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Distribution of Polycyclic Aromatic Sulfur Heterocycles in Three Saudi Arabian Crude Oils as Determined by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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The distribution pattern of polycyclic sulfur aromatics was established in three Saudi Arabian crude oils using a combination of liquid chromatography on a bonded Pd(II) phase and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The highest double bond equivalent (DBE) measured was 17 for the Arabian heavy crude oil and 14 for both Arabian medium and Arabian light crudes. The high DBE number indicates the presence of a large variety of parent ring systems; knowledge of them is important in the characterization of crudes with respect to their processing properties. A higher sulfur concentration was correlated with more alkyl carbons in the aromatic compounds and with a higher DBE. A representation of the mass spectral data in a pseudogram, a form that resembles a chromatogram, is introduced to facilitate the quick visual inspection and comparison of the mass spectral data.

Introduction

Due to the increasingly rare availability of low-sulfur crude oils, high-sulfur crudes are gaining ground for the production of low-sulfur fuels. Refineries can achieve this only through efficient desulfurization processes that lower the sulfur content to below the legal limits regulating transportation and heating fuels in many countries. Although many processes have been suggested and tested for desulfurization purposes, in practice, hydrodesulfurization (HDS), involving elevated temperatures and hydrogen pressures in the presence of, typically, Ni/Mo and/or Co/Mo catalysts, is the generally used process. Although it is quite effective for low-boiling and middle distillates such as gas oils, it has not yet been shown to operate as efficiently for high-boiling fractions like vacuum gas oils (VGO) or vacuum residues.¹

The reasons for this are at present not fully understood, but one hypothesis is that molecular characteristics influence the ease of removal of the sulfur. The polycyclic aromatic sulfur heterocycles (PASHs) are known to be a major chemical class of sulfur-containing compounds in crudes, and as the sulfur concentration usually goes up with the boiling range of the distillation fractions, it can be expected that the PASHs are predominant species in fractions of higher boiling points. Among the molecular characteristics that may have an influence on the ease of desulfurization are, in analogy to the known reactivity of more volatile compounds, the parent aromatic structures and the respective positions of alkyl groups. Using standard

compounds, it has been established that the resistance to hydrodesulfurization increases in the following order: thiophenes < benzothiophenes < benzonaphthothiophenes < tetrahydrobenzonaphthothiophenes < dibenzothiophenes.² A more recent investigation on VGO extended the observations to include a finer gradation in the difficulty of hydrodesulfurization as follows: nonaromatic sulfides < thiophenes ~ benzothiophenes ≪ catacondensed (“extended”) five-ring thiophenes ~ six-ring thiophenes < benzonaphthothiophenes ~ pericondensed (“compact”) five-ring thiophenes < C₀/C₁-dibenzothiophenes < C₂₊-dibenzothiophenes < (pericondensed) phenanthrothiophenes.³

It has also been reported that it is evident that the alkylation pattern has an influence on the resistance to HDS. Thus among the dibenzothiophenes of middle distillates, substituents in the 4 and/or 6 positions confer a high degree of stability to the compounds under HDS conditions and these accumulate in the desulfurized product.^{4–6} Recently, it was also noted that a methyl group in the 1 position of dibenzothiophene can have a similar effect.⁷ Structural studies of the PASHs present in a crude oil

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may therefore lead to information on its resistance to HDS and on the conditions needed for a successful process.

The classically preferred analytical technique for the characterization of PASHs in petroleum fractions has long been high-resolution gas chromatography (GC) because of the high-resolution capabilities with capillary columns and because of the presence of several sulfur-selective detectors on the market.⁸ The recent development of two-dimensional GC has further underlined this unrivaled position, especially since selective detectors have been shown to be capable of being linked to a GC \times GC system.⁹ However, the inherent weakness of GC is that only volatile compounds can be analyzed which means that aromatic compounds with a molar mass not much above 300 can be analyzed with a reasonable degree of accuracy. In a VGO with a boiling range of 340–530 °C, up to C₅-benzonaphthothiophenes (BNTs) could be detected as weak signals by GC.¹⁰ By contrast, in a VGO of somewhat lower boiling range,¹¹ up to C₁₂-BNT can be easily detected by mass spectrometry. For whole crudes, where the molar masses of PASHs can reach over 700 (see below), GC will therefore not be a choice.

Nuclear magnetic resonance (NMR) extends to the full molar mass range found in petroleum and has been used to obtain statistical information on high-boiling fossil fuels materials.¹² The information it provides includes the average number of different kinds of carbon and hydrogen atoms, for instance, the distribution of aromatic and aliphatic carbon atoms, and the distribution of the latter in different positions, like benzylic or terminal methyl positions. Although useful, it does not help much in establishing the distribution of sulfur on various ring systems and variation in their respective individual alkylation.

In recent years, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has started playing a significant role in characterizing thousands of compounds in complex crude oil samples.¹³ FT-ICR MS is favored over other MS techniques for the analysis of such ultracomplex mixtures because of its high mass resolving power and mass accuracy. Different soft ionization techniques, e.g., low-voltage electron ionization,¹⁴ electrospray ionization (ESI),¹⁵ field desorption ionization

(FDI),¹⁶ and atmospheric pressure photo-ionization (APPI)¹⁷ have been coupled to FT-ICR MS to characterize analytes without fragmentation. However, in the case of low-voltage electron ionization, its use is restricted to fairly volatile compounds.¹⁸ On the other hand, ESI and FDI are not suitable for relatively nonpolar aromatic compounds, such as PASHs. Recently, APPI has been used for the speciation of sulfur compounds in petroleum fractions, but the simultaneous production of protonated molecules, deprotonated molecules, and molecular ion radicals in the ionization source complicates its use for compositional assignments.¹⁷ Since none of the ionization techniques is highly suitable for the ionization of PASHs, we introduced the methylation of thiophenic compounds as a derivatization technique which converts the neutral thiophenes into ions in solution that can be easily transferred into the gas phase in the ESI source.¹⁹ This technique is also selective for sulfur heterocycles in the presence of an overwhelming amount of sulfur-free aromatic hydrocarbons which are left in the neutral state, thus lowering their ion concentration in the ICR instrument. This approach has made it possible to investigate the high molecular weight sulfur aromatics in a vacuum residue¹⁹ and in VGOs.¹¹

In the present work, the PASHs in three Arabian crude oils of different API gravities and sulfur levels, namely, Arabian heavy, Arabian medium, and Arabian light, are investigated by FT-ICR MS. The aim is to gain information that will allow a comparison of the distribution pattern of sulfur heterocycles in such different oils with respect to their parent ring systems and the number of alkyl carbon atoms associated with them. One goal is to explore the analytical methods that may be suitable for the identification of sulfur compounds in individual oils before and after a desulfurization process²⁰ to determine the extent of the desulfurization process in order to retune the desulfurization method accordingly.

Experimental Section

Three Arabian crude oils—Arabian heavy (AH), Arabian medium (AM), and Arabian light (AL)—were provided by Saudi Aramco, Saudi Arabia. The sulfur content and API gravity of AH, AM, and AL were 2.9, 2.5, and 1.8 wt %, and 27, 29, and 32, respectively. The sulfur content was measured on an ANTEK 9000 pyro-fluorescence sulfur analyzer (ANTEK Instruments, Düsseldorf, Germany) using the ASTM D-5453 method. Sigma-Aldrich (Taufkirchen, Germany) provided chemicals and HPLC grade solvents.

The aromatic fractions from the oils were isolated by a dual-packed (silica and alumina) open tubular column. The column was

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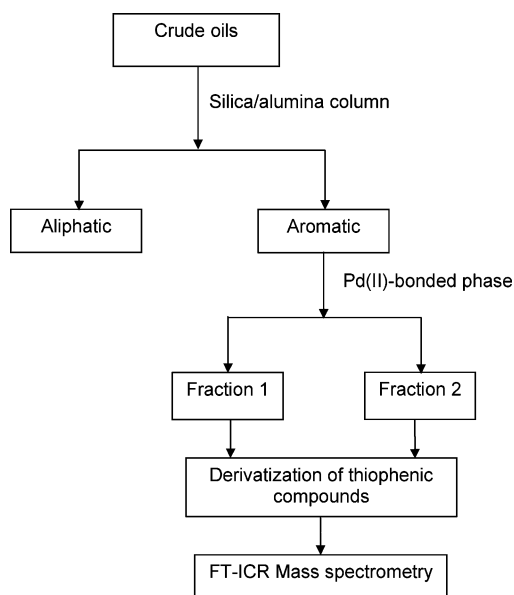


Figure 1. Analysis scheme of sulfur aromatics in crude oils as used in this work.

filled with 20 g of silica gel and 35 g of alumina (both were activated at 180 °C for 16 h separately). The aliphatic fraction was eluted with 120 mL of *n*-heptane whereas the aromatics were isolated with 360 mL of a mixture of *n*-heptane and toluene (2:1). The detailed analysis scheme is presented in Figure 1.

Ligand Exchange Chromatography. A Pd(II)-bonded silica phase was synthesized based on 10 μ m LiChrosorb Si 100 (Merck, Darmstadt, Germany) as described in the literature.^{21–23} The bonded silica gel was packed into a stainless steel column (250 mm \times 8 mm) using the slurry method with methanol as fluid. About 50 mg of the aromatic fraction from each crude oil was separated on the Pd(II)-bonded phase into two fractions. The first fraction (Pd-1) was eluted with cyclohexane:dichloromethane (7:3 v/v) over a period of 15 min, and the second fraction (Pd-2) was eluted after the addition of 0.5% isopropanol to the previous mobile phase. The flow rate was maintained at 3 mL/min throughout the separation.

Derivatization of Thiophenic Compounds. To each fraction, Pd-1 and Pd-2, was added 50 μ L of methyl iodide and 40 mg of silver tetrafluoroborate in 3 mL of 1,2-dichloroethane (DCE). The mixture was allowed to react at room temperature for 48 h to ensure complete methylation of all the sulfur compounds. Then, the filtrate was collected and the solvent evaporated by a stream of nitrogen flow to obtain the methyl thiophenium salts.¹⁹

FT-ICR Mass Spectrometry. Mass spectra were acquired using an APEX III Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a 7 T actively shielded superconducting magnet and an Agilent ESI source. The thiophenium salts were dissolved in a 1:1 (v/v) solution of dichloromethane/acetonitrile and injected in the infusion mode with a flow rate of 2 μ L/min detecting positive ions. The spray voltage was maintained at 4.5 kV. The ions were accumulated for 0.4 s in the octapole before transfer to the cyclotron cell. For a better signal-to-noise ratio, at least 64 scans were accumulated. Internal and external calibrations were done using a mixture of the Agilent electrospray calibration solution with the masses 622.028 96

and 922.009 80 and with the addition of indolacrylic acid with the masses 397.115 89 [$2M + Na$]⁺ and 584.17923 [$3M + Na$]⁺ covering the whole range of masses in the samples.

Data Analysis. All the masses obtained from the FT-ICR mass measurements were imported into an Excel spreadsheet. Each mass corresponds to the methylated form of a parent molecule since there were no observable signals from nonmethylated compounds under the conditions used. In order to assign an elemental composition of each original component, all the masses obtained as [$M + CH_3$]⁺ were converted to neutral masses by subtracting 15.022 93 from the measured masses. Then, IUPAC masses were converted to the Kendrick mass scale in the following way:²⁴

$$\text{Kendrick mass} = \text{IUPAC mass} \times (14.000\ 00/14.015\ 65)$$

Kendrick mass defect (KMD) = Kendrick nominal mass

(KNM) – Kendrick exact mass

The Kendrick nominal mass is obtained by rounding the Kendrick exact mass to the nearest integer. In this study, the masses were separated into different homologues by their nominal masses and Kendrick mass defect following a multiple sorting procedure reported elsewhere.²⁵ For simplicity, we have consistently used the DBE (double bond equivalent) concept in place of KMDs in this work. The DBE always represents the sum of the total number of rings and double bonds present in a compound and is calculated from the elemental formula obtained from the exact mass measurement.

Generation of Pseudograms. The individual peaks in the pseudograms were generated by the data obtained using the following Gaussian function in an Excel spreadsheet:

$$y(x) = a \cdot \exp(-((x - b)/c)^2)$$

where *a*, *b*, and *c* represent the relative abundance of the mass of interest, this particular mass, and the selected standard deviation, respectively.

Results and Discussion

The first step toward characterization of sulfur aromatics in petroleum is the isolation of the nonpolar aromatic fraction using a traditional adsorption chromatography. The subsequent separation of the aromatic fraction into two well-defined subfractions: fraction Pd-1 and fraction Pd-2 is performed using ligand exchange chromatography on a Pd(II)-containing stationary phase as shown in Figure 2. We reported earlier²⁶ that fraction Pd-1 contains all polycyclic aromatic hydrocarbons (PAH) together with thiophenes attached to aromatic rings in a noncondensed fashion, e.g., as phenylthiophenes, whereas fraction Pd-2 contains thiophenes attached to aromatic rings in a condensed way like benzothiophene and higher homologues.

After methylation at the sulfur atom, the derivatized sulfur compounds produced were investigated by FT-ICR MS. Subsequently, we assign elemental compositions to all compounds containing one sulfur atom based on the exact masses obtained. Due to the complexity of the sample, it is practically impossible to extract any information from the mass spectra without transforming the masses to the Kendrick mass scale. This was carried out based on the mass spectra of the condensed thiophenes from all three samples (shown in Figure 3).

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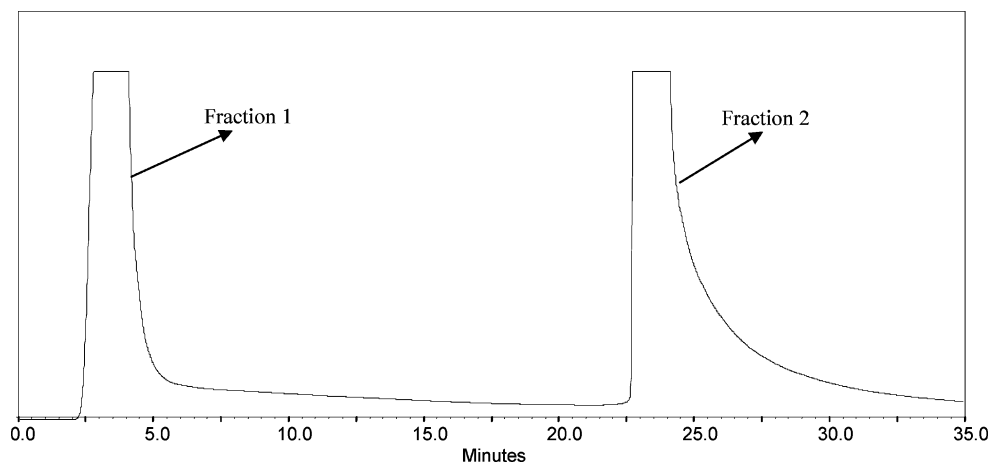


Figure 2. Fractionation on Pd(II)-bonded phase of the aromatic fraction from crude oils: (conditions) column dimension 250 mm \times 8 mm; solvent a mixture of cyclohexane and dichloromethane (7:3 v/v) for 15 min, then the same solvent mixture with added 0.5% isopropanol; flow rate 3 mL/min; UV detection at 254 nm.

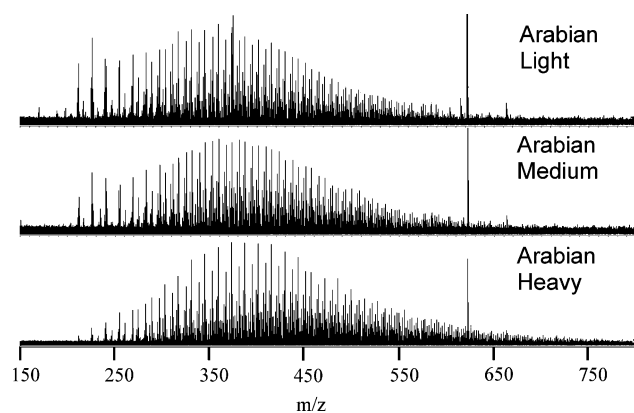


Figure 3. ESI FT-ICR mass spectra of condensed thiophenes in the three Arabian crude oils (fraction Pd-2) with the calibration peak at m/z 622.

The detailed transformation procedure together with an explanation of the Kendrick mass scale and the importance of the Kendrick plot is described in the literature.²⁷ Here, for simplicity, we also make use of the DBE (double bond equivalent) concept to convey essential information about the number of rings and double bonds. The DBE is derived in a straightforward manner from the elemental composition of a compound and always represents the sum of the total number of rings and double bonds in a compound.

Of the three samples, only AH contained detectable amounts of PASHs in the fraction Pd-1. In the second fraction of all three samples, we find one-sulfur-atom-containing compounds with DBEs up to 12. It is important to note that, for the lowest DBEs, practically only one parent ring system is likely (crude oils rarely contain appreciable amounts of alkenes so that the DBE is essentially made up of the number of rings and the number of aromatic double bonds) but, for higher DBEs, several parent ring systems are a possibility. At the moment, there is no conclusive way to tell which systems are predominantly present at a certain DBE. UV spectra can be helpful,¹¹ but the presence of minor components can easily be concealed by major components.

Arabian Heavy. In Figure 3, the ICR mass spectrum of the PASHs in fraction Pd-2 of the Arabian heavy is depicted. The

corresponding Kendrick plot is reproduced in Figure 4. The sulfur aromatics in this fraction range from DBE 6 to DBE 17. As expected from the workup, this verifies that any open-chain sulfides, tetrahydrothiophenes, dihydrothiophenes, thiophenes, naphthenothiophenes, and cycloalkenothiophenes (DBE = 0–5) have been removed chromatographically.

The strong presence of benzothiophenes (DBE 6) and dibenzothiophenes (DBE 9) illustrates that these two benzologues are the most abundant types of compounds expected in a crude oil. The magnitude of the mass spectrometric signals (in the Kendrick plots, the size of the circles is a rough measure of magnitude of the signal) decreases gradually from DBE 6 to DBE 8 as can be seen in Figure 4. The next higher compound types of appreciable abundance belong to the dibenzothiophene (DBE 9) series. It should be noted that from mass spectrometric data alone it is not possible to distinguish between dibenzothiophenes and the three isomeric naphthothiophenes but in crude oils naphthothiophenes are generally found in much lower quantities than dibenzothiophenes. The abundance of compounds of higher DBEs than 9 decreases gradually up to DBE 17.

The mass range for all compounds in this sample goes from ca. 200 to 750 Da. Lighter compounds, such as dibenzothiophene (184) and the monomethyldibenzothiophenes (198), that are known to be indigenous to crude oils, are not detected here due to their loss, probably during sample preparation which involves some evaporation of higher-boiling solvents (toluene). On the other hand, DBT and the C_1 -DBTs that are lost may well be minor representatives of the dibenzothiophenes since the summed magnitude of all isomers (compounds with a common x in the formula C_x -DBTs) increases to a maximum for a certain x which in the case of DBE 9 in AH equals 15. Since there are much fewer isomers possible for low values of x , each individual isomer at such an x may show a strong abundance although the sum of them is considerably lower than the sum of the abundances of all isomers of a higher x . Thus, the summed abundance of the C_{15} -DBTs is more than three times higher than the summed abundance for the C_3 -DBTs, but it is likely that no single C_{15} -DBT would be as abundant as the individual C_3 -DBTs are.

The benzothiophene series starts at mass 204 and goes up to 708 Da, indicating the presence of C_5 - to C_{41} -benzothiophenes. Again, the lower substituted compounds (C_0 – C_4) seem to be lost during the preparation process. DBE values of 7 are probably benzothiophenes with a naphthenic ring, either condensed or substituted to the aromatic system. This series contains

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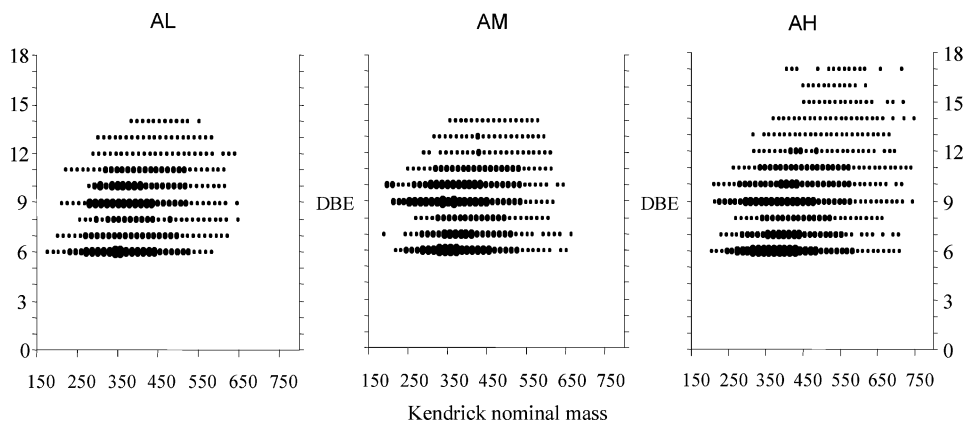


Figure 4. Kendrick plot of fraction Pd-2 from the three Arabian crude oils.

Table 1. Distribution of the Number of Alkyl Carbons at Different DBEs of Three Arabian Crude Oils^a

| typical compounds | DBE | parent mass | alkyl carbon distribution | | |
|---------------------------------|-----|-------------|---------------------------|-----------------|------|
| | | | AH | AM | AL |
| benzothiophenes | 6 | 134 | 5–41 | 6–37 | 3–32 |
| tetrahydrodibenzothiophenes | 7 | 188 | 3–37 | 0–34 | 1–31 |
| dihydrodibenzothiophenes | 8 | 186 | 6–36 | 6–30 | 5–33 |
| dibenzothiophenes | 9 | 184 | 2–40 | 2–31 | 2–33 |
| acenaphthenothiophenes | 10 | 210 | 0–36 | 0–32 | 5–29 |
| acenaphthylenothiophenes | 11 | 208 | 4–38 | 3–29 | 1–29 |
| benzonaphthothiophenes | 12 | 234 | 6–33 | 4–27 | 4–29 |
| naphthenophenanthrenothiophenes | 13 | 246 | 5–31 | 5–25 | 4–24 |
| pyrenothiophenes | 14 | 258 | 8–35 | 7–23 | 9–21 |
| chrysenothiophenes | 15 | 284 | 8–33 | nd ^b | nd |
| cholanthrenothiophenes | 16 | 296 | 11–24 | nd | nd |
| benzopyrenothiophenes | 17 | 308 | 7–32 | nd | nd |

^a The compounds mentioned in the left column are examples, not proven structures. ^b Here, nd refers to not detected.

from 3 to 37 CH₂-groups in the side chains. The next higher homologues (DBE 8) can be those of the dihydrodibenzothiophene series or benzothiophenes with two naphthenic rings containing from 6 to 36 carbon atoms as alkyl side chains. DBE 9 represents the series of dibenzothiophenes which is the most abundant series next to the benzothiophenes. Here, alkyl side chains are found with 2–40 carbon atoms. It can also be noticed that both benzothiophenes and dibenzothiophenes are not only strong in magnitude but possess the largest number of carbon atoms in the side chains.

As the DBE increases, the probability of finding isomeric parent compounds increases to a greater extent. For instance, the next higher series (DBE = 10) might consist of acenaphthenothiophenes (C₁₄H₁₀S), benzothiophenes with a phenyl group as a substituent, or dibenzothiophenes with a naphtheno ring. The compounds here contain up to 36 side alkyl carbons. Assigning carbon skeletons based on MS data alone to the compounds of higher DBEs becomes debatable because of the many possibilities. Putative structures and their alkyl carbon distributions are provided in Table 1.

We are able to find some compounds of unknown composition with one sulfur atom in fraction Pd-1. Figure 5 indicates that DBE 6 is the first and also the dominating series, followed by DBE 7. From DBE 8 to DBE 11, the number of compounds in the different series is smaller and of lower abundance. It is doubtful whether DBE 6 represents benzothiophenes, as would be the first assumption. Extensive studies on the Pd(II)-bonded

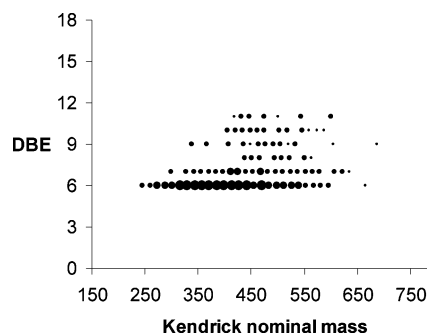


Figure 5. Kendrick plot of the Arabian heavy, fraction Pd-1.

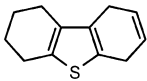
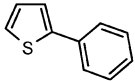
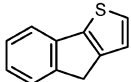
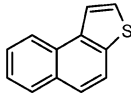
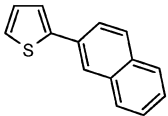
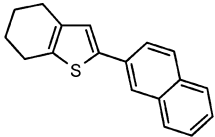
stationary phase with a variety of standard compounds showed that all benzothiophenes eluted in the second fraction.

DBE 7 can correspond to phenylthiophenes, albeit other structures are also known with this DBE that contain noncondensed thiophenes. Such thiophenes have been reported to elute in the Pd-1 fraction in our previous studies with reference compounds.²⁶ Higher DBEs, up to 11, can be presumed to represent compounds with different naphthenic rings or aromatic rings connected to a thiophene in a noncondensed way (Table 2). The case of naphtho[2,1-*b*]thiophene is not conclusive since only the parent compound has been studied so far. Most alkylated derivatives—as are expected to be dominant in crude oil—are more strongly retained on Pd(II) than their parent compounds. Therefore, alkylnaphththiophenes may be expected to elute in the Pd-2 fraction. The identity of the compounds that elute in the Pd-1 fraction thus needs to be clarified through further work. Since they are not detected in AM or AL, they are most probably thiophenes without condensed aromatic rings which are not of much concern in hydrodesulfurization processes since they are expected to be very easily hydrogenated.^{2,3}

Arabian Medium. The Pd-2 fraction shows the presence of sulfur aromatics, comprising DBEs 6–14 (Figure 4). The dominating series corresponds to the benzothiophenes and dibenzothiophenes. The highest mass recorded for dibenzothiophenes is 670 compared to 750 recorded for AH. The highest DBE is 14 versus 17 for AH. The distribution pattern of compounds at different DBEs is demonstrated in Table 1. We did not detect any S₁ compounds in the Pd-1 fraction.

Arabian Light. The sulfur aromatics in the Pd-2 fraction range from DBE 6 to DBE 14 (Figure 4). The most intense series is the same as that of AH and AM. They follow a similar pattern to those of the AM with a similar higher mass limit of about 650. Also, there is no significant difference in the

Table 2. Examples of Typical Sulfur-Containing Compounds Eluting in the First Fraction on the Pd(II) Phase

| possible structure | DBE | compound type | nominal mass |
|---|-----|--|--------------|
|  | 6 | Hexahydrodibenzothiophene | 190 |
|  | 7 | Phenylthiophene | 160 |
|  | 8 | 4H-Indeno[1,2- <i>b</i>]thiophene | 172 |
|  | 9 | Naphtho[2,1- <i>b</i>]thiophene | 184 |
|  | 10 | 2-(2-Naphthyl)thiophene | 210 |
|  | 11 | 2-(2-Naphthyl)tetrahydrobenzothiophene | 264 |

distribution pattern of compounds with different DBEs from that of AM (Table 1).

We have previously reported sulfur heterocyclic compounds from a vacuum residue from a different crude oil than the Arabian crude oils, with DBEs going up to 20 for S₁ compounds, some compounds containing two sulfur atoms, and a few containing three sulfur atoms with recorded masses reaching 850.¹⁹ We do not see a higher DBE than 17 and a higher mass than ca. 750 for S₁ compounds in these Arabian whole crude oils. In addition, we were also not able to find any detectable amounts of S₂- and S₃-compounds which may mean that their concentration in the whole crude is too low to be easily measured; they are expected to be concentrated in the heavier distillation fractions. Their absence in the mass spectra here does not exclude their presence in the Arabian crude oils.

Comparison with Gas Chromatographic Measurements.

Customary methods for the analysis of PASHs in crude oil rely heavily on GC. For components of lower molar mass, high-resolution GC methods are powerful; however, the inherent thermal limits for GC equipment, even considering the possibility of high-temperature gas chromatography, mean that this technique is satisfactory only for components of some volatility. For instance, in the literature, benzothiophenes with up to 16 alkyl carbon atoms have been found in a vacuum gas oil,¹⁰ but with the MS technique employed here, we have been able to find benzothiophenes with up to 30 alkyl carbon atoms in a somewhat lower boiling vacuum gas oil;¹¹ in a vacuum residue, we identified benzothiophenes with up to 47 side-chain carbon atoms using MS.¹⁹ Likewise, GC characterization was capable of identifying up to C₅-benzonaphthothiophenes (of molecular

weight 304 Da) in a crude oil.^{28,29} With the present MS method, we find benzonaphthothiophenes with no less than 33 alkyl carbons in the AH. Furthermore, the discrimination against higher-boiling compounds in GC distorts the pattern of the analytes if they have widely differing boiling points.

Similarly, the information obtained from GC-based research is limited not only with respect to masses but it seems also to aromatic size. The highest DBE reported was 12 (for benzonaphthothiophenes) in case of both vacuum gas oil¹⁰ and crude oil,²⁸ whereas the highest DBE goes up to 17 for AH and 14 for AM and AL as shown here. The limitation in information about the size of the aromatic system, which is highly important for different processes involved in the refining of crude oil, is thus overcome with mass spectral methods as has also been demonstrated, for instance, in a study of a Russian crude oil that indicated the presence of PASHs up to DBE 15.³⁰

Gas chromatography has the advantage that the information can be presented visually appealingly in the form of a gas chromatogram. Traditionally FT-ICR MS data are less clearly represented, for instance, by Kendrick plots such as those in Figures 4 and 5. In order to highlight the different abundancies of the masses, a color plot can also be produced with different colors for different abundancies. To facilitate the quick comprehension of such data, we prefer yet another graphical presentation that makes it considerably easier to visualize the

(28) Mössner, S. G.; Wise, S. A. Determination of polycyclic aromatic sulfur heterocycles in fossil fuel-related samples. *Anal. Chem.* **1999**, *71*, 58–69.

(29) Sugimoto, Y.; Tunnukij, K.; Miki, Y.; Yamadaya, S. Characterization of compound-class fractions of vacuum gas oil by using capillary GC and GCMS. *Sekiyu Gakkaishi* **1992**, *35*, 339–48.

(30) Poberii, A. Y.; Karmanova, L. P.; Lyapina, N. K. Group-structural composition of thiopheno-aromatic concentrates of 400–450. °C distillates of Usino heavy crude-oil. *Pet. Chem.* **1987**, *27*, 178–184.

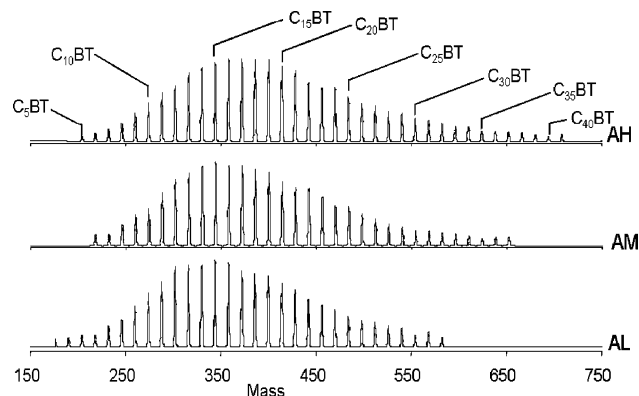


Figure 6. Pseudograms showing the distribution of alkylated benzothiophenes (C_xBT) of the three Arabian crude oils.

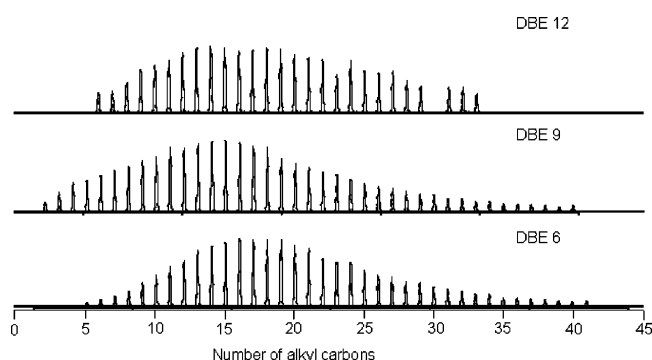


Figure 7. Pseudogram showing the distribution of alkylated condensed thiophenes of the Arabian heavy crude oil, with benzothiophenes at DBE 6, dibenzothiophenes at 9, and benzonaphthothiophenes at 12.

distribution pattern of the compounds of a certain DBE or to compare the substitution pattern of compounds of various DBEs. We convert the MS abundance data of each mass into a Gaussian peak, normalize the peak magnitude to the one of the most abundant peak, and then distribute the peaks along a mass scale, thus turning the mass spectral data into a visual form that resembles a chromatogram. This we call a pseudogram, examples of which are shown in Figures 6 and 7. This is in effect an elaboration of the traditional centroid presentation of mass spectral data but highlights the often overlooked basic principle of mass spectrometry as a separation technique in which ions are separated according to their m/z ratios. We wish to stress that the standard deviation of the Gaussian peaks selected here is an arbitrary value, does not have a physical meaning, and only serves the purpose of generating a chromatogramlike shape. This is in the tradition of the centroid presentation of mass spectra that has a standard deviation of zero and therefore also does not reflect a measured quality.

In Figure 6, the compounds of DBE 6 (corresponding to the alkylated benzothiophenes) from the three oils are represented in this manner, illustrating the ease with which the series of alkyl derivatives can be compared for different samples. It is

immediately clear that the most abundant members of these series carry 14–20 alkyl carbon atoms and that the number of alkyl carbons decreases from AH to AL.

A pseudogram is not a real chromatogram since all compounds with a common exact mass, i.e., compounds of a common nominal mass and a common DBE, appear together in one “peak”. A chromatographic technique would resolve many of those isomers into a host of smaller peaks, many of which would overlap with compounds of other masses and DBEs. The advantage of the pseudogram is that it gives quick information on the distribution of the alkyl substitution in a convenient form that the analytical chemist can use to evaluate visually. A chromatographic technique that would give this kind of graphic information must be able to analyze compounds of extremely different volatilities and to show no selectivity at all for isomers. Such a technique does not exist. Finally, it should be kept in mind that the mass spectral resolving power is enormously much higher than is apparent in Figures 6 and 7; the pseudograms are not meant to reflect this.

Another convenient way of using pseudograms is for comparing the alkylation pattern for different aromatic parent systems. In Figure 7, we depict this for the benzothiophenes (DBE 6), dibenzothiophenes (DBE 9), and benzonaphthothiophenes (DBE 12) in AH. Here, the mass scale of the pseudograms is adjusted so that “peaks” representing compounds of the same number of alkyl carbons are aligned along the x -axis. Thus, a quick glance is sufficient to learn that benzothiophenes and dibenzothiophenes are represented with higher alkyl numbers than the benzonaphthothiophenes and that the distribution of alkyl carbons has its maximum at somewhat larger numbers for benzothiophenes than for dibenzothiophenes and benzonaphthothiophenes.

4. Conclusions

The three crude oils studied here differ somewhat in sulfur content, ranging from 1.8 to 2.9%. The polycyclic aromatic sulfur heterocycles are shown to reflect this in that a higher sulfur concentration is correlated with the existence of larger ring systems and with a relatively larger number of alkyl carbon atoms in the side chains of the aromatic compounds. The pseudogram representation introduced here makes this very clear in a simple visual manner.

Furthermore, PASHs eluting in the Pd-1 fraction were detected only in the Arabian heavy crude. To our present understanding, this means that they contain thiophene rings which are not condensed with other aromatic groups, although they may contain aromatic substituents. Since such compounds were also seen previously in a vacuum residue¹⁹ of 4.55% sulfur, this may hint at a more complex mixture of parent ring structures in the heavier, more sulfur-rich materials. This will probably not be of concern in the hydrodesulfurization process since such compounds are likely to be reduced fairly easily.

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