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Nadine Tachon, Farid Jahouh, Michel Delmas, Joseph H. Banoub. Structural determination by atmospheric pressure photoionization tandem mass spectrometry of some compounds isolated from the SARA fractions obtained from bitumen. *Rapid Communications in Mass Spectrometry*, 2011, 25 (18), pp.2657-2671. 10.1002/RCM.5156 . hal-03469353

HAL Id: hal-03469353

<https://hal.science/hal-03469353>

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To link to this article: DOI:10.1002/RCM.5156
URL: <http://dx.doi.org/10.1002/RCM.5156>

To cite this version: Tachon, Nadine and Jahouh, Farid and Delmas, Michel and Banoub, Joseph H. (2011) Structural determination by atmospheric pressure photoionization tandem mass spectrometry of some compounds isolated from the SARA fractions obtained from bitumen. *Rapid Communications in Mass Spectrometry*, vol. 25 (n°18). pp. 2657-2671. ISSN 0951-4198

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Structural determination by atmospheric pressure photoionization tandem mass spectrometry of some compounds isolated from the SARA fractions obtained from bitumen

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We have identified compounds obtained from the SARA fractions of bitumen by using atmospheric pressure photoionization mass spectrometry and low-energy collision tandem mass spectrometric analyses with a QqToF-MS/MS hybrid instrument. The identified compounds were isolated from the maltene saturated oil and the aromatic fractions of the SARA components of a bitumen. The QqToF instrument had sufficient mass resolution to provide accurate molecular weight information and to enhance the tandem mass spectrometry results. The APPI-QqToF-MS analysis of the separated compounds showed a series of protonated molecules $[M+H]^+$ and molecular ions $[M]^{+*}$ of the same mass but having different chemical structures, in the maltene saturated oil and the aromatic SARA fractions. These isobaric ions were a molecular ion $[M_2]^{+*}$ at m/z 418.2787 and a protonated molecule $[M_5+H]^+$ at m/z 287.1625 in the saturated oil fraction, and molecular ions $[M_6]^{+*}$ at m/z 418.1584 and $[M_7]^{+*}$ at m/z 287.1285 in the aromatic fraction.

The identification of this series of chemical compounds was achieved by performing CID-MS/MS analyses of the molecular ions $[M]^{+*}$ ($[M_1]^{+*}$ at m/z 446.2980, $[M_2]^{+*}$ at m/z 418.2787, $[M_3]^{+*}$ at m/z 360.3350 and $[M_4]^{+*}$ at m/z 346.2095) in the saturated oil fraction and of the $[M_5+H]^+$ ion at m/z 287.1625 also in the saturated oil fraction. The observed CID-MS/MS fragmentation differences were explained by proposed different breakdown processes of the precursor ions. The presented tandem mass spectrometric study shows the capability of MS/MS experiments to differentiate between different classes of chemical compounds of the SARA components of bitumen and to explain the reasons for the observed mass spectrometric differences. However, greater mass resolution than that provided by the QqToF-MS/MS instrument would be required for the analysis of the asphaltene fraction of bitumen.

Crude oil is a mixture of naturally occurring hydrocarbons that can be refined into diesel, gasoline, heating oil, jet fuel, kerosene, and thousands of other petrochemical products.^[1] Bitumen is the residual or by-product obtained by fractional distillation of crude oil,^[2] and it is a highly viscous, black and sticky mixture of organic liquids, composed primarily of highly condensed chemical compound. It is the heaviest fraction of crude oil, has the highest boiling point and is also referred to as 'asphalt' or 'asphalt cement'.^[3] Bitumen is employed for different applications such as road engineering and for the solidification of waste. It is composed of two separable hydrocarbon fractions: the maltenes and the asphaltene.^[4,5] The maltene family can be divided into three hydrocarbon portions: the saturated oil, the aromatic oil and the resin. The constituents of bitumen are typically classified

by their solubility in organic solvents, in the following order: saturated, aromatic, resin, and asphaltene (SARA).^[6-8] The SARA fractionation starts with the removal of asphaltene by precipitation with a saturated hydrocarbon such as heptane.

Subsequent elution with a series of increasingly polar solvents yields the maltene fraction. Elution of the maltene with a non-polar solvent such as hexane affords the saturated fraction. Subsequent elution of the maltene fraction with toluene affords the aromatic fraction. The resin fractions are separated by using a more polar solvent.

Comparisons between the elemental composition and the spectroscopic properties of the maltene and asphaltene families indicate that the asphaltene are more aromatic than the maltene and that they also contain more heteroatoms.^[4,5] The average molecular weight calculated for the maltene aromatic oil fraction of bitumen is around 800 u and it has been shown that about 30% of the carbon atoms are part of aromatic rings.^[9] On the other hand, no identifiable chemical structures have been proposed for the resin fraction and very few studies dealing with the determination of the constituent chemical structures of maltene have ever been published.

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The asphaltene fraction has been studied extensively because of its role in oil field flow assurance and more recently because of its application as a geochemical marker that can indicate the geological structure of oil reservoirs. Optimizing the value of these sources and converting them into something other than blacktop (concrete bitumen) requires a detailed molecular-level understanding of the maltene and asphaltene families.^[10–12] Petroleum asphaltene are extremely complex substances consisting of thousands of compounds containing highly aromatic cores, long-chain aliphatic groups, heteroatoms (sulfur, nitrogen, and oxygen), as well as trace quantities of heavy metals (vanadium and nickel). Therefore, it is extremely difficult to elucidate the molecular structure of petroleum asphaltenes, and some fundamental aspects of asphaltene chemistry are still being debated.^[6–8,13] Recent structural models suggest that asphaltene molecules are composed of an aromatic core with an average of six condensed aromatic rings, substituted by *n*-alkyl groups averaging C-8 in length. In addition, bridging polymethylene groups may be present which connect the aromatic core to smaller aromatic and thiophenic rings. Most strikingly, the average asphaltene molecular mass is still unknown to within an order of magnitude. The average molecular weight of individual asphaltene molecules is less than 1000 u. However, it has been reported that the asphaltene molecules interact strongly in solution, forming colloidal aggregates, with very high apparent molecular weights.^[14] Over the past decades, several groups have probed the asphaltene molecular-mass distribution with a variety of analytical, chromatographic and molecular-diffusion-based techniques. These studies have included asphaltene pyrolysis, chemical reduction and oxidation (RICO) with catalysts together with the use of many analytical techniques such as H-1 and C-13 NMR, FT-IR, UV-vis spectra, Extended X-ray Absorption Fine Structure (EXAFS), ESR, and X-ray diffraction (XRD) to investigate the asphaltene structure at the molecular level.^[15–22] Despite the great differences in their ionization mechanisms, measurements using GC/EI-MS,^[23] CI-MS,^[24] field desorption ionization,^[25] electrospray ionization,^[26–28] and atmospheric pressure chemical ionization^[29] all give an asphaltene molecular-mass distribution that peaks in the range of 500–1000 u. However, measurements employing ²⁵²Cf plasma desorption and fast atom bombardment ionization show a pronounced tail, at times extending beyond 10000 u, and there was no experimental data suggesting that this high mass value corresponded to the formation of aggregates.^[16,30,31] Recently, two newly developed MS methods appear to have mitigated those concerns.^[26–28,32] Studies employing laser desorption/ionization mass spectrometry (LDI)^[33–35] and ion mobility mass spectrometry (IM-MS)^[35] indicate a high-molecular-weight limit of significantly less than 10000 u.^[36] Pomerantz and coworkers developed a two-step Laser Mass Spectrometry (L²MS) technique to measure the molecular mass distribution of asphaltenes.^[33,34] For the compositional analysis of petroleum-derived materials such as asphaltene, Marshall and coworkers used electrospray ionization with ultra high-resolution Fourier transform ion cyclotron resonance mass spectrometry to measure the polar N-, S- and O-containing compounds, and their different combinations.^[26]

In this manuscript, we describe the analysis of novel compounds isolated from the SARA fractions, namely the maltene fraction of bitumen, using photoionization mass

spectrometry (APPI-MS) and low-energy collision-induced dissociation tandem mass spectrometry (CID-MS/MS) with a hybrid QqToF-MS/MS instrument.

EXPERIMENTAL

Sample preparation

Bitumen was furnished by La Société des Pétroles Shell, Colombes, France. It has a penetrability (consistency at 25°C) of between 35 and 50 dmm and a ball and ring temperature (at which the bitumen reaches consistency) of about 52°C.

Asphaltene separation

The asphaltene fraction was precipitated with heptane with a mass ratio of bitumen/heptane of about 1:40 by refluxing for 2 h. Filtration was performed with a 4.5 µm pore size filter.

The asphaltene fraction was washed with heptane at room temperature, until the eluent was clear. It was then extracted from the filter with chloroform. The chloroform fraction was recovered using rotary evaporation under vacuum to afford the crude asphaltene fraction.

Maltene separation

The maltenes were separated by column chromatography on columns packed with silica gel. The silica (70–200 µm and surface area 550 m²/g) was activated at 250°C for 36 h. The solvents were introduced manually into the column from a flask. The elution of the saturated oil was performed using *n*-heptane, and the aromatic oils were then eluted using toluene. Finally, the extraction of the resin was carried out in two stages: first by elution with a 50:50 mixture of methanol and dichloromethane, and then by elution with 100 mL of dichloromethane and 100 mL of methanol.

After chromatographic separation, each fraction was dried to remove the solvent and weighed to calculate the final percentage composition. The solvents were removed by rotary evaporation under vacuum.

Characterization by thin-layer chromatography (TLC)

The aluminium TLC sheets (silica gel 60) were activated at 200°C for 36 h. The sheets were visualized with elution solvents under UV light (265 and 364 nm). The solvents used depended on the specific fractions being analyzed according to a previously established protocol.^[37]

IR Analysis

Viscous fractions, such as aromatics and saturated oil, were analyzed by ATR-FTIR whereas solid fractions, such as the resins and asphaltenes, were analyzed by other FTIR techniques.

APPI-QqToF-MS analysis

APPI-MS was performed using an Applied Biosystems (Foster City, CA, USA) API QSTAR XL MS/MS quadrupole orthogonal time-of-flight (QqToF)-MS/MS hybrid instrument having a moderate mass resolution of 18000 FWHM. APPI was performed with a PhotoSpray ion source (Applied Biosystems) operated at 1300 V and at a temperature of 400°C, with all

acquisitions performed in the positive ion mode. Samples were infused into the mass spectrometer with an integrated Harvard syringe pump (Harvard Apparatus Canada, Saint-Laurent, QC, Canada) at a rate of 0.1 mL/min. The auxiliary nebulizer gas (N₂) pressure was set at 25 psi, the nebulizer gas (N₂) pressure at 74 psi, and the curtain gas (N₂) pressure at 30 psi. The declustering potential (DP) was set at 100 V, and the focus potential (FP) was adjusted to 100 V. Toluene was selected as the dopant for its ability to undergo trouble-free photoionization at 8.83 eV. The eluent was composed of methanol/chloroform (1:1). No modifier was used to enhance ion production.

The mass calibration of the ToF analyzer in the positive ion mode was performed with the PhotoSpray ion source, using 1,2,3,5-tetra-*O*-acetyl- β -D-ribofuranose to observe the exact masses of the [M+H]⁺ ion [C₁₃H₁₉O₉]⁺ at *m/z* 319.1024 and the [M+H-AcOH]⁺ ion [C₁₁H₁₅O₇]⁺ at *m/z* 259.0812. Calibration for higher masses was performed with hexa-*O*-acetyl- β -D-lactopyranose to observe the [M+H]⁺ ion [C₂₈H₃₇O₁₉]⁺ at *m/z* 677.1929. The APPI mass spectra were recorded with higher DP values varying from 80 to 120 V.

Low-energy CID-MS/MS experiments

Product ion spectra were obtained on the same instrument as described above. Nitrogen was used as the collision gas for MS/MS analyses. A collision energy (CE) of 20 eV was used for all the CID-MS/MS analyses and the CAD (collision gas control) value of 4 remained unchanged for all the analyses. This ensured that all the MS/MS analyses took place under identical conditions and each acquisition allowed the precursor ion to remain abundant in the product ion spectra. We have used, in general, a high mass resolution for the MS/MS selection of the precursor ion for simplification of the analysis. In addition, re-confirmation of the various established fragmentation routes was effected by conducting a series of APPI in-source collision-induced experiments (APPI-QqToF-CID-MS/MS) on the same Applied Biosystems API QSTAR XL instrument. Fragmentation in the atmospheric pressure/vacuum interface was achieved by ramping the DP from 102 to 150 V, until the characteristic product ions were observed in the spectra. These ions were then selected as precursors for the subsequent MS/MS acquisitions. The fragmentation conditions were the same as in the MS/MS experiments described above.

RESULTS AND DISCUSSION

Precipitation of 10 g of a 35/50 bitumen afforded 1.3 g of asphaltenes after filtration. The residue contained maltenes diluted in *n*-heptane. After evaporation of the heptane, 2 g of maltenes separated by column chromatography afforded saturated oil, aromatic oil and resins (Table 1).

Although moderate mass resolution mass spectra (18000 FMHW) can provide the probable elemental composition of molecular and product ions for compound identification, there was no chromatographic separation attempted given the complexity of the SARA fractions. However, mass spectrometry provides an additional dimension of separation based on mass-to-charge ratio. Thus, the molecular weight

Table 1. SARA fractions obtained by precipitation with heptane

	Saturated oil	Aromatic oils	Resins	Asphaltenes
Fraction (% of total mass)	11	56	20	13

and product ion information provided by APPI-MS and tandem mass spectrometric analyses makes it possible to differentiate these species to some extent. The postulated chemical compositions indicated in Supplementary Tables S1–S10 (Supporting Information) were based on the accurate masses measured by APPI-QqToF-MS and the product ions observed in CID-MS/MS experiments.

The use of atmospheric pressure photoionization (APPI) has grown rapidly over the last decade and its popularity is due to its success in allowing the ionization of non-polar compounds, weak acids, and halogenated organic compounds. Unlike with ESI and APCI, photoionization is not based on charge affinity, which makes APPI the ideal tool for ionizing non-polar compounds. The principal mechanism for the photoionization of a molecule *M* is photon absorption and subsequent electron ejection to form the molecular ion [M]⁺. Because the photon energy typically is just above the ionization energy, the molecular radical ion is less susceptible to dissociation. In the presence of protic solvents the molecular radical cation [M]⁺ can attract a hydrogen atom during gas-phase ionization to produce the protonated molecule [M+H]⁺. Chromatographic separation prior to MS analyses presents many advantages for mixture analyses. However, APPI-MS makes it possible to analyze complex mixtures by direct injection into the source, without resorting to liquid chromatography (LC) to separate the components.^[38–41]

APPI-QqToF-MS analysis of the maltene fraction of the bitumen

APPI-MS of the saturated oil fraction

The saturated oil obtained had a white colour and was viscous. It was initially analyzed by TLC. The obtained spots of the oil were visualized with UV light (254 nm). It is noteworthy to mention that, although this fraction has been attributed as a saturated fraction, we have found that some of the molecules comprising this fraction did contain simple double-bond unsaturations. This was confirmed by analysis of the saturated oil fraction by ATR-FTIR spectroscopy (Supplementary Fig. S1, see Supporting Information) where the spectra obtained showed clear vibrational bands corresponding to C=C unsaturations. Other bands in the spectra are characteristic of CH₂ and CH₃ functional groups. Moreover, O-H stretching vibrations were also detected between 3200 and 3400 cm⁻¹. Subsequently, this oil was analyzed by atmospheric pressure photoionization mass spectrometry (APPI-MS) with a QqToF-MS/MS hybrid instrument.

Conventional APPI-MS showed a very simple mass spectrum containing several major ions. We have described these ions as the following: *m/z* 446.2980 as the molecular ion [M]⁺,

m/z 418.2787 as the molecular ion $[M_2]^{+*}$, m/z 360.3350 as the molecular ion $[M_3]^{+*}$, and m/z 346.2095 as the molecular ion $[M_4]^{+*}$; the base peak was identified as the protonated molecule $[M_5+H]^+$ at m/z 287.1625 (Fig. 1 and Supplementary Table S1, Supporting Information). These major ions were examined using low-energy CID-MS/MS analysis thus enabling us to obtain information about their chemical structures. It should be noted that the compounds identified herein are novel compounds, whose chemical identities have not previously been reported. Therefore, the chemical structures that we are presenting are tentative, as the identification is solely based on the MS analysis and we have given no consideration to the stereochemistry of the identified molecules. We were also aware of the necessity to provide adequate mass spectral evidence when proposing ion structures or confirming the presence of a particular compound in a complex sample matrix.^[42] Thus, the saturated oil fraction was deuterated and the observed masses are reported in Supplementary Table S1 (Supporting Information). We noticed a mass increase of 1 u for the molecular ion $[M_1]^{+*}$ at m/z 447.3082 which allowed us to confirm the presence of one labile proton in the structure of this molecule. A mass shift of 2 u was detected for the molecular ion $[M_2]^{+*}$ at m/z 420.2834 which corresponded to the presence of two exchangeable protons on the molecule. For the molecular ion $[M_4]^{+*}$ we observed a mass shift of 1 u at m/z 347.2198 which was assigned to the presence of one labile hydrogen on the molecule. Finally, no mass shift was observed for the molecular ion $[M_3]^{+*}$ at m/z 360.3410 or for the protonated molecule $[M_5+H]^+$ at m/z 287.1625, indicating that no exchangeable proton was present on these molecules. The extracted precursor ions $[M_1D]^{+*}$, $[M_2D_2]^{+*}$, $[M_3]^{+*}$, $[M_4D]^{+*}$ and $[M_5+H]^+$ were subjected to CID-MS/MS analyses which confirmed the previous assessments.

Low-energy CID-MS/MS of the molecular ion $[M_1]^{+*}$ at m/z 446.3005 extracted from the saturated oil fraction

The product ion scan of the molecular ion $[M_1]^{+*}$ at m/z 446.3005 afforded ions at m/z 428.2959, 388.2509, 370.2377, 328.2066, 316.1659, 287.1704, 232.1795, 215.1504, 157.0930, 155.0780 and 137.0955 (Fig. 2). The molecule was assigned a probable molecular formula of $[C_{23}H_{46}N_2O_2S_2]^{+*}$ and the proposed structure seems to contain two piperidine cycles linked by a S-S bond, with each piperidine ring substituted by either a $C_5H_{11}O$ or a $C_8H_{17}O$ aliphatic chain. The fragmentation of this precursor ion was quite straightforward with the formation of product ions containing both S-S-linked piperidine rings. Thus, the precursor ion afforded the product ion at m/z 428.2959 by elimination of water. The precursor ion also underwent consecutive losses of water (18 u) and $CH_3CH=CHOH$ (76 u) to afford the product ion at m/z 370.2377. Other product ions were produced by various eliminations on the aliphatic side chains attached to the piperidine rings in the precursor ion, such as m/z 388.2509 formed by loss of 58 u (C_3H_6O); m/z 328.2066 formed by loss of 118 u (C_2H_6O and C_4H_8O); m/z 316.1659 formed by the loss of 130 u ($C_8H_{18}O$); and m/z 287.1704 formed by loss of 159 u ($C_8H_{17}O$ and CH_2O).

The precursor ion also fragmented by cleavage at the S-S disulphide bond to afford a series of product ions containing one piperidine ring such as $[C_{10}H_{18}NOS_2]^+$ at m/z 232.1795; $[C_{11}H_{21}NOS]^{+*}$ at m/z 215.1504; $[C_8H_{15}NS]^{+*}$ at m/z 157.0930; and $[C_8H_{13}NS]^{+*}$ at m/z 155.0780. We have also identified one loss of the joint S-S-linked piperidine rings, which afforded the product ion $[C_9H_{13}O]^+$ at m/z 137.0955. The product ion masses and deviations from the calculated masses, and the deuterated product ion analogue are reported in Supplementary Table S2 (Supporting Information). The tentative CID fragmentation routes and the structures of the product ions are shown in Scheme 1.

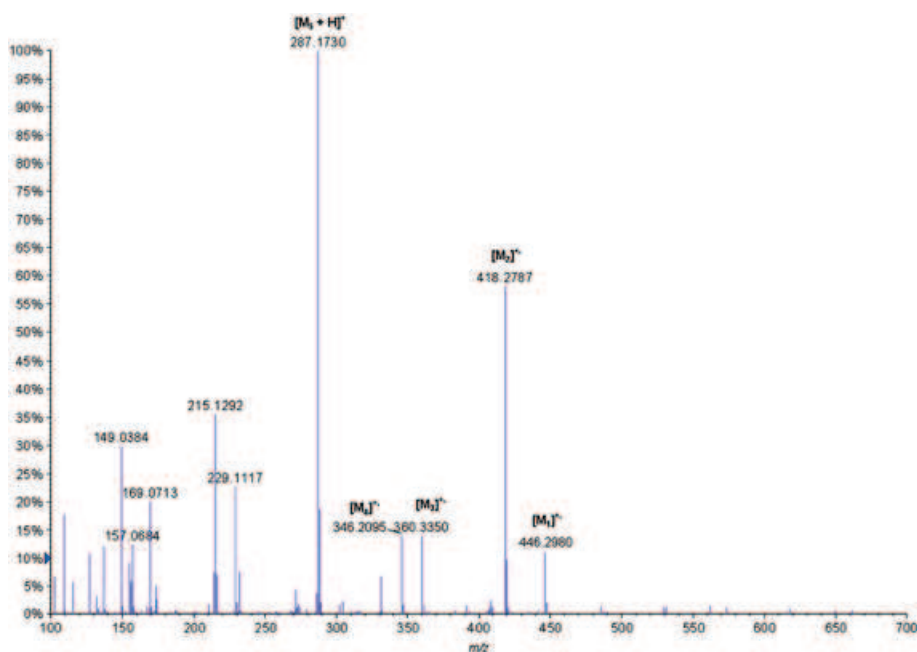


Figure 1. APPI-QqToF-MS of the maltene saturated oil fraction.

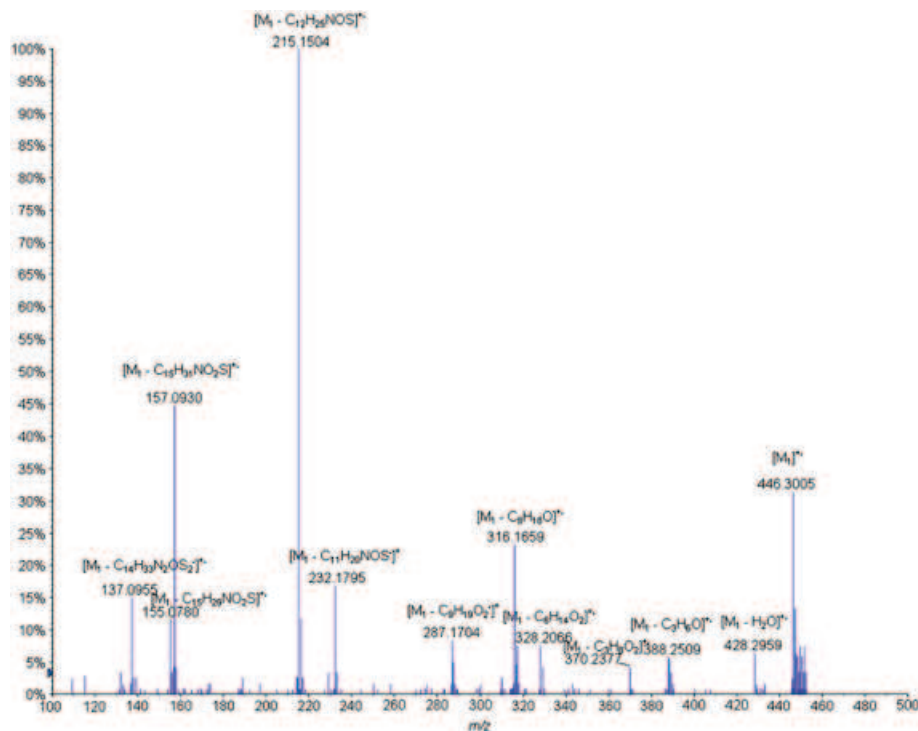


Figure 2. CID-MS/MS of the molecular ion $[M_1]^{+\bullet}$ at m/z 446.3005 extracted from the saturated oil fraction.

Low-energy CID-MS/MS of the molecular ion $[M_2]^{+\bullet}$ at m/z 418.2713 extracted from the saturated oil fraction

The product ion scan of the molecular ion $[M_2]^{+\bullet}$ at m/z 418.2713 afforded two main product ions at m/z 360.2295 and 287.1640 (Fig. 3). The molecule has a probable formula of $[C_{21}H_{42}N_2O_2S_2]^{+\bullet}$ and we propose that the structure contains two piperidine rings linked by an S-S bond, with each piperidine ring being substituted by either a $C_5H_{11}O$ or a $C_6H_{13}O$ aliphatic chain. The radical product ion at m/z 360.2295 was formed by elimination of a molecule of C_3H_6O from the precursor ion at m/z 418.2713. Elimination of a C_4H_8O (72 u) molecule and a $C_3H_7O^\bullet$ (59 u) radical from the precursor ion afforded the product ion at m/z 287.1640. The tentative CID fragmentation routes of the molecular ion $[M_2]^{+\bullet}$ at m/z 418.2713 and the structures of the product ions are shown in Scheme 2. The product ion masses and deviations from the calculated masses, and their deuterated product ion analogues are reported in Supplementary Table S3 (Supporting Information).

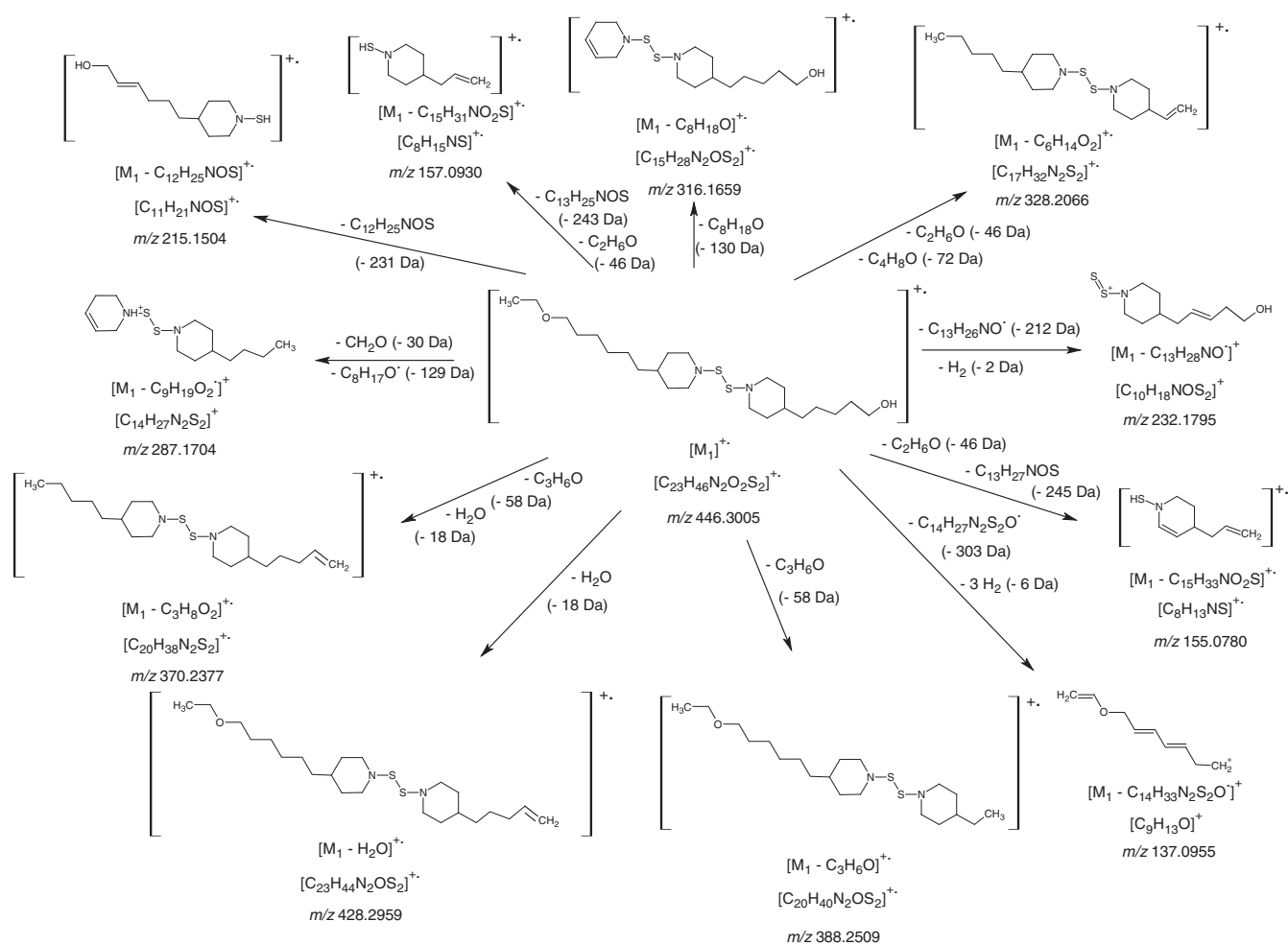
Low-energy CID-MS/MS of the molecular ion $[M_3]^{+\bullet}$ at m/z 360.3367 extracted from the saturated oil fraction

The molecular ion at m/z 360.3367 had a probable formula of $[C_{25}H_{44}O]^{+\bullet}$ and we propose that the molecule is composed of a cyclo-2,5-hexadiene attached to an aliphatic $(CH_2)_{14}$ chain which in turn is attached at the other end to a tetrahydropyran ring. CID-MS/MS analysis of $[M_3]^{+\bullet}$ at m/z 360.3367 produced a major product ion at m/z 156.1878 formed by elimination of two neutral fragments $C_6H_{10}O$ (96 u) and C_8H_{10} (106 u) (Fig. 4). The precursor ion eliminated the neutral fragment

C_2H_{40} (44 u) and a molecule of hydrogen to afford the product ion at m/z 314.2911. The $[M_3]^{+\bullet}$ ion also eliminated water by an intramolecular mechanism to afford the product ion at m/z 342.3230. A unique product ion at m/z 164.1585 was formed by loss of the major part of the alkylated chain, occurring as $C_7H_{14}O$ (114 u), C_6H_8 (80 u) and a hydrogen molecule. In addition, we noted the formation of product ions containing the tetrahydropyran ring only, such as m/z 210.1999, 128.1164 and 110.0715. Similarly, product ions containing the cyclo-2,5-hexadiene attached to the straight alkylated chain were formed at m/z 246.2312 and 228.1857. The tentative CID fragmentation pathways of the molecular ion $[M_3]^{+\bullet}$ at m/z 360.3367 and the proposed structures of the product ions are shown in Scheme 3. The product ion masses and deviations from the calculated masses of the product ions are reported in Supplementary Table S4 (Supporting Information).

Low-energy CID-MS/MS of the molecular ion $[M_4]^{+\bullet}$ at m/z 346.2096 extracted from the saturated oil fraction

The molecular ion of $[M_4]^{+\bullet}$ at m/z 346.2096 has been assigned the probable formula of $[C_{17}H_{34}N_2OS_2]^{+\bullet}$. Fragmentation of this ion afforded the following product ions: m/z 288.1659 formed by the loss 30 u (CH_2O group) and 28 u (C_2H_4); m/z 287.1590 formed by the loss of 28 u (C_2H_4) and 31 u (CH_3O^\bullet); m/z 215.0771 formed by the loss of 131 u, corresponding to a $C_7H_{15}N$ molecule and H_2O ; and finally the ion at m/z 157.0933 formed by the loss of the $C_7H_{13}NS$ (143 u) and C_2H_6O (46 u) molecules. The postulated CID-MS/MS fragmentation pathways are displayed in Scheme 4, the MS/MS



Scheme 1. Proposed structures of the product ions resulting from the CID-MS/MS of the molecular ion $[M_1]^+$ at m/z 446.3005 extracted from the maltene saturated oil fraction.

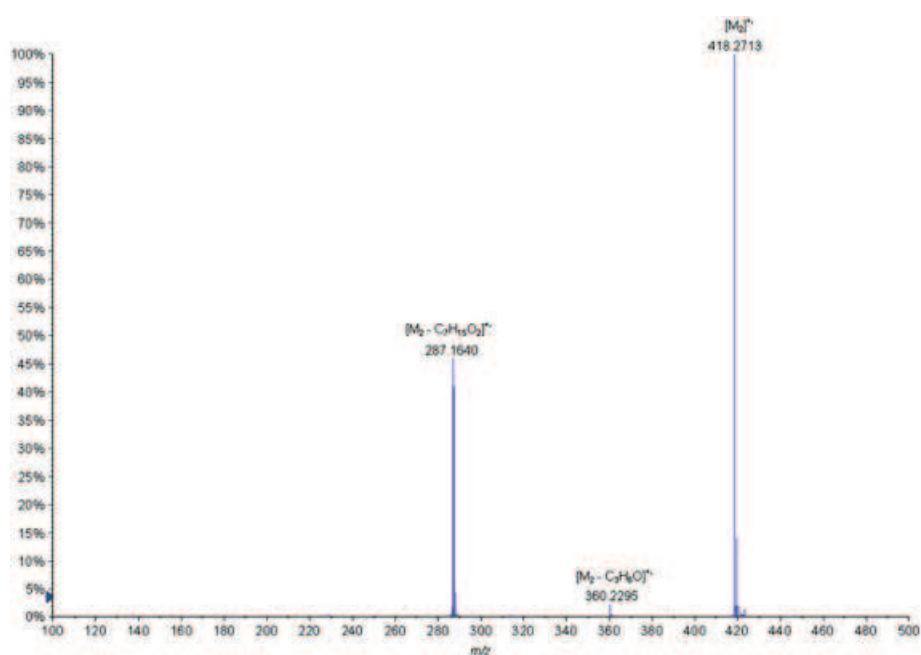
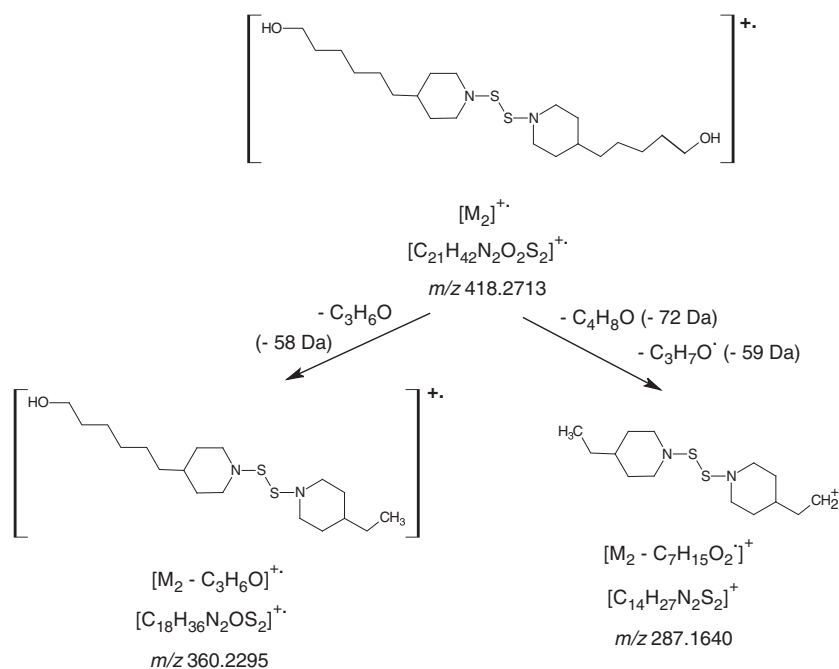


Figure 3. CID-MS/MS of the molecular ion $[M_2]^+$ at m/z 418.2713 extracted from the saturated oil fraction.



Scheme 2. Proposed structures of the product ions resulting from the CID-MS/MS of the molecular ion $[M_2]^+$ at m/z 418.2713 extracted from the maltene saturated oil fraction.

spectrum is shown in Fig. 5 and Supplementary Table S5 (Supporting Information) contains the experimental and calculated m/z values of the product ions, and the mass deviations. Supplementary Table S5 (Supporting Information) shows also the product ions resulting from the CID-MS/MS analysis of the deuterated molecular ion $[M_4D]^+$ at m/z 347.2140.

Low-energy CID-MS/MS of the protonated molecule $[M_5+H]^+$ at m/z 287.1625 extracted from the saturated oil fraction

CID-MS/MS of the protonated molecule $[M_5+H]^+$ at m/z 287.1625 (Fig. 6), whose formula was assigned as $[C_{14}H_{27}N_2S_2]^+$, afforded the following product ions: m/z 229.0835 formed by

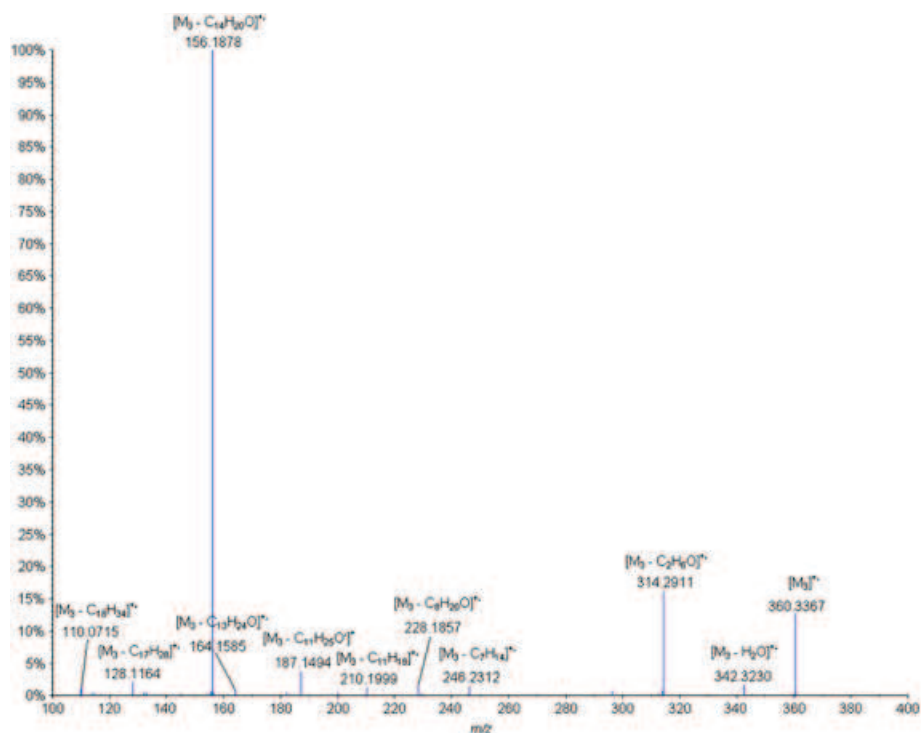
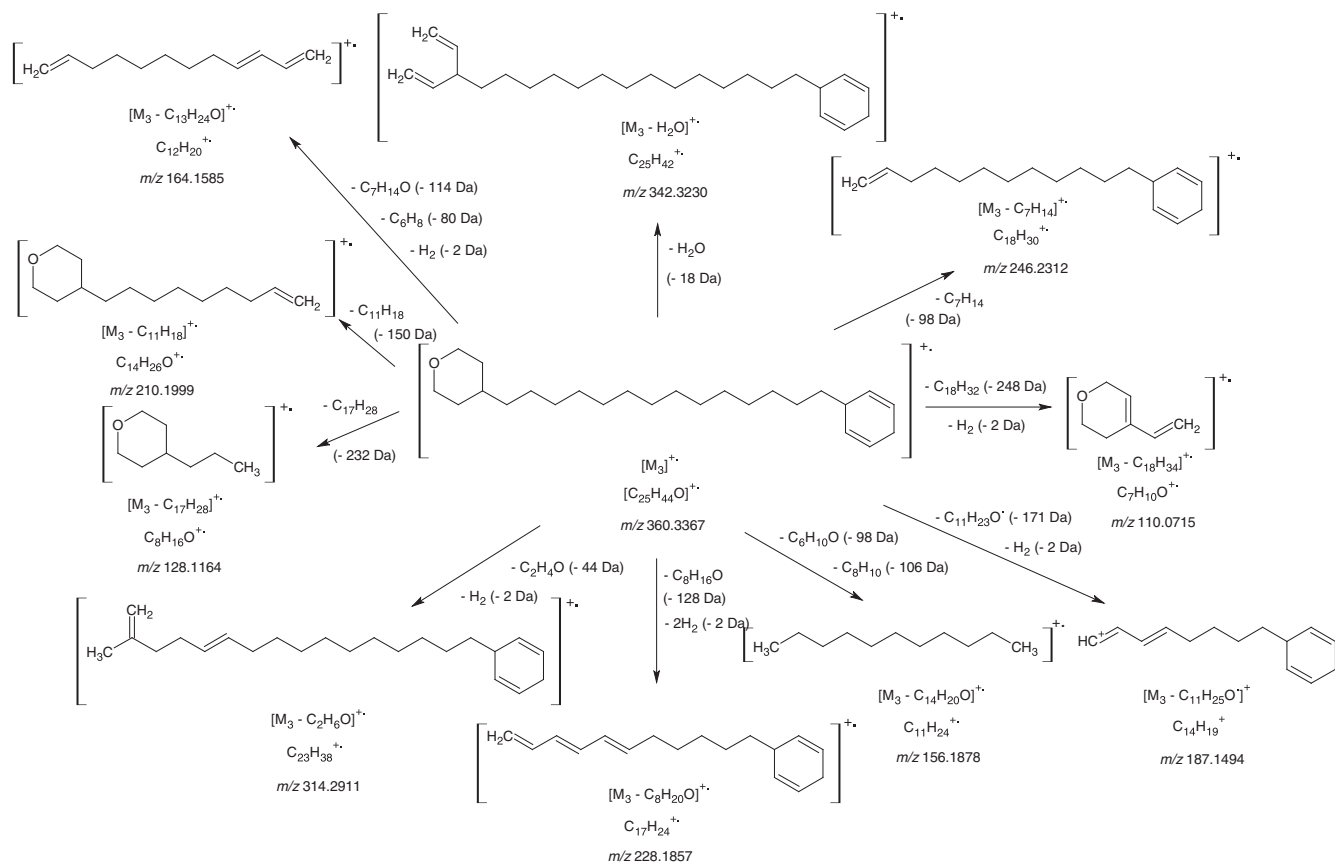


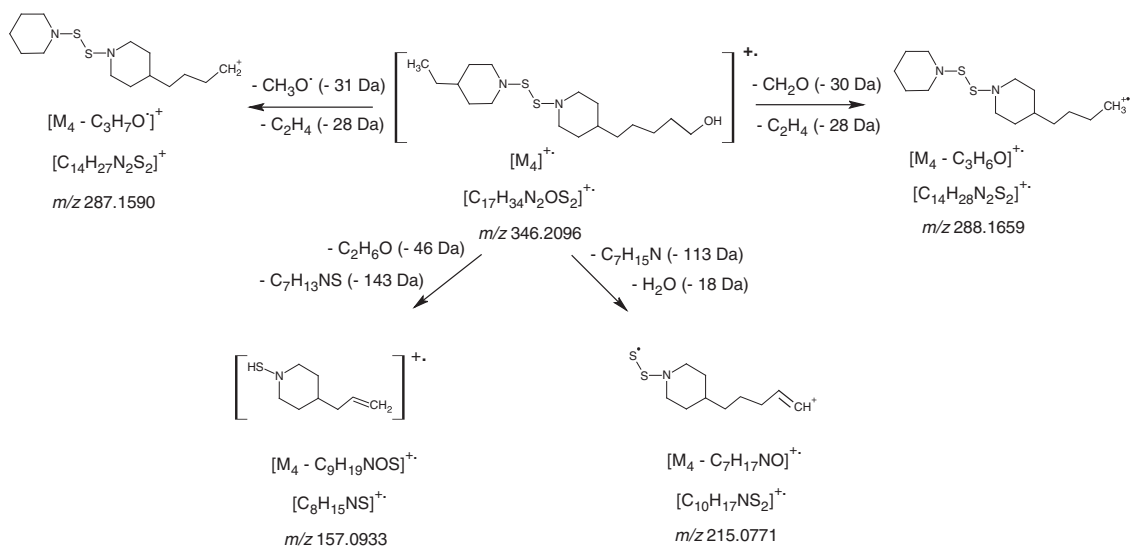
Figure 4. CID-MS/MS of the molecular ion $[M_3]^+$ at m/z 360.3367 extracted from the saturated oil fraction.



Scheme 3. Proposed structures of the product ions resulting from the CID-MS/MS of the molecular ion $[M_3]^+$ at m/z 360.3367 extracted from the maltene saturated oil fraction.

elimination of 58 u (C_4H_{10}) from the precursor ion; m/z 173.1200 formed by elimination of 114 u ($C_5H_8NS^*$) from the precursor ion; m/z 155.0710 formed by elimination of 132 u ($C_6H_{14}NS^*$) from the precursor ion; m/z 137.0327 formed by loss of 150 u ($C_7H_{20}NS^*$) from the precursor ion; and the ions at m/z 133.0050 and 115.0490 formed by the straightforward pathways explained in Scheme 5. The CID-MS/MS spectrum

is shown in Fig. 6 and the masses of the product ions are indicated in Supplementary TableS6 (Supporting Information). The proposed CID fragmentation routes and the structures of the product ions are shown in Scheme 5. Moreover, the molecule could not be deuterated due to the absence of exchangeable protons. It is interesting to note that the identified molecule contains at least one double bond in addition to the



Scheme 4. Proposed structures of the product ions resulting from the CID-MS/MS of the molecular ion $[M_4]^+$ at m/z 346.2096 extracted from the maltene saturated oil fraction.

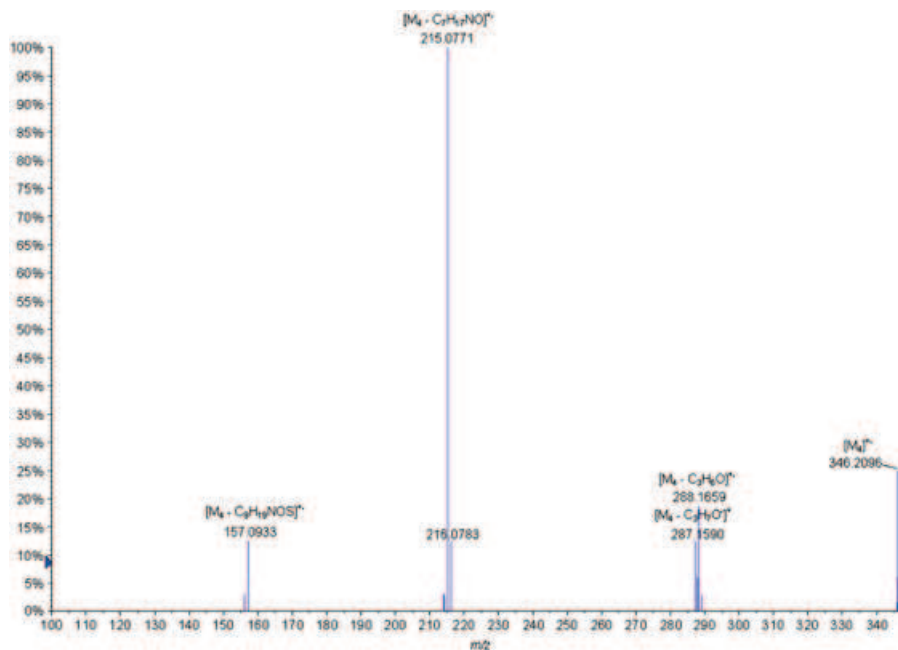


Figure 5. CID-MS/MS of the molecular ion $[M_4]^{+\bullet}$ at m/z 346.2096 extracted from the saturated oil fraction.

S- and N-heteroatoms. This is consistent with the results obtained by the UV and FT-IR analyses of the saturated oil fraction.

It should be mentioned that the protonated molecule $[M_5 + H]^+$ at m/z 287.1625 was isobaric with product ions formed from the molecular radical ions $[M_1]^{+\bullet}$ at m/z 446.2980, $[M_2]^{+\bullet}$ at m/z 418.2787 and $[M_4]^{+\bullet}$ at m/z 346.2095; all extracted from the same saturated oil fraction. To ensure that we were dealing with a different isobaric molecule and not an

ion formed from one of these molecular radical ions by nozzle CID fragmentation, we performed APPI-MS analysis of this saturated oil fraction with a series of lower DP values. It was noted that the abundance of the ion at m/z 287.1625 did not drop off when the mass spectra were recorded, thus indicating that this ion is representative of a new compound and eliminating the possibility that it was formed from the molecular radical ions.

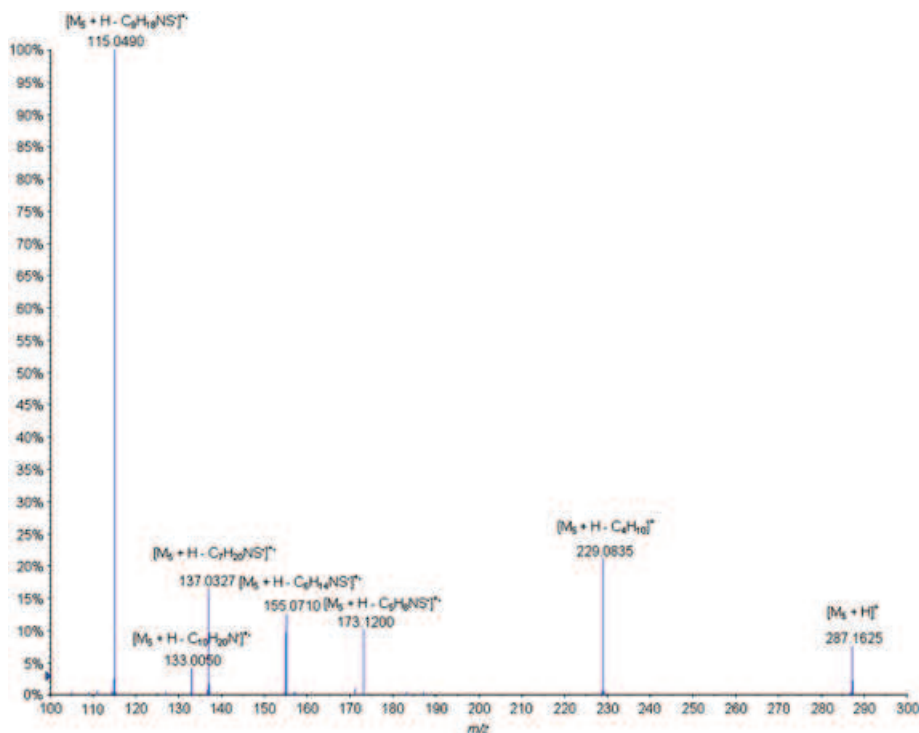
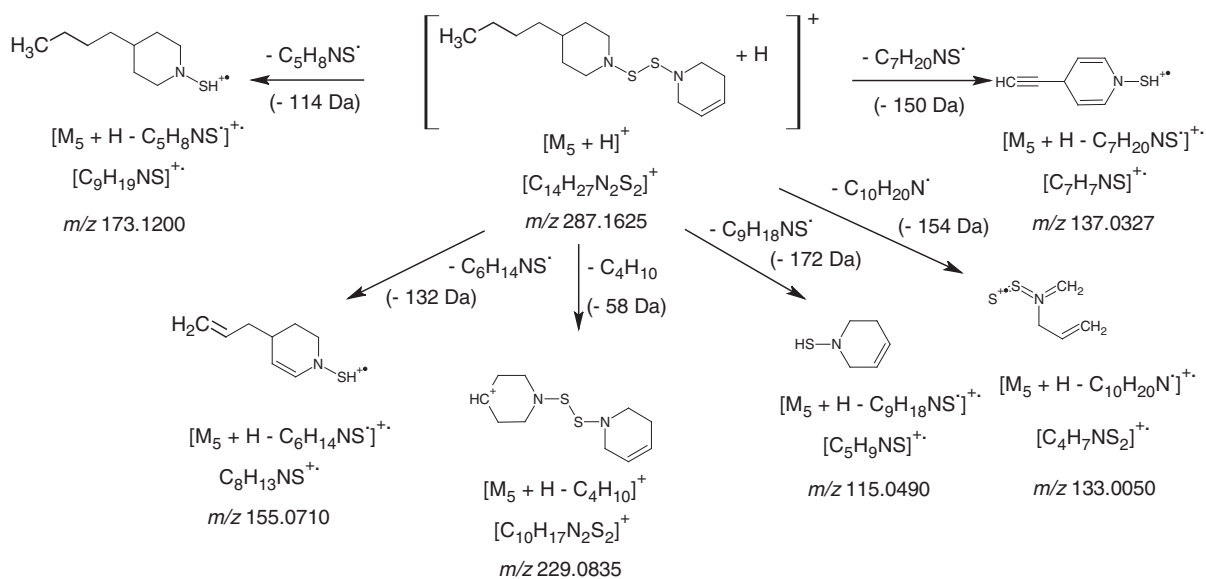


Figure 6. CID-MS/MS of the protonated molecule $[M_5 + H]^+$ at m/z 287.1625 extracted from the saturated oil fraction.



Scheme 5. Proposed structures of the product ions resulting from the CID-MS/MS of the molecular ion $[M_3]^{+\bullet}$ at m/z 360.3367 extracted from the maltene saturated oil fraction.

APPI-MS of the maltene aromatic oil fraction

The aromatic oil recovered was a brown-orange viscous liquid. TLC indicated the presence of several spots composed of a brown central part and a wide outlying part, which were visualized by UV radiation (254 and 365 nm).

The ATR FT-IR spectrum of this fraction is very simple (Supplementary Fig. S2, see Supporting Information). The absence of vibrational bands between 3000 and 3600 cm^{-1} is an indication of the absence of polar groups in the aromatic oil. The four intense vibrational bands at 690, 730, 800, and 860 cm^{-1} are characteristic of twisting aromatic C-H bonding. The other vibrational bands are characteristic of aliphatic and aromatic C-H and C-C bonding.

The APPI mass spectrum of the aromatic fraction is much more complex than that obtained for the saturated

fraction (Fig. 7, Supplementary Table S7, Supporting Information). A quick perusal of this mass spectrum indicates that separating all the molecules present in this fraction and studying their structures would be a mammoth task, quite laborious and thus time-consuming. As the majority of the molecules exhibit ions in the mass range m/z 200–800, we presume that the average molecular weight 800 u generally assumed^[9] for similar maltene aromatic fractions may actually be different for this fraction. Although the spectrum is extremely complex, we noted the presence of some very intense ions at m/z 418.1584, 346.1605, 287.1285, 215.1309 and 149.0714. We successfully extracted only the ions at m/z 418.1584 and 287.1285 for CID-MS/MS analysis. Attempts to obtain interpretable structures from the ions at m/z 346.1605, 215.1309 and 149.0714 failed, as these ions were obviously mixtures of different isobaric ions, which of

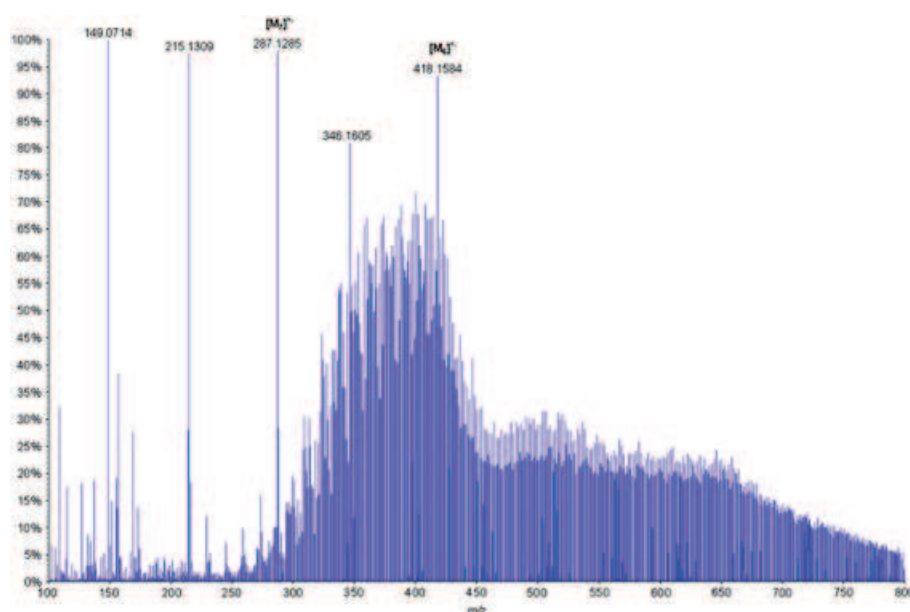


Figure 7. APPI-QqToF-MS of the maltenes aromatic oil fraction.

course were difficult to separate with the moderate resolution of our QqToF-hybrid instrument.

Low-energy CID-MS/MS of the molecular ion $[M_6]^{+\bullet}$ at m/z 418.1590 extracted from the aromatic fraction

CID-MS/MS analyses of the major ions formed in the conventional APPI-MS spectra were performed in order to propose tentative chemical structures for the molecules forming this fraction; specifically, the molecular ions $[M_6]^{+\bullet}$ at m/z 418.1590 and $[M_7]^{+\bullet}$ at m/z 287.1285.

The CID-MS/MS analysis of the molecular ion $[M_6]^{+\bullet}$ at m/z 418.1590 to which we assigned a formula of $[C_{26}H_{26}O_3S]^{+\bullet}$ afforded a series of product ions, which were quite different from the ones obtained by CID-MS/MS of the molecular ion $[M_2]^{+\bullet}$ at m/z 418.2787 extracted from the saturated oil fraction. These product ions m/z 418.1584 were: m/z 403.1291 formed by elimination of a methyl radical from the precursor ion; m/z 389.1145 formed by loss of an ethyl group from the precursor ion; m/z 375.1512 formed by loss of the $C_2H_3O^\bullet$ radical (43 u) from the precursor ion; m/z 287.0940 produced by combined losses of 131 u ($C_6H_{11}OS^\bullet$) from the precursor ion; and the ion at m/z 229.0852 produced by two different successive retro-Diels-Alder reactions and the loss of the CH_2SCH_3 radical from the precursor ion. The structure assigned to the product ion at m/z 156.0922 is in agreement with the proposed structure of this complex molecule and provides strong evidence that this ion was formed from the second ring of this aromatic compound. This also indicates that the CH_2SCH_3 chain is contiguous to an oxygen atom, belonging to the next adjacent aromatic ring. Finally, the product ions at m/z 137.0602 and 115.0560 were also produced from the precursor ions by a series of conventional elimination reactions. The CID-MS/MS spectrum is shown in Fig. 8 and the masses of the product ions are reported in Supplementary Table S8 (Supporting Information).

The tentative CID fragmentation routes and the structures of the product ions are shown in Scheme 6. Obviously, we were not successful in the synthesis of the deuterated analogue of this molecule as this compound did not contain any exchangeable hydrogens.

Low-energy CID-MS/MS of the molecular ion $[M_7]^{+\bullet}$ at m/z 287.1281 extracted from the aromatic fraction

As observed previously the CID-MS/MS product ion spectrum of the molecular radical ion $[M_7]^{+\bullet}$ at m/z 287.1281 to which we assigned the formula $[C_{20}H_{17}NO]^{+\bullet}$ was different from that obtained for the product ion scan of the protonated molecule $[M_5+H]^+$ at m/z 287.1625 extracted from the saturated oil fraction. The CID-MS/MS of the $[M_7]^{+\bullet}$ ion afforded the following product ions: m/z 272.1144 formed by elimination of a methyl radical from the precursor ion; the radical ion at m/z 258.1024 produced by the neutral loss of $CH_2=NH$ (29 u) from the precursor ion; m/z 257.0997 produced by the loss of the CH_2N^\bullet radical (28 u) and H_2 (2 u) from the precursor ion; m/z 245.0953 created by the loss of the $C_2H_4N^\bullet$ radical (42 u) from the precursor ion; the radical ion at m/z 230.1072 formed by loss of C_2H_3NO (57 u), corresponding to the partial side chain of the precursor ion; and, finally, the product radical ions at m/z 216.1065 and 115.0683 formed by a series of conventional elimination reactions. The CID-MS/MS spectrum is shown in Fig. 9 and the masses of the product ions are reported in Supplementary Table S9 (see Supporting Information). These seem to confirm that the molecular radical ion $[M_7]^{+\bullet}$ has a chrysene-type structure containing a fused *N*-methylmorpholine ring. The tentative CID fragmentation routes and the structures of the product ions are shown in Scheme 7. Therefore, the two main molecules identified in the maltene aromatic fraction, $[M_6]^{+\bullet}$ and $[M_7]^{+\bullet}$, obviously have a very strong aromatic character. In this case, the absence of the aliphatic chains was noted; however, the presence of heteroatoms must be underlined.

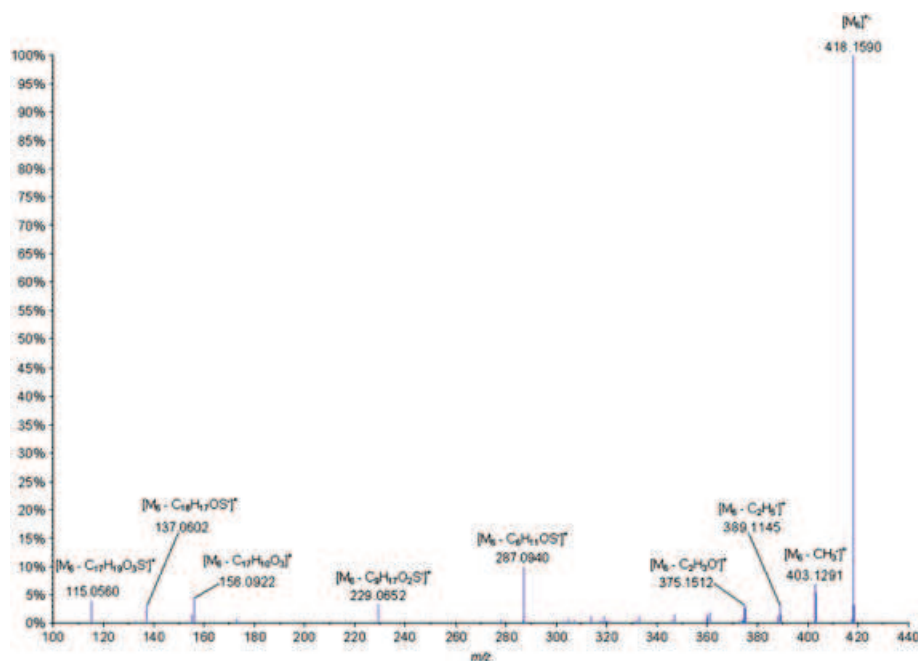
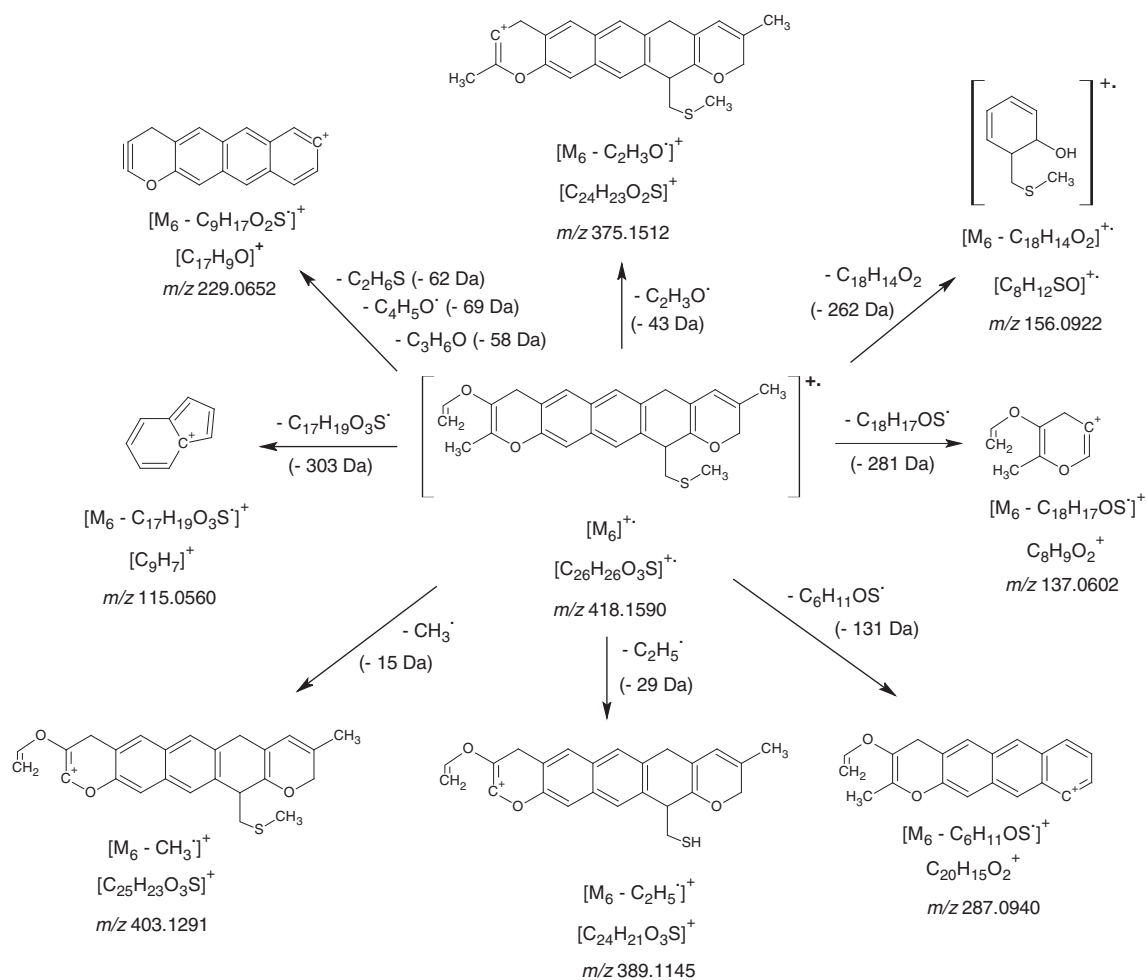


Figure 8. CID-MS/MS of the molecular ion $[M_6]^{+\bullet}$ at m/z 418.1590 extracted from the maltene aromatic oil fraction.



Scheme 6. Proposed structures of the product ions resulting from the CID-MS/MS of the molecular ion $[M_6]^+$ at m/z 418.1590 extracted from the aromatic oil fraction.

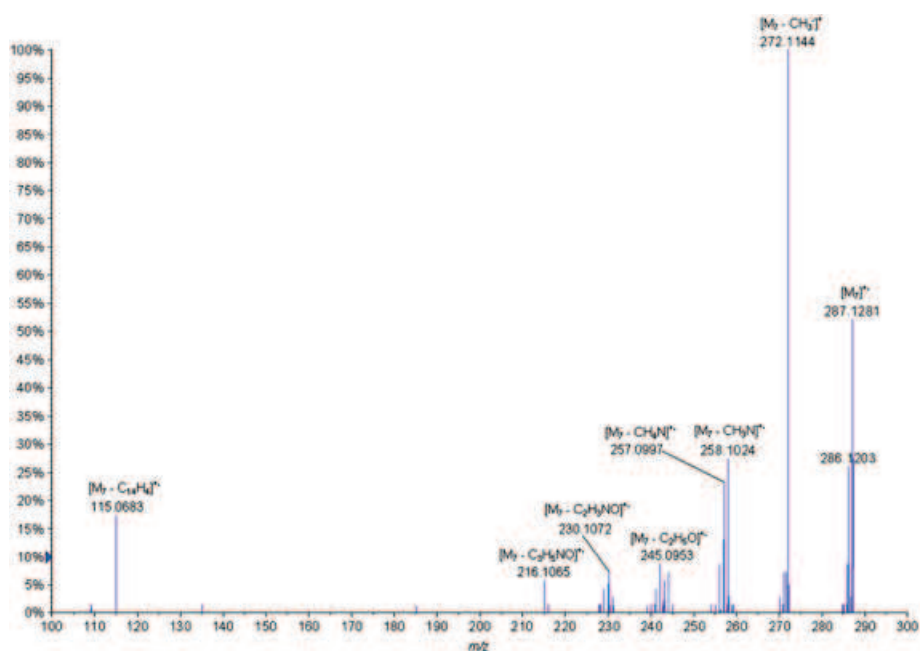
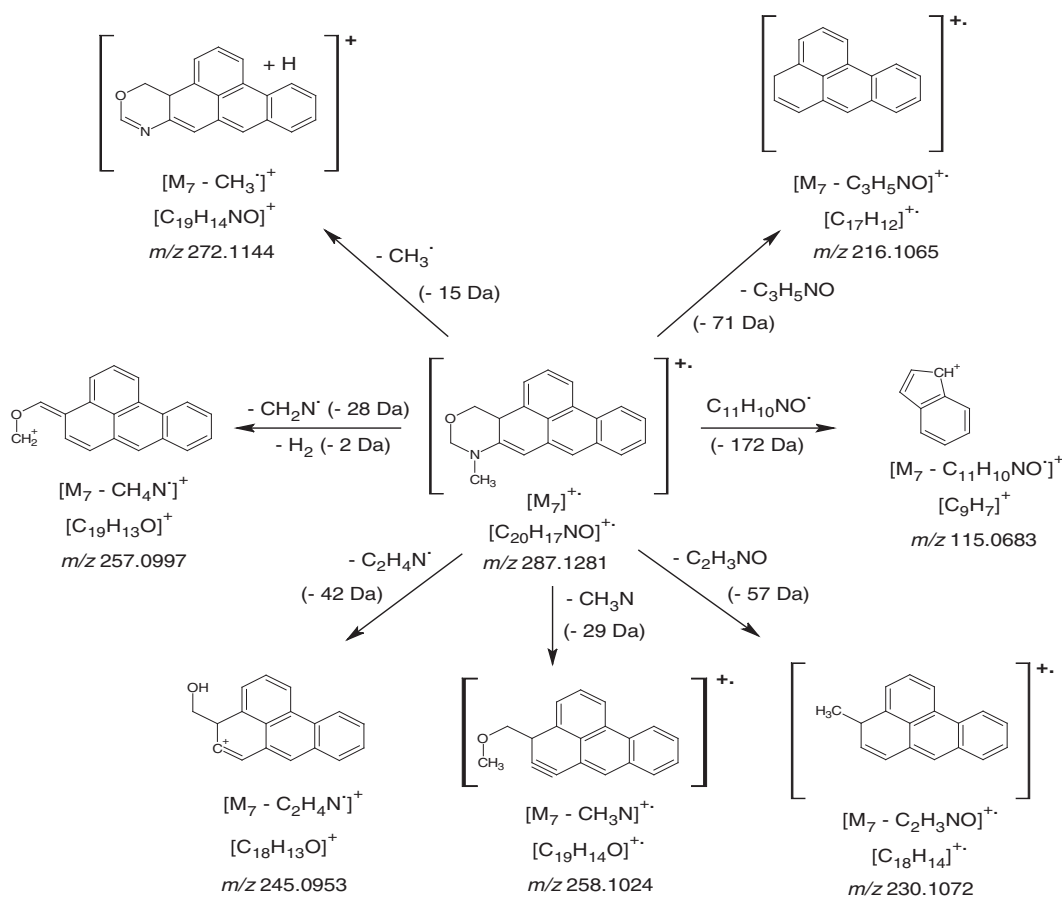


Figure 9. CID-MS/MS of the molecular ion $[M_7]^+$ at m/z 287.1281 extracted from the maltene aromatic oil fraction.



Scheme 7. Proposed structures of the product ions resulting from CID-MS/MS of the molecular ion $[M_7]^{+\bullet}$ at m/z 287.1281 extracted from the aromatic fraction.

APPI-QqToF-MS analysis of the maltene resin fraction of the bitumen

The maltene resin fraction is a brown-black solid and its FT-IR spectrum was more complex than those of the two other maltene fractions. It presented vibrational bands in the range of 3000 to 3600 cm^{-1} that suggest the presence of polar groups containing diagnostic OH and NH_2 bonds, together with bands corresponding to aromatic functions.

The APPI-MS spectrum of the resin fraction was very similar to that of the aromatic oil fraction, indicating that it was severely contaminated with this fraction. Therefore, as would be expected, the low-energy CID-MS/MS analyses had no diagnostic ability. It became clear, after performing the CID-MS/MS of the individual predominant precursor ions – $[M_8]^{+\bullet}$ at m/z 418.2713, $[M_9]^{+\bullet}$ at m/z 346.2129 and $[M_{10}]^{+\bullet}$ at m/z 287.1519 – that these mixtures contained large amounts of other individual isobaric precursor ions, such as $[M_2]^{+\bullet}$ at m/z 418.2787, $[M_4]^{+\bullet}$ at m/z 346.2095 and $[M_5+H]^+$ at m/z 287.1625 obtained from the saturated and aromatic maltene oil fractions.

APPI-QqToF-MS analysis of the asphaltene fraction of the bitumen

The asphaltenes were precipitated from the bitumen as a black powder. The FT-IR spectrum of this fraction is nearly the same as that of the resins.

The APPI-QqToF-MS analysis of asphaltenes showed a very complex spectrum containing a multitude of overlapping ions in the range of m/z 100 to 1000 (Fig. 10). The average molecular weight was centred on 600 u, and no ions appeared in the m/z 1000 to 2000 range. Although the APPI-MS spectrum of the asphaltene fraction was as complex as that of the maltene aromatic oil fraction, we were able to identify a series of prominent ions such as m/z 607.4206, 579.4434, 446.2456, 418.2308, 355.1704 and 331.21550. It is noteworthy that when the APPI-QqToF-MS spectrum was recorded with higher asphaltene concentrations, the spectra obtained were identical; however, the peaks obtained were broader, indicating a stronger heterogeneity and no ions at higher m/z values were observed.

The APPI-MS ions were extracted for further CID-MS/MS studies. Unfortunately, repeated attempts to obtain accurate masses of the product ions formed from the extracted molecular ion species at m/z 607.4206, 579.4434, 446.2456, 418.2308, 355.1704 and 331.21550 were unsuccessful, yielding large errors in these measurements. All the CID-MS/MS analyses of these precursor ions gave us a difference (Δm) of around 100 ppm between the accurate mass (experimentally measured) and the exact mass calculated (theoretical mass), which was unacceptable when trying to propose correct structures.^[29] This discrepancy seems to be associated with the mass resolution of the QqToF-MS/MS hybrid instrument (ca. 18000 FWHM) which we used to determine the possible formulae of these ions. For the

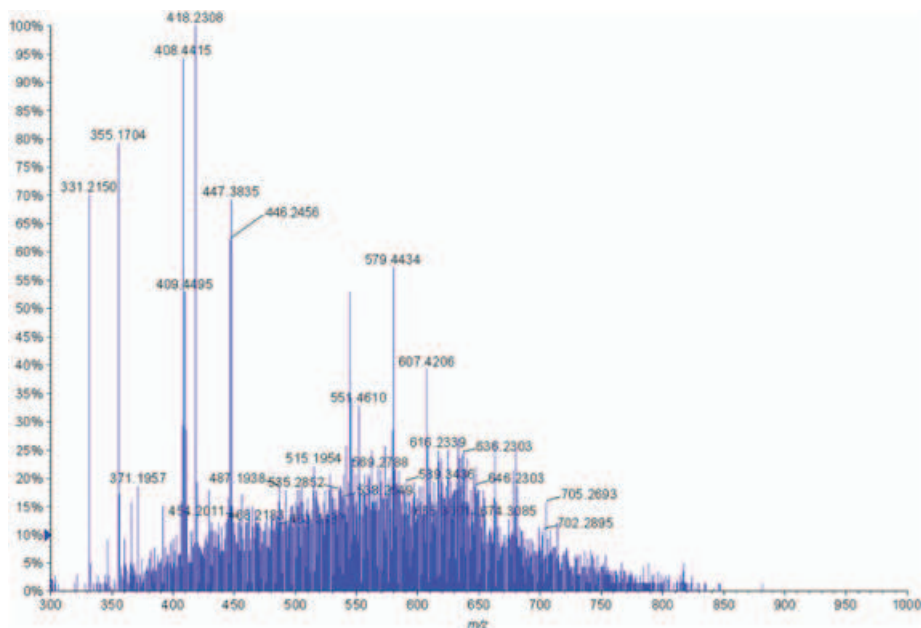


Figure 10. APPI-Qq-TOF-MS spectrum of the asphaltene fraction.

determination of the exact masses of these product ions, higher mass resolution instruments, such as FT-ICR or Orbitrap mass spectrometers, are thus needed. This is especially true, as we believe that some of the CID-extracted precursor ions are indeed mixtures of several precursor ions with isobaric masses, which certainly complicates this investigation.

CONCLUSIONS

In this study, we have demonstrated the use of APPI-QqToF-MS and low-energy CID-MS/MS analyses using an atmospheric pressure photoionization source. This method was used to identify compounds obtained from the SARA components of bitumen, namely, the maltene saturated oil and the aromatic SARA fractions. This shows the capability of MS/MS experiments to differentiate between isobaric ions obtained in the mass spectrometry of the maltene fractions and to understand the reasons between their observed mass spectrometric CID fragmentation differences. We have also shown that there are significant differences in the various CID-MS/MS analyses of the isobaric protonated molecules $[M+H]^+$ and molecular radical ions $[M]^{+\bullet}$ extracted from the saturated oil and the aromatic SARA fractions. The mechanisms behind these observed MS/MS differences were explained by proposed different breakdown processes of the precursor ions. The difference between the simplicity of the FT-IR spectra and the complexity of the APPI mass spectra underlines the chemical homogeneity of each family. Thus, the molecules in the maltene saturated oil fraction seem to be composed mainly of two piperidine rings bridged by an S-S group, with each of the piperidine rings being substituted with either an alkyl or alkylated alcohol or an ether. It also contains a molecule formed of a cyclo-2,5-hexadiene attached to an aliphatic alkylated chain $-(CH_2)_{14}-$ which in turn is attached to a tetrahydropyran ring. The aromatic oil fraction of the maltene fraction is composed of compounds with polycyclic aromatic rings containing both S and N heteroatoms and

short aliphatic chains. Although the asphaltene fraction studied herein was n-heptane-insoluble, it was soluble in toluene. It is known that the quantity of separated asphaltenes depends on the method used to separate the maltene and asphaltene fractions. Thus, it seems logical to expect the presence of mixed fractions during the SARA purification process.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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