



Argentation chromatography for the separation of polycyclic aromatic compounds according to ring number

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ABSTRACT

Crude oils are the most complex mixtures known and every speciation method relies on a simplification of their complexity. Argentation chromatography is shown to be superior to traditional liquid chromatographic ways of separating aromatic compounds based on the number of aromatic carbon atoms. A silver(I) mercaptopropano silica gel allows an efficient group separation of polycyclic aromatic compounds to be achieved. The usefulness of this phase is demonstrated for SRM 1582 Wilmington crude oil and a diesel fuel. Furthermore, the phase can also be used for semi-preparative purposes to collect fractions for further analysis with high resolution mass spectrometry. Orbitrap mass spectra are obtained here for the polycyclic aromatic sulfur heterocycles and it is demonstrated that they can contain one to five naphtheno rings.

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1. Introduction

Fossil fuels are going to be the major energy source in the world for many years to come despite the drawbacks associated with their combustion. Next to a replacement of these sources by renewable energy forms, a more efficient and clean use of the fossil materials can contribute to alleviating the climate disturbances caused by the increase in atmospheric carbon dioxide. In attempts to improve the efficiency of the industrial processing of fossil materials, especially of petroleum, knowledge of the molecular structures of crude oil components is desirable which means that analytical methods for detailed studies of them are required.

In refineries severe problems like precipitation of petroleum components and clogging of pipelines and valves, leading to interruption of the continuous production, can be caused by compounds containing multiple rings. These can contain large aromatic systems that occur naturally in the so-called asphaltene fraction of the oil or formed in refinery processes from saturated cyclic precursors. Ultimately they may be converted into coke through removal of hydrogen [1]. Despite this being a serious technical problem, there is a lack of analytical methods that can give information on the distribution of multi-ring compounds in petroleum.

Scattered examples of polycyclic partially hydrogenated compounds have been known for a long time. Low-voltage mass spectrometry helped in recording a large number of naphthenologs of aromatic compounds that were detected through their molecular weight. Naphthalenes and benzothiophenes with up to five naphtheno rings were described after a complex work-up procedure from a distilled sample of a Prudhoe Bay crude [2] and benzothiophenes with one or two naphtheno rings (in a 3:1.2:1 ratio) were found in a Siberian petroleum [3]. Other Siberian oils were likewise presumed to contain up to trinaphthenobenzothiophenes but it was recognized that these are isomeric with dibenzothiophenes and therefore not separable using MS [4]. Other similar compounds identified in fossil material are sulfur-containing steranes [5]. A review listing such compounds is available, but many of the literature sources quoted are difficult to obtain [6]. Partially saturated nitrogen-containing polycyclic aromatic compounds have been analyzed in coal liquids by tandem mass spectrometry [7]. Partially saturated nitrogen and sulfur compounds are suggested to act as inhibition species in the hydrodesulfurization of fuels [8,9].

The reports mentioned invariably involve gas chromatography–mass spectrometry (GC–MS) for the analysis. However, it must be kept in mind that recording the molecular ion in MS itself does not identify the ring system. Thus the monoaromatic thienosterane mentioned above, with eight alkyl carbon substituents, is isomeric with a diaromatic tetrahydrodibenzothiophene with a total of 13 alkyl carbon substituents, both exhibiting

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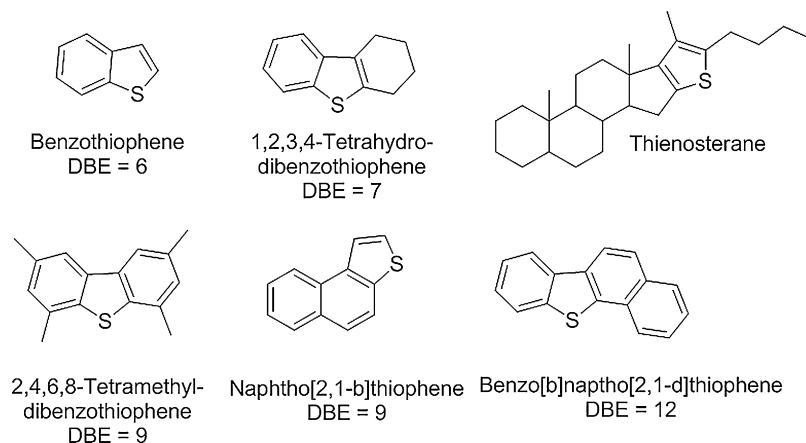


Fig. 1. General structures of selected PASHs.

the elemental composition $C_{27}H_{42}S$ (see Fig. 1). Additional evidence is therefore necessary for obtaining information on the ring system.

In this paper we present a method for analyzing complex mixtures of polycyclic aromatic compounds that contain naphtheno rings. It rests on the efficient separation of the different aromatic compounds based on the number of aromatic rings, followed by high resolution mass spectrometry. Thus the chromatographic step defines the size of the aromatic system, and then the elemental composition, as determined by MS, reveals the number of naphtheno rings. This chromatographic step must be highly efficient to preclude coelution of aromatic compounds of different sizes that may yield identical m/z values in mass spectrometry. In an earlier paper [10] we identified a β -cyclodextrin stationary phase as the most suitable of several tested phases for these purposes, but in such complex samples as crude oil there was still considerable overlap between compound classes of different aromatic sizes. This is caused by the extensive alkylation of the aromatic compounds present in petroleum. Here we now present result on a much more efficient phase for this separation, based on silver ions.

Since we have previously intensely investigated polycyclic aromatic sulfur heterocycles (PASH) in crudes, it was natural to concentrate on this class of compounds in an attempt to study such multi-ring compounds. Some results on polycyclic aromatic hydrocarbons (PAH) will also be given (see Supplementary Data). However, we expect that the conclusions drawn should be more general since experience shows that PASHs and PAHs are very closely related in their structural characteristics.

2. Experimental

2.1. Sample and chemicals

The Wilmington crude oil was obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA). The Spanish diesel sample was obtained from Repsol, Spain (for analytical results, see Supplementary Data).

Chemicals for synthesis and HPLC grade solvents are supplied by Sigma–Aldrich (Taufkirchen, Germany). All reference compounds were synthesized in our laboratory [11].

2.2. Preparation of the stationary phases and columns

Silver(I)-mercaptopropano silica gel was synthesized with $10\ \mu\text{m}$ LiChrosorb Si 100 (Merck, Darmstadt, Germany). The silica was dried at $130\ ^\circ\text{C}$ for 24 h. 10 g of silica were stirred in a solution of 15 mL 3-mercaptopropanotrimethoxysilane in 50 mL dry toluene

for 24 h at $80\ ^\circ\text{C}$. The resulting bonded silica gel was filtered off and washed with toluene and methanol. The obtained mercaptopropano silica gel was dried at $50\ ^\circ\text{C}$ over night. The silica gel was suspended in 250 mL of an aqueous solution of silver nitrate (0.1 M) and stirred for 3 h. After filtration the resulting silver(I) mercaptopropano silica gel was washed with water and methanol and dried at $50\ ^\circ\text{C}$ over night.

The amount of silver loaded on the stationary phase was determined by atomic absorption spectroscopy. 100 mg of the stationary phase was suspended in 5 mL of concentrated nitric acid and refluxed for 15 min to release the silver ions. The silver amount was determined to 1.7 mmol/g for the stationary phase. The amount of sulfur in the mercaptopropano stationary phase was determined to 1.78 mmol/g using elemental analysis [12].

The modified silica was packed into stainless steel columns ($250\ \text{mm} \times 4.6\ \text{mm}$) at 400 bar using a Knauer pneumatic pump. The slurry method was used with methanol as solvent. After packing the column was flushed first with acetone and then with 200 mL cyclohexane/dichloromethane (7:3) to allow normal phase chromatography.

2.3. Methylation

The collected fractions were dissolved in 2 mL of 1,2-dichloroethane and $40\ \mu\text{L}$ of methyl iodide was added and the vial wrapped with aluminum foil to limit the risk of photochemical decomposition of the sample. Silver tetrafluoroborate (60 mg) was added and the mixture stirred overnight. The precipitated silver iodide was removed by filtration and washed with 1,2-dichloroethane. The thiophenium salts were obtained by evaporation of the filtrate. Finally, the salts were dissolved in 2.0 mL acetonitrile and kept in the refrigerator at $-18\ ^\circ\text{C}$.

2.4. High-resolution mass spectrometry

Mass spectra were obtained using a Thermo Scientific Exact Orbitrap Mass Spectrometer (Thermo, Dreieich, Germany). The samples were dissolved in acetonitrile and injected with a flow rate of $5\ \mu\text{L}/\text{min}$ in the ESI(+)-mode with N_2 as sheath gas. The measurements were carried out with an ion spray voltage of 3.6 kV, a tubus lens voltage of 135 V, a skimmer voltage of 20 V and a capillary temperature of $275\ ^\circ\text{C}$.

The Kendrick mass scale sorts homologues of a compound family according to their number of double bond equivalents [13]. The IUPAC mass for a CH_2 group is converted to 14.00000 Da according

to the following equation, after subtraction of 15.02293 for the methyl group.

$$\text{Kendrick mass} = \text{IUPAC mass} \times \left(\frac{14.00000}{14.01565} \right)$$

The identification of homologous series as they appear in petroleum is now simplified. Additionally, compounds with the same number of double bond equivalents have the same Kendrick mass defect, which is determined by the equation

$$\text{Kendrick mass defect} = \text{Kendrick nominal mass} - \text{Kendrick mass}$$

The Kendrick nominal mass is the Kendrick mass rounded to the nearest integer. The Kendrick mass defect can be directly related to the number of double bond equivalents (DBE) which can be determined after an assignment of the molecular formulas.

2.5. UV/VIS absorption measurements

A Shimadzu Recording Spectrometer UV-1800 was used for the UV absorption measurements at a concentration of 0.001 M solution in cyclohexane.

2.6. Isolation of the PASH and PAH fractions of a crude oil

300 mg of Wilmington crude oil was separated into aliphatic and aromatic compounds using a gravity-fed column (250 mm × 16 mm) filled with alumina that had been activated at 50 °C over night. Aliphatics were eluted with cyclohexane and the aromatic fraction with cyclohexane/dichloromethane in a ratio of 1:1 (v:v). The solvents were removed by evaporation. The aromatic fraction was further separated by HPLC into PAHs and PASHs on a palladium(II)-mercaptopropano stationary phase (Pd(II)-MPSPG) [14].

2.7. Separation of PASHs

A gradient elution with cyclohexane (CH)/dichloromethane (DCM) with an increasing amount of isopropanol (IP) was used for the isolation of the fractions on the silver(I) mercaptopropano silica. Benzothiophenes were eluted with CH/DCM 7:3, dibenzothiophenes with CH/DCM 7:3 + 0.2% IP and benzonaphthothiophenes with CH/DCM 7:3 + 5.0% isopropanol. The separation was repeated three times and the corresponding fractions were combined for gas chromatographic and mass spectral investigations. Benzothiophenes were collected between 2 and 20 min, dibenzothiophenes from 20 to 47 min and benzonaphthothiophenes from 47 to 60 min at a flow rate of 2.5 mL/min.

2.8. Separation of PAHs

The PAH fraction of a diesel fuel was separated on silver(I) mercaptopropano silica using a gradient with

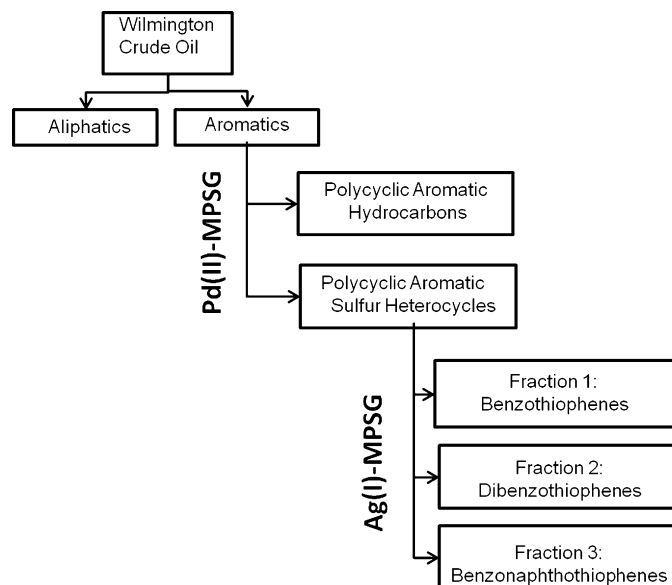


Fig. 2. Separation scheme for the analysis of the Wilmington crude oil.

cyclohexane:tetrahydrofuran (9:1). The first fraction was collected from 1.0 to 4.5 min, the second fraction from 4.5 to 12 min and the last fraction from 12 to 18 min at a flow rate of 2.0 mL/min. The separation was repeated three times and the corresponding fractions were combined for gas chromatographic and mass spectral investigations. These data are reported in [Supplementary Data](#).

3. Results and discussion

The oil investigated here is a Wilmington crude oil, identical to the one that was used by the National Institute of Standards and Technology to prepare the standard reference material SRM 1582 but it was not taken from an ampoule sold as SRM but from the batch used to prepare the SRM. We preferred this oil, that is available to every researcher, so that the results can be checked in other laboratories using the same material, thus eliminating inter-samples variabilities. The PASHs in SRM 1582 have been analyzed in detail by gas chromatography [15] but it should be kept in mind that many aromatic compounds in crude oil are not volatile enough for GC analysis.

Schemes for crude oil analysis routinely rely on the SARA fractionation as the first step, this being a normal-phase fractionation of compounds that elute with eluents of different polarity. In this work the second fraction from such separations is studied; it contains PAHs, PASHs and oxygen heterocycles. To isolate the PASHs, this aromatic fraction was next fractionated on a Pd(II) containing stationary phase using ligand exchange chromatography (LEC)

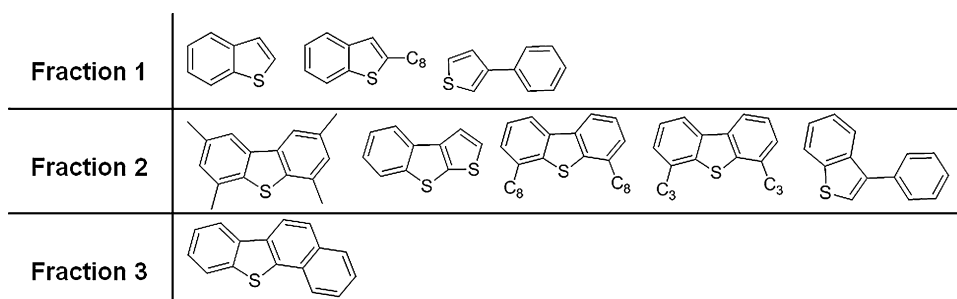


Fig. 3. Elution of selected standard compounds into different groups on the Ag(I) MPSPG phase.

as described in detail elsewhere [14,16]. This LEC is based on a reversible donor–acceptor interaction between palladium ions and the sulfur atoms. The sulfur containing aromatic compounds adsorb on the stationary phase until they are eluted as a group with a competitive mobile phase. Such stationary phases have been used to great advantage in research on sulfur compounds [16,17].

The preprepared fraction containing only the PASHs was further separated into subfractions containing compounds with different numbers of π -electrons. This was done using argentation chromatography which is shown to be much more efficient than traditionally used phases for separations according to the number of π -electrons. Reversible complexes are formed between silver ions in the stationary phase and unsaturated compounds. The Dewar–Chatt–Duncanson model [18] invokes a donor binding from the $p\pi$ -orbital of the olefinic or aromatic double bond into an unoccupied 5s- and 5p-orbital of the silver ion. A weak back-binding from the occupied 4d-orbitals of the silver into the unoccupied non binding $p\pi^*$ orbitals of the double bond is possible [19]. The strength of this bond is small enough for the smaller aromatic compounds that it can be broken by additives to the mobile phase and thus the aromatics elute. A stepwise gradient is used to elute fractions that only contain members of the same number of aromatic rings.

The simplest such stationary phase consists of a silver salt deposited on a carrier, e.g. silica. This has the disadvantage that silver ions may leak from the column when stronger eluents are introduced. To avoid this, cation exchangers have been loaded with Ag^+ [20], e.g. for the separation of lipids and fatty acids. However, these phases generally have low capacity and are not suitable for the larger amounts necessary in the present investigations. A silver loaded mercaptopropano phase has been described and the separation of a few single PAHs [21] was demonstrated, but the phase does not seem to have found any further utility.

Here we use this phase in the third dimension (after silica gel and Pd(II)-MPSG; see Fig. 2) to separate the PASHs into three subfractions. The first one includes substituted benzothiophenes (BT) with 8 π -electrons, the second one dibenzothiophenes (DBT) with 12 π -electrons and the third fraction benzonaphthothiophenes (BNT) (16 π -electrons). An important question regards the retention of alkyl derivatives that preferably should have similar retention times as the parent compounds. This was first tested using a series of standard compounds synthesized for this purpose.

Derivatives containing longer alkyl chains should in principle have approximately the same interactions with the stationary phase since these are developed through the π system of the aromatic ring and the Ag^+ ions. The alkyl chains are not expected to play a decisive role there. However, they will interact more strongly with the mobile phase the longer the chain is and the possibility that these interactions finally become so strong that the retention times will shorten considerably cannot be neglected. Therefore, it is necessary to investigate also compounds with longer alkyl chain that are known to occur in crudes [22,23]. Some PASHs containing one or two octyl chains were therefore synthesized and their elution times determined using the same gradient which was used for the separation of the crude oil. That reference compounds containing different substituents are cleanly separated according to the size of the aromatic system is depicted in Fig. 3. The retention times within a group deviated less than 3 min from each other. This also included compounds with two catacondensed thiophene rings (PAS_2H).

The dependence of the retention times on the number of double bonds is much larger than that exhibited by any of the other phases we have investigated, for instance aminopropanosilane, tetrachlorophthalimide and β -cyclodextrin [10]. Thus the Ag^+ containing stationary phase presents a superior way to isolate groups of PASHs according to the size of the aromatic system. We restrict ourselves here to compounds containing up to four aromatic rings

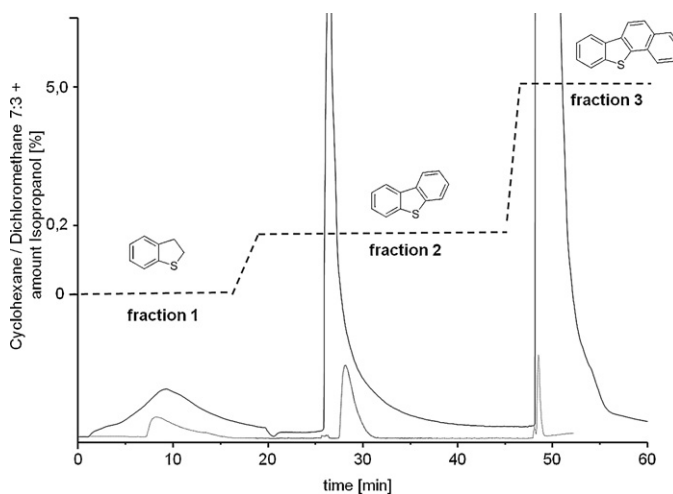


Fig. 4. Separation of a standard PASH mixture and a PASH fraction of the Wilmington crude on a silver(I)-mercaptopropano silica gel stationary phase (250 mm \times 4.6 mm). Conditions: mobile phase cyclohexane/isopropanol step gradient elution, 2.5 mL/min, room temperature, UV detection at 254 nm.

but it has been shown that with a stronger eluent it is easily possible to elute at least a compound like perylene with five aromatic rings [21].

Fig. 4 shows the resulting chromatogram of the separation of a simple standard mix of BT, DBT and BNT as well as the separation of the PASH fraction of the Wilmington crude oil. It is clear that only the aromatic system and not the sulfur atom interacts with the Ag^+ ions since the PASHs elute in a similar fashion to the PAHs (see below). Three subfractions were collected from the oil PASH fraction and were further analyzed for possible group type overlap. A comparison of the gas chromatograms of the BT and the DBT fractions showed the absence of BTs in the second fraction (see Fig. S3 in Supplementary data).

UV spectrometry was shown to detect the presence of 0.25 mol.% of 2,4,6,8-tetramethyldibenzothiophene in the benzothiophene fraction at 335 nm where BTs do not absorb (see Figs. S4–S6 in Supplementary data) but no absorption was detected at this wavelength in the BT fraction. In the mass spectrum of the BT fraction about 18% of the summed signal abundances are derived from compounds that have the same hydrogen deficit as DBTs. However, these signals must be derived from isomeric BTs (see below) since DBTs would show UV absorption of a magnitude that would be easily detected. Thus the fractionation on the Ag^+ phase achieves a very clean separation, as required for the next step, the MS analysis.

3.1. High resolution mass spectrometry

Electrospray ionization high resolution MS was used to obtain detailed information on the compounds in the three fractions. This ionization technique is a gentle method with no fragmentation of the analytes and thus preferred here, but it is effective only for polar compounds. The sulfur compounds are therefore methylated with methyl iodide [24] at the sulfur atom to methyl thiophenium ions that are readily detected. There are no studies on how quantitative this method is with respect to different ring systems. On a synthetic scale, BT, DBT and BNT gave yields of 68%, 78% and 82%, respectively [25], but our attempts to use thin-layer chromatographic analysis of the methylation product showed that no compounds of R_f values typical of the non-methylated aromatics were seen. Likewise, a very high recovery of 95% of the sulfur in the methylated fraction was determined for a high-sulfur Arabian crude [26] so odds are that

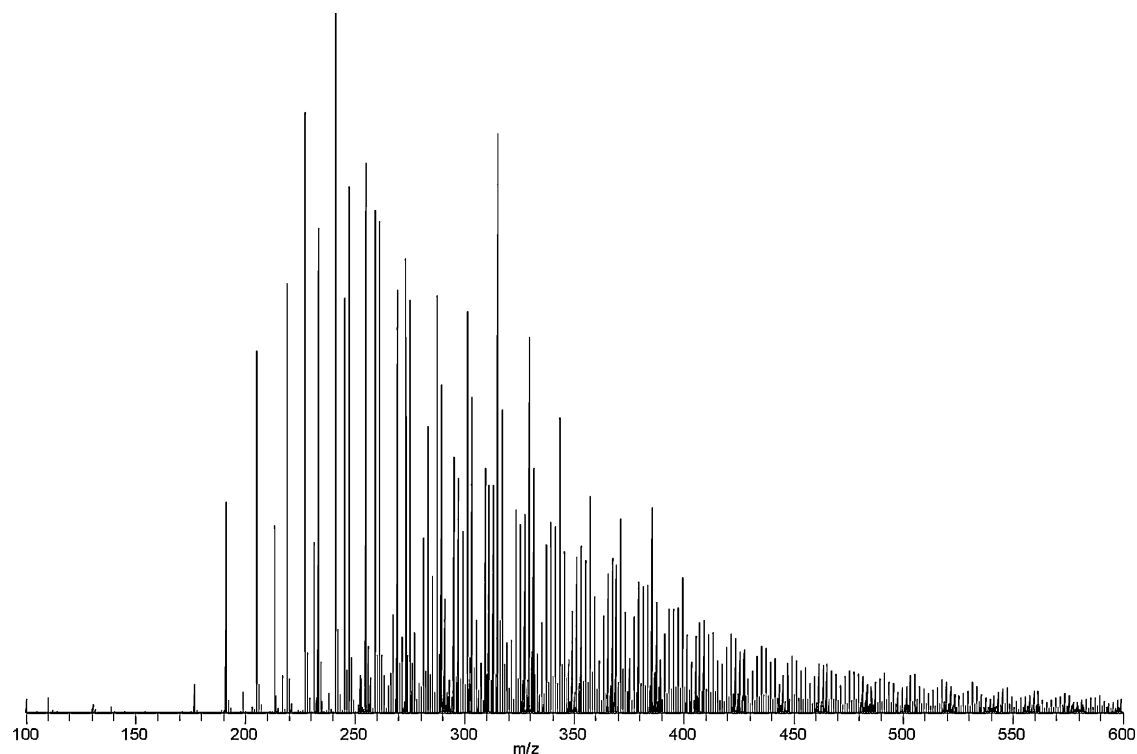


Fig. 5. High resolution mass spectrum from an Orbitrap measurement of the PASH fraction of the Wilmington crude oil.

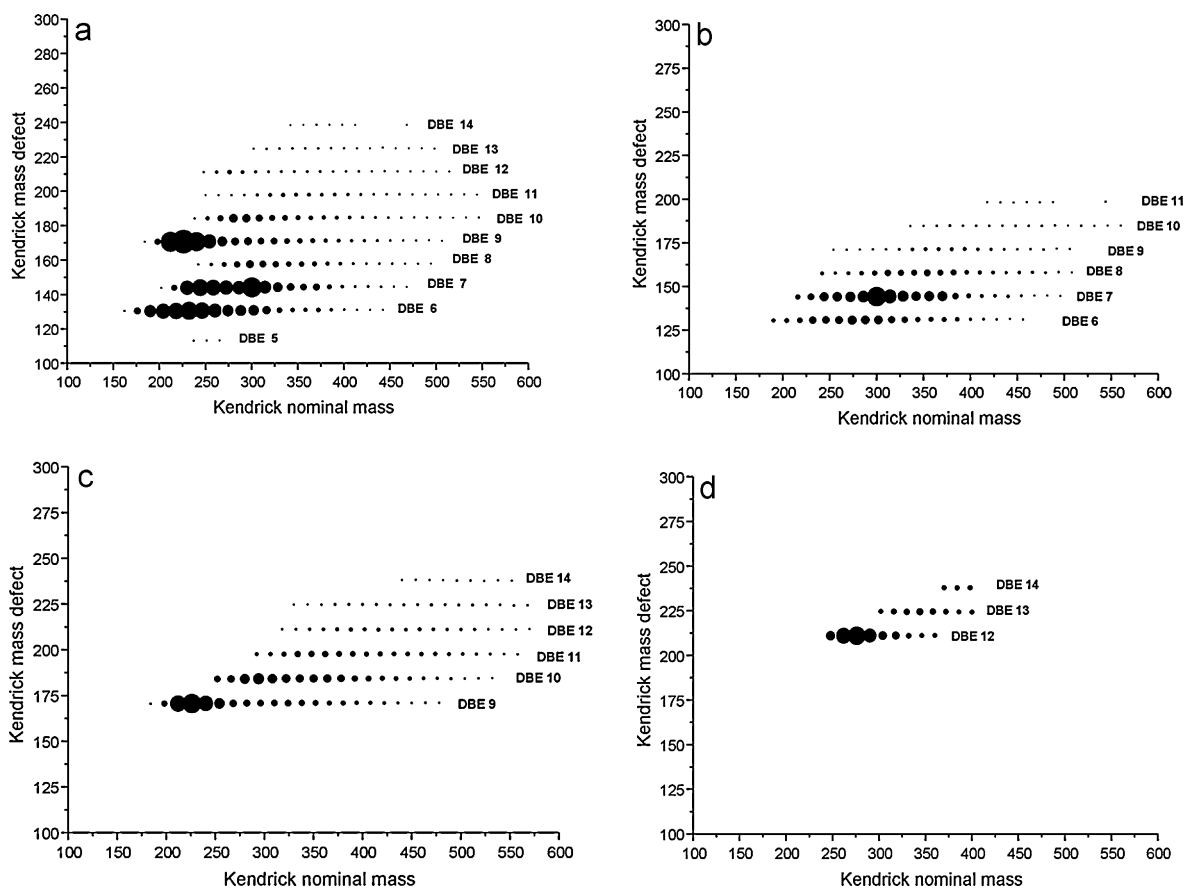


Fig. 6. Kendrick plots of the PASHs in the Wilmington crude. (a) Kendrick plot of the whole PASH fraction before the separation on Ag(1)-MPSG; (b) Kendrick plot of fraction 1 (BTs) from the separation on Ag(1)-MPSG; (c) fraction 2 (DBTs); and (d) fraction 3 (BNTs).

no significant part of the sulfur compounds will be missed in this derivatization.

Fig. 5 shows the resulting broadband mass spectrum of the whole PASH fraction after methylation. The complexity of the sample as well as the mass distribution is visible at once. The PASHs show nominal masses from m/z 180 to above 600. The elemental composition of each signal can be calculated from the exact masses measured, and from this the hydrogen deficit and the double bond equivalents (DBE) of the compounds are obtained. The plot of DBE vs. the Kendrick masses gives plentiful insight into the composition of the three PASH fractions of the Wilmington crude (Fig. 6a–d).

3.2. Kendrick plots

Kendrick plots were generated for all three fractions collected from the separation on the silver(I) mercaptopropano phase. Mass values for singly charged ions in a mass range from 100 to 600 Da were used. The Kendrick plot of the whole PASH fraction before the separation on Ag(I)-MPSG indicates the presence of compounds with DBEs from 6 to 14 (Fig. 6a). As thiophenic compounds without further catacondensed aromatic rings elute in the PAH fraction during the separation on the Pd(II) phase [14], they do not appear in the plot.

The BT fraction on the Ag(I) phase shows compounds with DBEs from 6 to 11 (Fig. 6b). A DBE of 6 corresponds to the BT series that displays compounds with four to 24 CH_2 groups. The amount of BTs with C_1 and C_2 substitution is so low that they do not appear in the plot. DBE 7 corresponds to compounds like tetrahydrodibenzothiophenes. Here between 4 and 22 substituent carbon atoms are visible, the most abundant being 8 carbon atoms. A DBE of 8 most likely represents benzothiophenes with two naphtheno rings, but indanylthiophenes and indenothiophenes are also conceivable. The next higher series with a DBE of 9 is suggested to represent BTs with three naphtheno rings.

Two situations should be conceptually separated, namely those in which a naphtheno ring is condensed onto the aromatic system and those in which a cycloalkyl group is connected either directly to the aromatic system or through an alkyl chain. The DBE will be the same in both cases. Both kinds of compounds were suggested to occur among the (sulfur-free) hydrocarbons in West Siberian oils [26] but they cannot be differentiated by MS.

Fraction 2 does not contain any compounds with a lower DBE than 9 (Fig. 6c), showing that alkylbenzothiophenes are successfully separated from their higher homologues. Dibenzothiophenes containing 0–20 substituent carbon atoms are identified at DBE 9. The next higher DBE corresponds to DBT with one naphtheno ring, acenaphthenothiophenes or BT with one phenyl substituent. Compounds with substituents ranging from 0 to 20 carbon atoms are present. Two naphtheno rings attached to DBT or phenanthro[4,5-*bcd*]thiophene (PT) lead to a DBE of 11 and such compounds would appear in this chromatographic fraction. C_2 – C_4 -PTs have been found in a heavy vacuum gas oil [27] but in the present crude oil they do not seem to be of any significance. The DBE 11 compounds start at a molar mass of 292 which would correspond to C_6 -PT. Since the alkylation of all other compounds start with one or two carbon atoms, we assume that this should be the case for PT also and therefore do not favor this assignment for this particular crude.

DBEs from 12 to 14 are derived from additional aliphatic rings attached to the DBT basic structure. That demonstrates that both BTs and DBTs have up to five naphtheno rings attached. Naphthothiophenes are isomeric with DBTs and would appear in the same fraction as these but they are not generally recorded in crude oil.

Fraction 3 (Fig. 6d) consists mainly of compounds exhibiting a DBE of 12, corresponding to the benzonaphthothiophenes (BNT), 13 and 14 but the signals are appreciably weaker than for the BTs and DBTs. Benzonaphthothiophenes with 2 to 10 carbon atoms in

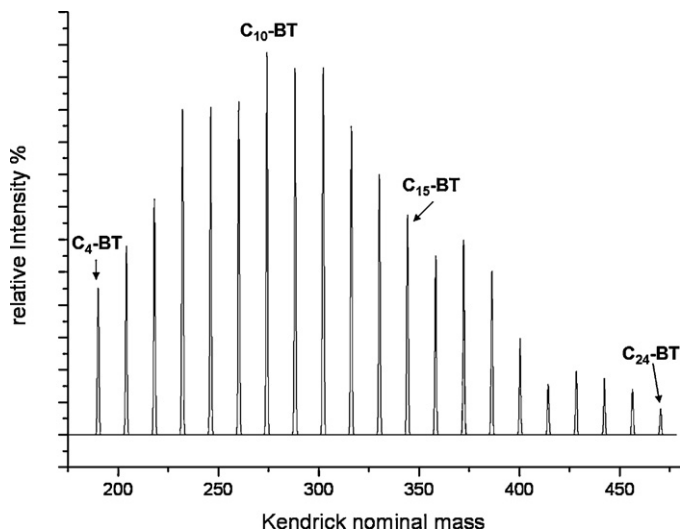


Fig. 7. Pseudogram of the benzothiophene series at DBE 6.

the substituents are identified at DBE 12. The carbon number for the heaviest members detected in the three series BT, DBT and BNT is 32, 32 and 26, respectively. The possible signals of compounds of higher aromaticity than BNT were too weak to be distinguished from the noise.

3.3. Pseudograms

Another visually easily accessible way of presenting the results of complex broadband mass spectra are so-called pseudograms. Pseudograms resemble gas chromatograms and it is possible to compare intensities of compounds within a particular DBE, aiding strongly in obtaining quick information on the sample [17]. Pseudograms are calculated using a Gaussian distribution for each mass, obtained by adding a standard deviation to the MS signals.

Fig. 7 shows the pseudogram for the BT series with DBE 6. The most abundant compounds are benzothiophenes with ten carbon atoms in the side chains with a mass of 274. The DBT series with a DBE of 9 is dominated by trimethyldibenzothiophenes with a mass of 226.

4. Conclusions

The silver(I)-mercaptopropano stationary phase is introduced for the separation of polycyclic aromatic sulfur heterocycles in crude oils according to their number of double bonds. It is easy to prepare and shows a much better separation according to the number of π -electrons than other investigated phases do. For the first time benzothiophenes as well as dibenzothiophenes with up to five aliphatic rings are identified as components of the Wilmington Crude oil of SRM 1582.

The separation of polycyclic aromatic hydrocarbons as illustrated for a diesel is also improved in comparison to separations on aminopropyl stationary phases. Even though the separation is not quite as clear as it is the case for the PASHs, a better pre-separation into two-ring and three-ring aromatics is easily achieved.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.11.006.

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