Molecular studies of Asphalt, Mummy and Kassel earth pigments: their characterisation, identification and effect on the drying of traditional oil paint
Languri, G.M.

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2. Asphalt: Characterisation of the 19th-century Hafkenscheid asphalt pigment. Markers and biomarkers

Abstract

Asphalt has been used since antiquity for various purposes and by painters since the 17th century. Asphalt as a pigment material with a known pre 19th century provenance is extremely rare. The analytical pyrolysis techniques of Direct Temperature resolved Mass Spectrometry (DTMS) and Pyrolysis Gas liquid Chromatography coupled with Mass Spectrometry (Py-GC/MS) were applied to characterise a unique “asphalt” sample from a painting materials collection dating from the early 19th century. The provenance of this sample was investigated by comparison with a sample from present day floating asphalt from the Dead Sea.

DTMS demonstrated a complex envelope of ions from hydrocarbons ranging past m/z 1000 in both samples. Both samples showed evaporating sets of compounds as well pyrolysing materials evolving from asphaltenes. Asphaltenes network polymers were marked by aliphatic cross-links releasing alkenes and alkanes, and aromatic centres releasing alkylbenzenes, alkylnapthalenes, alkylantracenes, alkylphenanthenes, alkylbenzothiophenes. Hopanoid hydrocarbons and C-ring monocyclic aromatic steroid hydrocarbons were among the biomarker compounds identified. Particularly striking were homologous series of alkylbenzothiophenes and alkyl-dibenzothiophenes with long hydrocarbon chains that could be traced with DTMS and confirmed by DTMS/MS.

The results indicate that the early 19th century 'asphalt' sample from the Hafkenscheid collection is indeed natural asphalt that shows many similarities to the Dead Sea asphalt sample, which is therefore proposed as the possible region of provenance.
Introduction

Asphalts as classified by Yen [1] are divided in “natural asphalts”, found in sediments and rocks, and “artificial asphalts, mainly petroleum-derived asphalts and to a lesser extent, coal tar, water-gas tars, and their pitches”. The “recorded” history of asphalt use starts about 38,000 BC in the Paleolithic period [2]. The varied utilisation of asphalritic material includes: its use in agriculture and ship building as an adhesive and waterproofing agent, its use in construction as mortar and cement, its use for lighting and heating or as a weapon (e.g. as component of Greek fire), the decorative use as a coating of art objects or in the making of paints or varnishes and its utilisation in medicine and embalming [2, 3, 4, 5]. Many of its uses disappeared in the course of history. In the 19th century with the development of photography, asphalt came back as a light sensitive substance in the making of “heliographs” [6]. Since early in the 20th century, the presence of asphalt in sediments is used as an indicator of the existence of buried oil fields [4].

Asphalitic materials have been used in paintings at least since the 17th century, but the pinnacle of its use was reached in the 18-19th century. Paint defects in the 18-19th century paintings, seen as darkening and the formation of premature drying cracks are often associated with its use. Recently, Bothe [7] has reviewed the complexity of asphalt utilised in paintings from the 18th and 19th century. In some cases asphalitic materials were used as such i.e. directly mixed with cold oil. In other cases various preparatory measures were taken (heating, specific solvents, addition of resins) to ensure that the asphalitic particles dissolved completely. In some cases, the asphalt was roasted before use (Mérimée recipe) [8]. The variety of preparatory methods for use in paint makes it difficult for the analytical chemist to develop suitable analytical methodology. White has used the distribution of hopanes in extracts from paint samples as marker compounds on the assumption that these are specific for asphalitic materials [9]. Hopanes are primarily part of the solvent extractable maltenic fraction of asphalts, and may be lost from the painting by solvent cleaning. Hopanes are of low abundance in the asphaltene fraction, which has a better chance of surviving in a painting that has been cleaned several times. For these reasons, hopanes are not completely reliable markers for the presence of asphalt in paintings. It is also unclear whether hopanes are always present in an asphalitic oil paint considering the many different recipes and preparation methods.

Asphalts are emulsions of cross-linked flat sheets of polycyclic aromatic and heterocyclic hydrocarbons (asphaltenes) “dissolved” in a mixture of lower molecular weight aliphatic and alicyclic hydrocarbons (maltenes) [1]. Depending on the geological origin, there may be a substantial amount of sulphur compounds present, presumably contributing S-linkages to the network polymer system. Aliphatic hydrocarbon chains with variable chain length (C₂-C₄₀) link most of the aromatic centres. Pyrolysis of asphalt results in the thermal dissociation of the asphaltene fraction which breaks the cross-links resulting in sets of straight chain alkanes and alkenes and a large number of isomers of alkylated mono- and polycyclic aromatic hydrocarbons [10]. Maltenes in such an asphalt will evaporate in the low temperature pyrolysis experiments. The maltenic fraction contains hopanoid hydrocarbons, aromatic steroids, alicyclic and aliphatic hydrocarbons that are used as biomarker molecules by geochemists [11]. The traditional way to analyse asphalt samples consists of fractionation of the complete sample, by solvent extraction, into maltenes
Asphalt pigment

and asphaltenes. The maltenes are then analysed by on-column GC/MS, while the asphaltenes are investigated by Py-GC/MS.

Direct Temperature Mass Spectrometry, a fast fingerprinting method particularly suited for the recognition of many classes of compounds, achieves a physical separation between low molecular weight compounds by evaporation and cross-linked fractions of a sample by gradually raising the temperature of the filament probe [12, 13]. An asphalt sample will be physically separated during DTMS into a fraction evaporating at low temperature equivalent to the maltenes and fractions relating to the asphaltenes at higher temperature. It has been shown before that the thermal extract data of a sample (LT of DTMS) is equivalent to the classic solvent extract DTMS data [14]. The analytical process at high temperature under DTMS conditions is equivalent to in source pyrolysis mass spectrometry [12]. Under Py-GC/MS conditions in the Curie point pyrolysis system available at FOM-AMOLF these evaporating and pyrolysing fractions are injected directly into the GC column, analysed collectively and usually not as separate fractions [15]. The analytical approaches used provide complementary information.

Numerous citations exist which describe asphalt as the cause of the "craquelure anglais" in the paintings of 19th century [16, 8]. Artists liked the beautiful brown warm mellow tone and the glaze-like transparency of asphalt containing paint when applied in thin layers. This may be the reasons for its purported extensive use. In the 18th century, two varieties of ‘asphalt’ are mentioned: natural or native asphalt and artificial ‘asphalt’ [16]. In early 19th century England, a third variety was introduced, an ‘asphalt’ originating from coal tar [16]. The natural asphalt was described as a brownish-black [16] solid material, in fact always deep black in colour (when pure, [17]) and viscous at relatively early stages of degradation, while brown and friable in more advanced stages of alteration [18]. Asphalt was first roasted and ground because it could not be dissolved in oil directly [16]. Carlyle et al. call this kind of asphalt “real asphalt”. Artificial ‘asphalt’ was said to be a by-product of the manufacture of lampblack or pitch, with possibly additions of poor drying balsams. This variety is soluble in vegetable oils. The most common ‘asphalt’, the coal tar type, is mentioned as an ‘inferior’ variety that would result in paint that never dries completely [16]. Paint manufacturers and/or painters themselves [19] also adulterated asphalt with other geo-materials during paint preparation.

It is not clear whether all of the asphalt marker compounds that can be identified with analytical methods will survive on a painting considering the oil paint preparation process, the strongly oxidising conditions during ageing and the loss by evaporation and the various solvent cleaning methods used by conservators and restorers. Perhaps the more cross-linked fractions have a better chance of survival under these conditions. It is unclear what kind of asphalt could have been available in the 19th century. Egypt, the Dead Sea area, France, Germany, Switzerland, China, Italy and Trinidad are mentioned as sources of real asphalt. [8] Gettens and Stout [20] have suggested that asphalt from the Dead Sea area has probably been used in European painting. Petroleum production started after 1860 so asphalt in earlier paintings must have relied on open pit sources [7] or floating blocks such as those from the Dead Sea area [4, 6].

The Hafkenscheid collection of pigments [21, 22] dating from the late 18th and early 19th century provided the opportunity to analyse an asphaltic material that was available to colourmen and painters of that period.

The collection represents the product assortment supplied by the Amsterdam firm “Michiel Hafkenscheid and Son” in “Painting Materials, Turpentine and Gums”
during the first three decades of the 19th century. Nowadays, the Hafkenscheid Collection is kept in the custody of the Teylers Museum in Haarlem, The Netherlands. The collection consists of about 370 samples, inorganic materials (ores, powdered pigments, abrasives, inert fillers) and organic materials (unprepared vegetable and animal dyes, tannins, organic pigments, gums and resins, several glues). A great number of the analysed materials proved to be early 19th century standard pigments [21, 22]. The Hafkenscheid collection is one of the few surviving collections of pigments and paint materials for painters from the early 19th century and unique in the Netherlands. The single “asphalt” sample present in the collection had not been characterised. Although some oxidation may have occurred in the last 200 years of exposure to the atmosphere, the sample is treated as a natural intact asphalt for analytical purposes.

In this paper, the analytical pyrolysis methodology presented is designed to provide information on the presence of asphalt in oil paint. Comparative analytical data on asphalt containing oil paint samples are not the subject of this chapter and will be published elsewhere. Attention is given to the distribution of marker compounds released by Py-GC/MS and DTMS techniques from the complete sample as is the usual practice when microgram amounts of oil painting sample are analysed. The objective is to identify the sample from the Hafkenscheid collection as an asphalt and to correlate its composition with possible sources. The supposition of a Middle Eastern origin of the Hafkenscheid sample was tested by comparison with a reference sample from a floating asphalt block collected in the Dead Sea (Israel) analysed under the same conditions and by comparison with data from the literature. The asphalt sample from the Hafkenscheid collection (sample HS) and a Dead Sea reference asphalt (sample DS) were also compared with the analytical pyrolysis data from large MOLART reference collection of asphalts, but reporting of these data is outside the scope of this paper.

**Experimental**

**Samples**

The ‘asphalt’ from the Hafkenscheid Collection [21, 22] was kindly made available by the Teylers Museum in Haarlem (The Netherlands). Labelled as sample HS, the Hafkenscheid sample consisted of small amorphous lumps of black glossy material. Sample HS was compared with a type I Dead Sea [4] asphalt sample (sample DS), provided by Dr. Arie Nissenbaum (Weizmann Institute of Science, Israel). Portions of both samples were completely soluble in dichloromethane (DCM).

**Sample preparation**

The samples (5-10 μg) for DTMS were dissolved in 15-25 μl of DCM. An aliquot of 1-2 μl of this solution was added on the Pt/Rh filament of a direct insertion probe for in-source analysis. Typically 10 μg of sample is used for Py-GC/MS. The samples were dissolved in DCM, applied to a ferromagnetic wire (Curie point 770 °C) and dried in vacuo. After drying the sample wire was inserted into a glass liner, placed in the cold compartment of the pyrolysis unit, flushed with helium and then
moved into the pyrolysis chamber (220 °C) of the FOM 5LX Curie point pyrolysis unit [23].

*Direct Temperature-resolved Mass Spectrometry (DTMS) and Direct Temperature-resolved Mass Spectrometry Mass Spectrometry (DTMS/MS)*

DTMS experiments were carried out on a JEOL JMS SX-102 double focussing mass spectrometer (B/E). A direct insertion probe equipped with a resistively heated Pt/Rh filament was used. The filament (Pt/Rh 9:1, 100 μm) was heated with a rate of 0.5 A/min to an end temperature of about 800 °C. Ions were generated by EI (16 eV) in an ionisation chamber kept at 190 °C, accelerated to 8 kV, analysed from m/z 20-1000 (about 1 s cycle time) and post-accelerated to 10 kV. A JEOL MS-MP 9020D data system was used for data acquisition and processing. The DTMS spectra were obtained under low energy (16 eV) electron impact conditions to minimise fragmentation reactions of the ions.

DTMS/MS experiments were carried out on a JEOL JMS-SX/SX 102A tandem mass spectrometer (B/E/B/E). Collision Induced Dissociation (CID) was performed in the third Field Free Region using helium as a collision gas (1.5 10⁻³ Pa). The voltage of the collision cell was 2 kV. The same conditions as for DTMS were used concerning the probe, ion generation, acceleration and post-acceleration of ions and acquisition. The ions were analysed from m/z 0 to 375 at about 1 s cycle time. The resolution used was 3000.

*Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS)*

The experiments were carried out with a FOM-5LX Curie-point pyrolysis unit mounted on a Carlo Erba series 8565 HRGC MEGA 2 gas chromatograph. For separation a fused silica SGE BPX5 column (25 m, 0.32 mm i. d., 0.25 μm film thickness) used with helium as a carrier gas at a flow rate of 2 ml/min. For both samples the oven temperature was programmed from the initial 35 °C (for 0 min.) to a final 320 °C (for 10 min), with a ramp of 4 °C /min. The column was interfaced directly to a JEOL JMS DX-303 double focussing (E/B) mass spectrometer or a JEOL JMS-SX/SX 102A tandem mass spectrometer (B/E/B/E), using a home-built high temperature interface. Ions were generated by electron impact ionisation (70 eV) in the ionisation chamber, accelerated to 3 kV, respectively 8 kV, mass separated and post-accelerated to 10 kV before detection. The mass range was scanned from m/z 35-500, respectively m/z 40-800, with a cycle time of 1 s. A JEOL MS-MP 9020D data system was used for data acquisition and processing.

*Results and discussion*

*Bulk analysis: δ¹³C isotopic values*

δ¹³C Isotopic measurements on archaeological asphalt samples have been used as a proxy for their provenance [4, 5, 24]. The δ¹³C data on the Hafkenscheid (HS) and Dead Sea (DS) asphalt samples are listed in Table 1 together with values
from the literature. The isotopic values of HS matches that of DS very closely. Comparison with values of other Dead Sea asphalts published by Nissenbaum [4, 24] show a good match. Comparison with literature carbon isotopic data on asphalt and asphalt containing artefacts from the Mesopotamian area [5] shows significantly different values.

Table 1. Stable carbon isotope data (δ C\(^{13}\)) for sample HS and DS and asphalts available in the 19th century [5, 24].

<table>
<thead>
<tr>
<th>Asphalt sample</th>
<th>(\delta C^{13})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(VPDB units for HS and DS, PDB units for the other samples)</td>
</tr>
<tr>
<td>HS</td>
<td>-29.26 ± 0.10 %</td>
</tr>
<tr>
<td>DS</td>
<td>-29.31 ± 0.10 %</td>
</tr>
</tbody>
</table>

Asphaltenes (i.e. the C\(^{13}\) enriched fraction) of Middle Eastern asphalts; [5]

<table>
<thead>
<tr>
<th></th>
<th>(\delta C^{13})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Israel (Dead Sea) floating blocks</td>
<td>-29.4 (-29.1)–(-29.5)</td>
</tr>
<tr>
<td>archaeological</td>
<td></td>
</tr>
<tr>
<td>Iraq           archaeological</td>
<td>-27.6–(-28.6)</td>
</tr>
<tr>
<td>Syria          archaeological</td>
<td>-25.0–(-26.7)</td>
</tr>
<tr>
<td>Iran</td>
<td>-26.1–(-28.0)</td>
</tr>
</tbody>
</table>

The data obtained support the hypothesis that the Hafkenscheid asphalt may have its origin in present day Israel. However, according to Nissenbaum [25] asphalt from Hasbeya, Southern Lebanon, is “very similar geochemically to Dead Sea asphalt and most certainly has the same source and thermal history. This deposit has also been used since ancient times, and travellers to the area said it was quarried even in the 19th century”. As far as known to the current researcher, no recent detailed geochemical work has been done on the Hasbeya asphalt.

**Analytical pyrolysis studies**

The results from the DTMS and Py-GC/MS analysis of the asphalt sample from the Hafkenscheid collection (sample HS) are presented in Fig. 1, Fig. 4a, Fig. 5, Fig. 7a, Fig. 8a, Fig. 9a and Fig. 10a. Similar results obtained for the Dead Sea asphalt (sample DS) are shown in Fig. 2, Fig. 3, Fig. 4b, Fig. 6, Fig. 7b, Fig. 8b, Fig. 9b and Fig. 10b. Identified compounds are listed in Table 2. The number of compounds in pyrolysates of asphalt is very high, so mass chromatography of selected compounds was used to trace specific compounds and their distribution. Peaks were identified on the basis of their 70 eV mass spectrum and retention time. In some cases the identification of the mass spectra was complicated due to co-elution and/or their relatively low abundance of certain compounds.
DTMS and DTMS/MS data

The spectra of sample HS (Fig. 1b and 1c) and DS (Fig. 2b and 2c) show the classical characteristics of an asphalitic material: unresolved envelopes of hydrocarbon fragment ion series extending beyond mass 1000 (truncated at m/z 700 in the figures). The TIC of both asphaltic samples show fractions evaporating at relatively low temperature (maltenes) as well as fractions evolved by pyrolysis of cross-linked fractions (asphaltenes) at higher temperature (see Fig. 1a and Fig. 2a).

In the DTMS spectrum of the maltene fraction of HS (Fig. 1b), ions of specific compounds e.g. m/z 253 indicative of C- ring monoaromatic steroids (and m/z 267 from methylated isomers) are observed above the ion envelope. These compounds are well known markers for mature oil [11] and their presence is confirmed by GC/MS (see below). Other specific fragment ions of lower abundance in HS (Fig. 1b) are m/z 191 from hopanoid and related pentacyclic hydrocarbons, m/z 217 from regular steranes and m/z 231 (and m/z 245 from methylated isomers) from triaromatic steroids. At mass ranges higher than m/z 300, a series of peaks of low relative abundance are observed above the ion envelope suggesting the presence of several homologous compound series.

In the DTMS spectrum of the evaporated fraction of DS (Fig. 2b) the highest peak above the ion envelope is m/z 175 accompanied by m/z 161 and m/z 189 at mass differences of 14 amu. The second high peak is observed at m/z 253 for C- ring monoaromatic steroids accompanied by a peak at m/z 267 (from methylated isomers). Other peaks of interest including peaks at m/z 191 for hopanes, 217 for regular steranes, 231 for triaromatic steroids and its methylated isomer at m/z 245 are of much lower abundance. After m/z 300 several series of peaks with mass increments of 14 amu are observed. The most predominant of these series shows peaks at m/z 288 + m(CH_2), in which m varies from 1 to 20. The series starts with a few peaks of a relatively high abundance, followed peaks maximising at m/z 372 and then diminishing towards 568 (see details in Fig. 2d). The m/z values of this series in Fig. 2d suggest a homologous series that can be assigned to alkylated benzothiophenes, regular steranes or triaromatic steranes. DTMS/MS of m/z 358 shown in Fig. 3 shows the characteristic fragment ions (m/z 161, 175 and 189) of an alkylbenzothiophene with an alkyl chain length C_{12}H_{25}. Other ions in this series analysed by DTMS/MS and information obtained by Py-GC/MS confirm that the peak series m/z 288 + m(CH_2) belongs to a series of alkylbenzothiophenes. The high peaks in the DTMS profile (Fig. 2b) at m/z 161, 175 and 189 are the fragment ions corresponding to alkylbenzothiophenes (see Table 2). Two other series are seen in the DTMS spectrum of DS one of which shows peaks at m/z 310 + k(CH_2), in which k= 1-14 has the highest relative abundance but still quite low when compared to the previous series. The envelope of the series diminishes towards higher m/z range. DTMS/MS and Py-GC/MS identified this series as due to alkylated dibenzothiophenes. The series showing peaks at m/z 370, 398, 412, 426, 440, 454, 468, 482, 496, are of a much lower abundance in the spectrum (Fig 2b and 2d), but are tentatively identified as a series of hopanes based on the Py-GC/MS data.

The homologous series of compounds in the DTMS of the DS asphalt are not very prominent in the HS asphalt. However, DTMS/MS and Py-GC/MS studies of the HS asphalt confirm the presence of a series alkylbenzothiophenes with peaks at m/z 330 + n(CH_2), where n= 1-10. The distribution follows the shape of the ion envelope, with slightly higher values at m/z 358 and m/z 428 (Fig. 1d). From the series of hopanes, as suggested for DS, just a few peaks are present in the data of HS. Only the
Fig. 1. DTMS fractionation of sample HS: (a) TIC of DTMS spectrum, (b) evaporation fraction, (c) the high temperature fraction, (d) detail of a series of compounds seen in (b); • was used to mark the series of alkylbenzothiophenes and ■ for a series of hopanes.
Fig. 2. DTMS fractionation of sample DS: (a) TIC of DTMS spectrum, (b) evaporation fraction, (c) the high temperature fraction, (d) detail of series of compounds seen in (b); '○' was used to mark the series of alkylbenzothiophenes, ' ▽ ' for series alkyldibenzothiophenes and ' ■ ' for series of hopanes.
peaks at m/z 398, 412, 426 and 440 with a relatively low abundance are visible above the envelope.

Both DS and HS DTMS evaporation spectra (Fig. 1b and 2b) show fragment ions of alkanes (m/z 43, 57, 71) and alkynes (m/z 55, 69, 83, 97, 111, 125). Other fragment ions like m/z 95, 109, 123 or m/z 129, 143, 157, 171 or m/z 169, 183, which differ by 14 amu, are observed but their significance is not clear.

The high temperature part of the DTMS spectra of HS and DS (Fig. 1c and 2c) mainly show fragment ions from paraffinic hydrocarbons (alkanes, alkenes and alkadienes) resulting from the thermal degradation of the paraffinic links between the aromatic sheets structures. The pyrolysed fractions in the HT part of the DTMS spectrum of HS and DS show less variation compared to their evaporated fraction.

The highest peaks above the ion envelope in the DTMS data of the high temperature fraction of HS (Fig. 1c) are observed as fragment ions for alkanes (m/z 43, 57, 71, 85), alkynes (m/z 41, 55, 69, 83, 97, 111, 125, 139, 153), alkadienes (m/z 67, 81, 95, 109, 123, 137) and a very high peak at m/z 125, possibly from alkylthiophenes. Above m/z 300 a few peaks of very low relative abundance can be still observed at m/z 412, 440, 454 and also at m/z 316, 344, 372, 414, 442, 470 and 512. These mass peaks are originating from the same series as seen in the evaporated fraction.

In the high temperature DTMS of DS (Fig. 2c) the highest peaks observed are the fragment ions for alkanes (m/z 43, 57, 71, 85), alkynes (m/z 41, 55, 69, 83, 97, 111, 125, 139) and alkadienes (m/z 67, 81, 95, 109, 123, 137). Other peaks of higher abundance above the ion envelope are fragment ions at mass increments of 14 amu from alkylbenzothiophenes at m/z 161, 175, 189 and 203. Peaks of low relative abundance at higher than 300 m/z range form two series observed or in part already observed in the evaporated fraction. A first series shows peaks differing by 14 amu starting at m/z 288 till m/z 568, which is identical the alkylbenzothiophenes series to the highest series seen in the evaporated fraction. This suggests that these compounds are partly adsorbed or encapsulated in the asphaltene network. Another series displaying peaks between m/z 300 and m/z 566, differing by 14 amu, are tentatively identified as an unsaturated alkylbenzothiophenes series originating from the asphaltene network by thermal cleavage.

**Fig. 3. MS/MS of m/z 358 of sample DS.**
Py-GC/MS data

The Py-GC/MS data of HS and DS show homologous series of straight chain hydrocarbons of normal alkenes and alkanes (see the TIC in Fig. 4a and 4b, Table 2). At low elution temperature the n-alkenes and n-alkanes are separated (marked in Fig. 4a and 4b and Table 2 as ‘c: 1’/c: 0’ in which ‘c’ is the number of carbon atoms present in the molecule).

Table 2. List of compounds identified in the TIC of Py-GC/MS data of the sample HS and sample DS.

<table>
<thead>
<tr>
<th>Classes of compounds</th>
<th>MW</th>
<th>Important EI fragment ions (m/z)</th>
<th>Label</th>
<th>Sample HS</th>
<th>Sample DS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aliphatic cross links</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkanes</td>
<td>85</td>
<td></td>
<td>c: 0</td>
<td>+ (C2-C35)</td>
<td>+ (C7-C34)</td>
</tr>
<tr>
<td>Alkenes</td>
<td>83</td>
<td></td>
<td>c: 1</td>
<td>+ (C7-C34)</td>
<td>+ (C7-C34)</td>
</tr>
<tr>
<td><strong>Alkylbenzenes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>78</td>
<td>78, 77, 63, 51</td>
<td>B</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C1-benzene (toluene)</td>
<td>92</td>
<td>92, 91, 65, 51</td>
<td>B1</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C2-benzene</td>
<td>106</td>
<td>106, 105, 91, 77</td>
<td>B2</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C3-benzene</td>
<td>120</td>
<td>120, 119, 105, 91, 77</td>
<td>B3</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Alkynaphthalenes</strong></td>
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<tr>
<td>Naphthalene</td>
<td>128</td>
<td>128, 102</td>
<td>N</td>
<td>+</td>
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<tr>
<td>C1-naphthalene</td>
<td>142</td>
<td>142, 115</td>
<td>N1</td>
<td>+</td>
<td>+</td>
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<tr>
<td>C2-naphthalene</td>
<td>156</td>
<td>156, 141, 115</td>
<td>N2</td>
<td>+</td>
<td>+</td>
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<tr>
<td>C3-naphthalene</td>
<td>170</td>
<td>170, 155</td>
<td>N3</td>
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<td>+</td>
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<tr>
<td><strong>Alkylbenzothiophenes</strong></td>
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<td></td>
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<tr>
<td>C1-benzothiophene</td>
<td>148</td>
<td>148, 147</td>
<td>BT1</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C2-benzothiophene</td>
<td>162</td>
<td>162, 161, 147</td>
<td>BT2</td>
<td>+</td>
<td>+</td>
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<tr>
<td>C3-benzothiophene</td>
<td>176</td>
<td>176, 175, 161, 147</td>
<td>BT3</td>
<td>+</td>
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<td>C4-benzothiophene</td>
<td>190</td>
<td>190, 189, 175, 161, 147</td>
<td>BT4</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Alkyl dibenzothiophenes</strong></td>
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<tr>
<td>C1-dibenzothiophene</td>
<td>198</td>
<td>198, 197, 165</td>
<td>DBT1</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C2-dibenzothiophene</td>
<td>212</td>
<td>212, 211, 197, 184</td>
<td>DBT2</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C3-dibenzothiophene</td>
<td>226</td>
<td>226, 225, 211</td>
<td>DBT3</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C4-dibenzothiophene</td>
<td>240</td>
<td>240, 239, 225</td>
<td>DBT4</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td><strong>Hopanoid compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C29-hopane</td>
<td>412</td>
<td>191</td>
<td>H29</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>C31-hopane</td>
<td>426</td>
<td>191</td>
<td>H31</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

1 up to C26 the alkene-alkane peaks are resolved
2 up to C26 the alkene-alkane peaks are resolved
3 detected as methyl-substituted benzene
4 detected as dimethyl-/ethyl- substituted benzene
5 detected as trimethyl-/dimethyl, ethyl-/ normal or isopropyl- substituted benzene
6 detected as α and β methyl- naphthalene
7 detected as α-α', α-β , β-β, β-β', α-β dimethyl- naphthalene
8 detected as trimethyl- naphthalene
9 detected as 17a, 21β (H)-30-hopane
10 detected as 17a, 21β (H)-29-homohopane, isomers 22S and 22R
Table 2 continued.

<table>
<thead>
<tr>
<th>Classes of compounds</th>
<th>MW</th>
<th>Important EI fragment ions (m/z)</th>
<th>Label</th>
<th>Sample HS</th>
<th>Sample DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C32-hopane11</td>
<td>440</td>
<td>191</td>
<td>H32</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(22S, 22R)</td>
<td>(22S, 22R)</td>
</tr>
<tr>
<td>Terpanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gammacerane (C30)</td>
<td>412</td>
<td>191</td>
<td>G12</td>
<td>+</td>
<td>+?</td>
</tr>
<tr>
<td>C-ring monoaromatic steroids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C27-monoaromatic steroid13</td>
<td>366</td>
<td>253</td>
<td>MA27</td>
<td>+?</td>
<td>+?</td>
</tr>
<tr>
<td>C28-monoaromatic steroid14</td>
<td>380</td>
<td>253</td>
<td>MA28</td>
<td>+?</td>
<td>+?</td>
</tr>
<tr>
<td>C29-monoaromatic steroid12</td>
<td>394</td>
<td>253</td>
<td>MA29</td>
<td>+?</td>
<td>+?</td>
</tr>
</tbody>
</table>

At higher retention temperatures, separation is not achieved and the n-alkene + alkane peaks are simply marked with their carbon number. HS shows a distribution of straight chain resolved hydrocarbons in Fig. 4a ranging from C6 to C31 (alkenes) and from C7 to C35 (alkanes), on top of an unresolved envelope of other hydrocarbon compounds starting near the C15 hydrocarbon. The GC conditions chosen leave compounds unresolved till C7 in the Py-GC/MS data. The alkenes are resolved from alkanes till C26H54. A similar distribution is observed for sample DS with aliphatic chains ranging from C6 to C31 (alkenes) and from C7 to C34 (alkanes) (Fig. 4b). The straight chain hydrocarbons result from the aliphatic cross bridges in the asphaltene macromolecule [1] by thermally induced radical cleavage processes during pyrolysis leading to homologous series of alkanes and alkenes. The isoprenoidic compounds phytane and pristane are absent in the Py-GC/MS data of both samples suggesting that biodegradation processes have been severe [11].

Mass chromatogram generation was used to trace specific biomarker compounds (Fig. 5-6) and alkyl-aromatic sheet structures (Fig. 7-10). The relative distribution of the compounds identified in this way allows the tracing of the original source and the geothermal maturity of an asphalt. Connan et al. [5] has shown this successfully for archaeological materials from Mesopotamia. The identified compounds are given in Table 1 with structures of typical markers (aliphatic cross-links such as alkanes and alkenes, aromatic sheet compounds such as alkylbenzenes, alkylnaphthalenes and alkylbenzo thiophenes) and biomarkers (steroid and hopanoid compounds) present in asphalt illustrated in Scheme 1.

---

11 detected as 17α, 21β (H)-29-bishomohopane, isomers 22S and 22R
12 detected as gammacerane (G)
13 tentatively identified as C27H44 C-ring monoaromatic steroids, probably isomers (I 20S and/or V 20S) in the 1st group of peaks, (I 20R + V 20R and/or II 20S) in the 2nd group of peaks, (II 20R) in the 3rd group of peaks [11]
14 tentatively identified as C28H44 C-ring monoaromatic steroids, probably isomers (I 20S and/or V 20S) in the 2nd group of peaks, (II 20S and/or I 20R + V 20R) in the 3rd group of peaks, (II 20S and/or II 20R) in the 4th group of peaks [11]
15 tentatively identified as C29H44 C-ring monoaromatic steroids, probably isomers (I 20S + V 20S) in the 3rd group of peaks, (I 20R + V 20R) in the 4th group of peaks, (II 20R) in the 5th group of peaks [11]
Mass chromatograms of characteristic fragment ions of C-ring monoaromatic steroids MAx (m/z 253), various steroid skeletons (m/z 217 + 231 + 245 +253 + 267) and hopanes Hi (m/z 191) are plotted in Fig. 5 of HS and Fig. 6 of DS. M/z 217 is a common fragment ion for 14α (H)-steranes. M/z 231 and m/z 253 (245 and 267 for their methyl substituted compounds) represent common fragments for triaromatic steroids and monoaromatic steroids (MA), [11]. Only the C-ring monoaromatic steranes, m/z 253 form a predominant mass chromatogram profile in the Py-GC/MS data of HS (Fig. 5b and 5c). The other steranes form an unresolved envelope. This is also observed in DS (Fig. 6b and 6c).

Fig. 4. Py-GC/MS TIC of sample HS (a) and sample DS (b); the presence of dibutyl phthalate is marked with ‘*’. 
Scheme 1. Structures of specific asphalt markers and biomarkers.
Although there could be a bias about the influence of the thermal exposure during the analytical process on the steroid distribution, no influence was found when distribution in maltenes analysed by on-column GC/MS and thermally extracted fractions in Curie point Py-GC/MS of a standard reference asphalt provided by Shell were compared (chapter 5). The ion profiles of the monoaromatic steroids in HS and DS are almost identical to the literature [11, 26] and show a series

Fig. 5. Partial mass chromatograms of (a) alkanes as markers for aliphatic cross-links (m/z 85), (b) C-ring monoaromatic steroids MA (m/z 253), (c) steroid hydrocarbons (m/z 217+231+245+253+267) and biomarker (d) hopanes H (m/z 191) in Py-GC/MS data of sample HS.
Chapter 2

of non-rearranged steranes and rearranged C-ring monoaromatic steranes ranging from C_{27} to C_{29}. Peters and Moldowan [11] list eight known compounds in petroleum. Four of them match the non-rearranged 5(H), 10(CH_{3}) C-ring monoaromatic steranes: I (5β, 10β), II (5α, 10β), III (5α, 10α), IV (5β, 10α). The other four structures, V (5β, 10β), VI (5β, 10α), VII (5α, 10α) and VIII (5α, 10β) correspond to the rearranged 5(CH_{3}), 10(H) C-ring monoaromatic steranes.

Fig. 6. Partial mass chromatograms of (a) alkanes as markers for aliphatic cross-links (m/z 85), (b) C-ring monoaromatic steroids MA, (m/z 253), (c) steroid hydrocarbons (m/z 217+231+245+253+267) and biomarker (d) hopanes H, (m/z 191) in Py-GC/MS data of sample DS.
They specify that only structures I, II and V, shown in Scheme 2, are the most common and used in quantification of MA steroids [11].

**Scheme 2.** Most common structures of non-rearranged C-ring monoaromatic steroids (structures I and II) and rearranged C-ring monoaromatic steroids (structure V). [11, 26]

According to the literature five groups of peaks are expected and symmetrically distributed around the middle one. The first group contains two peaks of the C\textsubscript{27} homologues. The second group has four peaks, the first two for the C\textsubscript{27} homologues and the last two for the C\textsubscript{28} homologue, possibly reversed [11]. The third group includes a C\textsubscript{27} homologue, two peaks for the C\textsubscript{28} homologues and one peak for the C\textsubscript{29} homologues. The fourth group has two C\textsubscript{28} homologues and one peak for the C\textsubscript{29} homologues. The last group is in fact just one peak, a C\textsubscript{29} homologue. The corresponding isomers for each homologue in the group are given in Table 3.

**Table 3. Isomers of C-ring MA steroids.** [11]

<table>
<thead>
<tr>
<th>Group</th>
<th>C\textsubscript{27}</th>
<th>C\textsubscript{28}</th>
<th>C\textsubscript{29}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st}</td>
<td>120S, V 20 S</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2\textsuperscript{nd}</td>
<td>120R + V 20R, II 20S</td>
<td>120S, V 20S</td>
<td>-</td>
</tr>
<tr>
<td>3\textsuperscript{rd}</td>
<td>II 20R</td>
<td>II 20S, I 20R + V 20R</td>
<td>I 20S + V 20S</td>
</tr>
<tr>
<td>4\textsuperscript{th}</td>
<td>-</td>
<td>II 20S, II 20R</td>
<td>I 20R + V 20R</td>
</tr>
<tr>
<td>5\textsuperscript{th}</td>
<td>-</td>
<td>-</td>
<td>II 20R</td>
</tr>
</tbody>
</table>

In the data from both HS and DS, these five groups of peaks are observed, with a similar relative distribution around the middle group as mentioned above. The peaks shown in the m/z 253 partial mass chromatogram (Fig. 5 and 6) and listed in Table 2 are tentatively identified as C-ring MA steranes on the basis of the presence of the specific fragment m/z 253 and the rather good match of their relative distribution with the data from literature. Due to their low relative abundance and the complexity of the asphaltene compound envelope, the corresponding parent ions could not be discriminated from isobaric alkylbenzothiophenes molecular ions. The C–ring MA’s in Fig. 5 and 6 were tentatively identified as the first group being C\textsubscript{27} homologues, the second group C\textsubscript{27} and C\textsubscript{28} homologues, the third group C\textsubscript{27}, C\textsubscript{28} and
Fig. 7. Partial mass chromatograms of alkylbenzenes $B_i$ of sample HS (a) and sample DS (b) in Py-GC/MS data; the isomers are marked with '•' and '▲' to distinguish between two consecutive homologues.
Fig. 8. Partial mass chromatograms of alkynaphthalenes $N_i$ of sample HS (a) and sample DS (b) in Py-GC/MS data; the isomers are marked with ‘•’.
Fig. 9. Partial mass chromatograms of alkylbenzothiophenes $BT_i$ of sample HS (a) and sample DS (b) in Py-GC/MS data; '●' is used to mark the saturated compounds and '○' the unsaturated homologues.
Fig. 10. Partial mass chromatograms of alkyl dibenzothiophenes DBT$_i$ of sample HS (a) and sample DS (b) in Py-GC/MS data; the isomers are marked with ‘●’.
Chapter 2

C_{29} homologues, the fourth group C_{28} and C_{29} homologues and the fifth group as the C_{29} homologues. No diasteranes (m/z 259) are present in sample HS and DS but these compounds are not expected in a Dead Sea asphalt type [5].

The hopanes in HS (C_{27} to C_{32}) have a low relative abundance with respect to the MA’s but their mass spectra are recognisable. Relatively abundant in Fig. 5 are the Tm (C_{27}) trisnorhopane isomer, norhopane (C_{29}), hopane (C_{30}), homohopane (C_{31}) 22S and 22R isomers and the tentatively identified bishomohopane (C_{32}) 22S and 22R isomers. The T, trisnorhopane isomer is not present, but a peak with a similar relative retention time but a parent ion at m/z 368 appears before the T_m. The peak between the C_{31} and C_{32} hopanoid homologues could be identified as gammacerane. [11].

The abundance of hopanes in DS (C_{29} to C_{31}) is relatively low compared to the data available in the literature on other Dead Sea asphalt samples [5, 27]. In Fig. 6 the trisnorhopane isomer T_m (C_{27}), norhopane (C_{29}), hopane (C_{30}) are positively identified, while homohopane (C_{31}) 22S and 22R isomers and bishomohopane (C_{32}) 22S and 22R isomers are tentatively identified on the basis of relative retention time and some characteristic mass peaks. The peak between the C_{31} and C_{32} hopanoid homologues is tentatively identified as gammacerane.

The Dead Sea asphalt sample analysed and the asphalt sample from the Hafkenschei collection contain a large number of algal-derived steroid biomarkers mainly present as C-ring monoaromatic steroid hydrocarbons. Both samples have a low abundance of bacterially derived hopanoid markers.

Aromatic hydrocarbons released from asphaltenes in HS and DS are present as alkylbenzenes, alkylnaphthalenes, alkylanthracenes, alklyphenanthrenes, alkylbenzothiophenes and alkyl dibenzothiophenes. Alkylbenzenes (m/z 91, 105, 119) are shown in Fig. 7a and 7b. Alkylnaphthalenes (m/z 142, 156, 170) are given in Fig. 8a and 8b. Alkylbenzothiophenes (m/z 148, 162, 176) are shown in Fig. 9a and 9b. Alkyl dibenzothiophenes (m/z 198, 212, 226, 240) are shown in Fig. 10a and 10b. Alkylanthracenes and alklyphenanthrenes are not shown. There is good degree of similarity in the distribution of all these marker compounds between HS and DS. These aromatic subunits are typical for asphaltenes [5] and good evidence that the Hafkenschei sample was indeed a natural asphalt. The data obtained for the HS and DS samples were compared to several other asphalts kindly provided by Shell Research and Technology Centre in Amsterdam. All marker compounds are present in these samples but their relative distribution can differ between asphalts of different origins. The presence of the sulphur containing benzo thiophenes (BT) and dibenzothiophenes (DBT) [5] is another indication for the asphaltic nature of the Hafkenschei sample. Both dibenzothiophenes and aromatic steroids are considered to be the most reliable markers for asphalt by Connan et al. [5] due to their resistance against bacterial degradation.

Conclusions

The DTMS and Py-GC/MS data confirm that the Hafkenschei "asphalt" is indeed a natural asphalt sample. The distribution of the "biomarker" compounds is not unlike asphalts from the Middle Eastern region, but further comparative studies on natural asphalts available in the 19th century should be performed to assure its provenance. The match with the Dead Sea reference sample is good considering the history of the samples. The Hafkenschei sample has been exposed to air for about 200 years and it is not unlikely that this will have an effect on the sulphur containing compounds in the asphalt. Moreover studies by Connan et al. [5] have shown that
asphalts near the Dead Sea may differ in composition due to exposure or thermal history. The methodology applied exposes a large number of marker compounds that may be very useful for asphalt characterisation in asphalt pigmented paints from paintings. Preliminary studies of asphalt pigmented paints in the FOM-AMOLF laboratory have already shown that such markers can be traced. The proposed methodology is also very applicable to the extremely small samples that may be obtained from paintings. A complicating factor in painting studies will be the paint manufacturing process. The data show that many characteristic markers for asphalt can be evaporated or released by pyrolysis. So any paint manufacturing pretreatment involving roasting of the asphalt will likely result extensive or even complete loss of the marker compounds identified. In addition, restoration treatment of paintings often implies exposure to solvents, which may displace or even extract solvent sensitive materials such as the maltene fraction. In the case of asphalt, the solvent extractable biomarker compounds are especially sensitive, putting a bias on the validity of hopanes as markers of asphalt in paintings with an unknown history of preservation. The asphaltene fractions of asphalt are much less likely to be effected by solvent cleaning and thus may provide a rich potential source of asphalt markers in paintings.

References


