils[25], is one of the most important from an analytical and environmental point of view. As stated above, RP-18 is suitable for a first isolation step, even if it is not possible to obtain a sufficiently homogeneous PAH fraction for analysis. This can be achieved by a two-step fractionation (see Fig. 1), using a second micro-column of aluminium oxide. The choice of this stationary phase is based upon its class frac-

TABLE I

RECOVERY OF HYDROCARBONS FROM THE RP-18 MICRO-COLUMN

Hydrocarbon	Recovery (%)	S.D. (%)
n-C_8	93	4
n-C_9	93	6
n-C_{10}	92	6
n-C_{12}	92	5
n-C_{14}	98	7
n-C_{16}	95	5
n-C_{20}	95	6
n-C_{22}	93	6
n-C_{24}	93	7
n-C_{28}	95	5
n-C_{30}	96	5
n-C_{32}	95	6
n-C_{36}	93	5
Decylbenzene	91	6
Octylbenzene	95	5
p-Cymene	92	6
Hexylbenzene	93	6
Mesitylene	91	6
Butylbenzene	95	4
Cumene	97	4
Propylbenzene	96	5
Ethylbenzene	95	4
o-Xylene	93	4
m-/p-Xylene	95	4
Toluene	92	6
Naphthalene	93	6
1-Merhylnaphthalene	94	7
Acenaphthylene	93	5
Acenaphthene	91	6
Fluorene	92	6
Phenanthrene	90	6
Anthracene	90	7
Fluoranthene	92	7
Pyrene	93	5
Chrysene	95	6
Benzo[a]pyrene	92	5
Perylene	97	5
Dibenz[ah]anthracene	95	5
Benzo[ghi]perylene	97	5
1,2-4,5-Dibenzopyrene	93	5
3,4-8,9-Dibenzopyrene	95	5

tionation power for PAH, with eluents of increasing and definite $\varepsilon°$ (the solvent strength parameter in liquid–solid chromatography)[24,26,31–33]. The second 2.5 ml portion of n-hexane (b) used for the elution of the PAH fraction on RP-18 was passed through an aluminium oxide column and then discarded; in the next 7 ml of n-pentane–dichloromethane (6:4) the majority of methyl-substituted PAHs with two
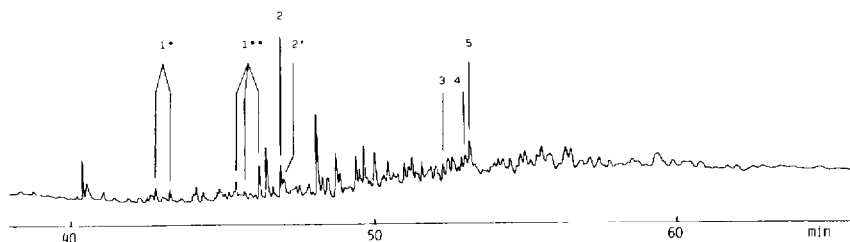
Fig. 3. Gas chromatogram of PAH fraction having greater then four rings for LA crude. Peaks: 1* and 1** = methylchrysenes; 2 = benzo[e]pyrene; 2' = benzo[a]pyrene; 3 = indeno[1,2,3-cd]pyrene; 4 = picene; 5 = benzo[ghi]perylene.

to four rings were also eliminated, and in 3 ml of dichloromethane it was possible to obtain an homogeneous greater than four-ring fraction, containing only traces of residual methyl-PAHs with four rings.

GC[34]/GC–MS[35,36] analysis confirms the homogeneity of this fraction (see Fig. 3); the very low concentration of methylchrysenes (1*, 1**) is of particular interest. Some other components of the mixtures were identified as benzopyrenes, indeno-pyrenes, picenes and corresponding methyl derivatives, together with some polycyclic compounds containing sulphur. Fig. 3 shows the gas chromatogram of some compounds whose identification is important for their carcinogenic properties: benzo-[e]pyrene (2); benzo[a]pyrene (2'); indeno[1,2,3-cd]pyrene (3); picene (4); benzo-[ghi]perylene (5). It should be noted that with this new fractionation method it is possible to enrich the PAH fraction. The maximum capacity of the method is normally 50 mg of crude, but when the percentage of Asphaltenes is low it is possible to analyze up to 100 mg of sample without altering the PAH fraction. In this way the sensitivity of the method is increased 5–10 times with respect to other methods that do not use deasphaltening procedures.

These results are of great analytical interest, because with the micro-fractionation method it is possible to save time by eliminating tedious extraction methods and also the formation of micelles[13], artefacts and loss of volatile hydrocarbons such as methyl-substituted benzenes and naphthalenes, due to heating. It is important to note that there was a high recovery, as shown in Table II, where the percentage of PAHs with greater then four rings is given for the most critical conditions (evaporation to 0.05 ml).

TABLE II

RECOVERY OF PAHs WITH MORE THAN FOUR RINGS

The recoveries are average values from five determinations.

Hydrocarbon	Recovery (%)	S.D. (%)
Benzo[a]pyrene	90	5
Perylene	97	5
Dibenz[ah]anthracene	93	6
Benzo[ghi]perylene	97	6
Coronene	93	6
1,2-4,5-Dibenzopyrene	90	5
3,4-8,9-Dibenzopyrene	90	6

TABLE III

COMPARISON BETWEEN CHROMATOGRAPHIC AND EXTRACTION METHODS

Crude oil	Asphaltenes (%)	
	Chromatography*	Extraction
TJ	5.7	6.8
LA	3	2.8
EM	2.9	3.2
RU	2	1.6

* The measurements were performed on 500 mg of sample by using a column (11 cm × 1 cm) filled with 5.7 g of RP-18.

This important family of environmental compounds contains highly oxidizable components[37-39], such as benzo- and dibenzopyrenes. With this method is it possible to identify such compounds in complex mixtures, without changing their composition, even when they are present at trace levels.

Fractionation of the crude oil portion remaining on the column after elution with n-hexane

Elution of the crude oil portion insoluble in *n*-hexane was achieved with toluene. The content of this fraction was analyzed by UV spectroscopy and gravimetric measurements on the residue obtained by evaporating the solvent. The results were compared with those obtained with the usual extraction methods (see Experimental) for the following samples: TJ (South America), LA (Middle East), EM (Africa), RU (Russia).

As shown in Table III there is good agreement between the two series of results. Furthermore the UV spectra of the toluene fractions, obtained with the two above-mentioned techniques, were similar, with differences only in the maximum of absorption at 287 nm. Such data confirm the presence of Asphaltenes in these fractions. Finally, there is a direct relationship between the absorbance values and the percentages of Asphaltenes determined gravimetrically.

Loading experiments carried out on RP-18 columns containing different amounts of stationary phase showed that the maximum operating limit was 3 mg of Asphaltenes per gram of RP-18. Above this limit the hydrocarbon fraction was contaminated by Asphaltenes. In the case of TJ crude oil, which has a high percentage of Asphaltenes (see Table III), it would be necessary to use an RP-18 column with a larger amount of stationary phase. By using the above-mentioned micro-column, the *n*-hexane fraction contains some Asphaltenes, and it was necessary to pass it through 0.45-μm filters to eliminate those compounds.

In conclusion, the measurements of the absorption maximum at 287 nm of the toluene fraction obtained from the RP-18 micro-column indicate the percentage of Asphaltenes in a crude oil. It is thus possible to evaluate the maximum quantity of sample for chromatographic separations, or for its characterization for industrial processing[36,40].

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