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Direct Insertion Probe–Mass Spectrometry: A Useful Tool for Characterization of Asphaltenes

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The direct insertion probe–mass spectrometry (DIP–MS) technique, routine analysis for labile and polar samples, is based on the introduction of samples directly into the ionization chamber, followed by their vaporization and eventual ionization by electronic impact. In this work, a new application of the DIP–MS technique to the analysis of asphaltenes, a complex mixture derived from the *n*-pentane-insoluble fraction of crude oil, is proposed and described. They can be detected without previous separation, as a function of their boiling point and volatility, by programming a suitable probe temperature ramp that behaves as a fractional distillation. Particular attention is devoted to the data processing that allows for a deeper evaluation of the mass spectra according to the vaporization propensity of the single compounds. Differences are evidenced between the samples on the basis of the evolution of their mass spectra.

1. Introduction

In recent years, the analysis of low-volatile mixtures, such as heavy-oil fractions or bitumens, has rapidly gained increasing importance, because of the exploitation of oil reservoirs of low quality (tar sands, ultra-heavy oils, etc.). Gel permeation chromatography (GPC), vapor pressure osmometry (VPO), and high-temperature simulated distillation are common analytical methods applied for the study of these materials,¹ although suffering of limitations, as recently evidenced.² Several spectroscopic methods have also been considered for the class analysis of these mixtures during the last few decades: Fourier transform infrared (FTIR),³ near-infrared (NIR),⁴ transmitted-light FTIR microspectroscopy,⁵ nuclear magnetic resonance (NMR),⁶ and fluorescence.⁷ Conventional gas chromatography fails in elution of so poor-volatile complex matrices, and even liquid chromatography^{8,9} shows several limitations caused by the poor solubility in the most convenient solvents.¹⁰ Laser desorption mass spectrometry proved to be suitable for the analysis of these systems, but a lot

of work has to be performed for the optimization of the desorption parameters.^{11–13} Matrix-assisted laser desorption/ionization (MALDI) is also an effective and fast technique for studying asphaltenes;^{14–17} it operates in a wide *m/z* range but needs a complex optimization of the experimental variables (e.g., laser power, ion-exchange voltage, sample pretreatment and loading, and composition of the matrix). Electrospray- and atmospheric-pressure-photo-ionization Fourier transform ion cyclotron resonance mass spectromscopies (ESI– and APPI–FTICR–MS) are now applied to study asphaltenes with high accuracy,^{14,15} although with expensive instruments and time-consuming data management.

The direct insertion probe–mass spectrometry (DIP–MS) technique has been applied for the analysis of samples for more than 30 years.¹⁶ It is based on the introduction of the samples directly into the ionization chamber, followed by their vaporization and eventual ionization by electronic impact. Because this technique is often mentioned as a fast alternative for polar or thermally labile samples (e.g., aromas) that do not require gas-chromatographic separation, it has been considered of poor scientific relevance and only as a secondary application on solid and insoluble samples characterized by high boiling point or hindrance that prohibit or limit analysis by chromatographic methods.¹⁷

Asphaltenes are the most complex component of crude oil, defined as the toluene-soluble and *n*-heptane-insoluble mixture, with poorly known structure and a large variety of chemical and physical properties.^{18–20} The general agreement about the constituent molecular fragments of asphaltenes

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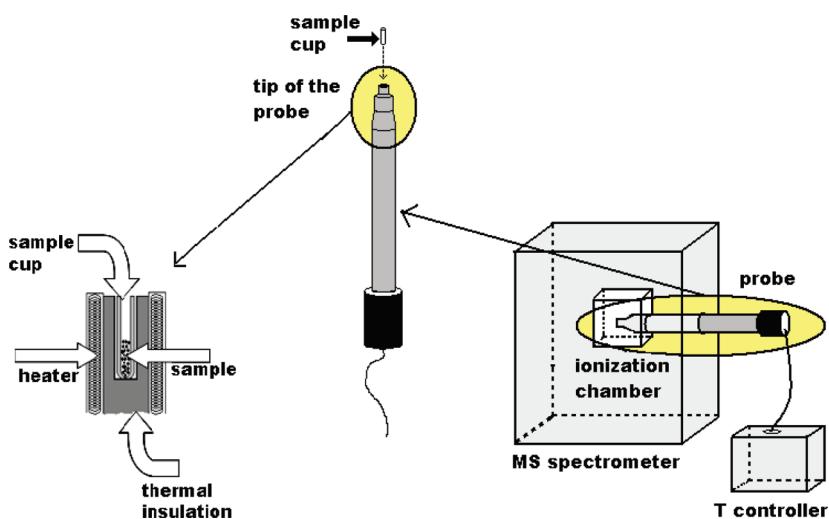


Figure 1. Schematic representation of the DIP-MS apparatus.

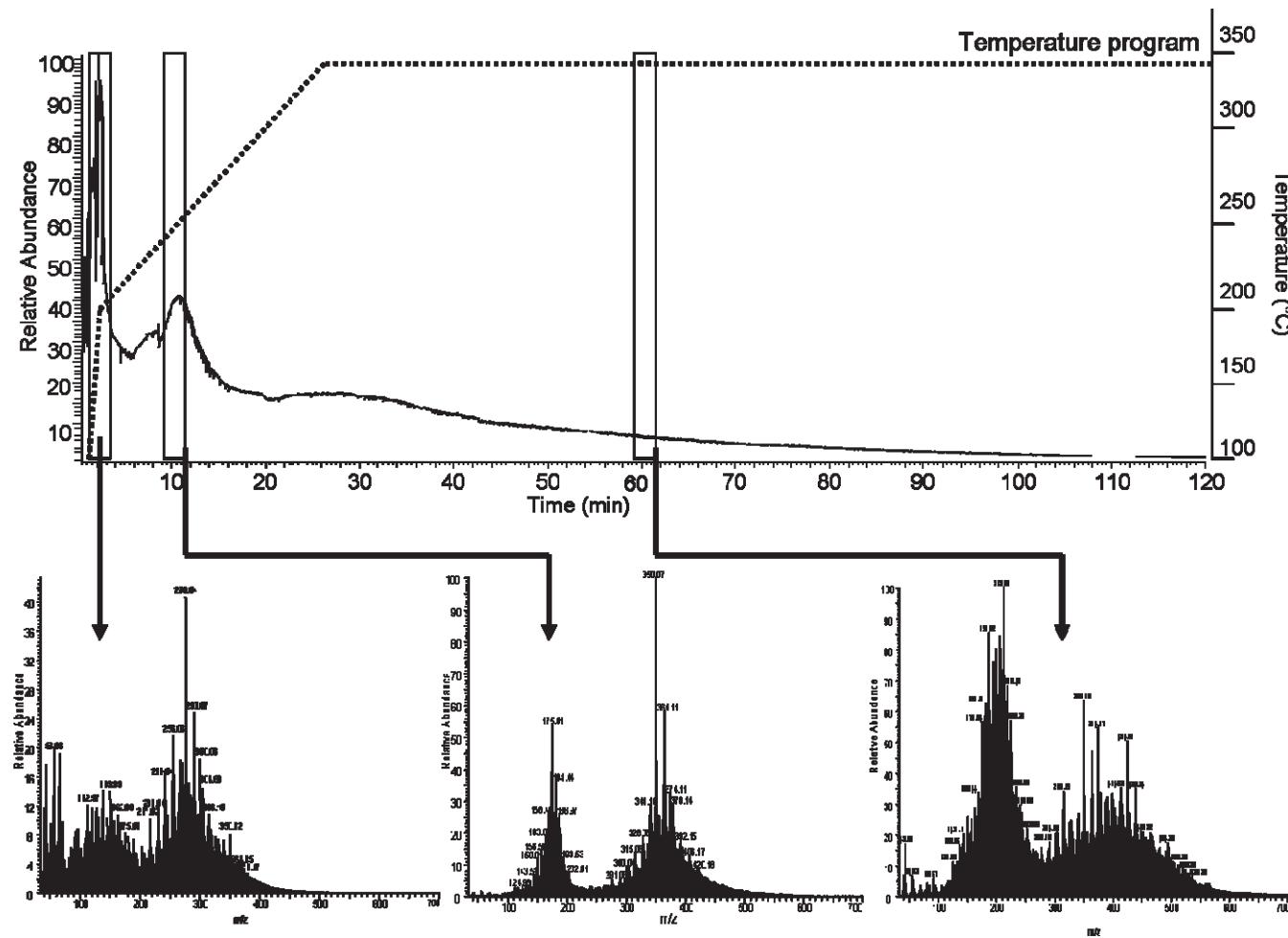


Figure 2. DIP-MS analysis of one asphaltene: (top) TIC profile obtained with DIP-MS analysis of asphaltene A and (bottom) corresponding mass profiles at three selected ranges of desorption temperature (120–220, 240–260, and 340 °C, from left to right, respectively).

describes them as condensed aromatic systems carrying alkyl, cycloalkyl, and heteroatom constituents,²¹ in monomeric or

polymeric form, with molecular weight from 400 to 4000 Da.²² Recently, the average molecular weight of asphaltenes is estimated to be distributed between 500 and 1000 Da in one

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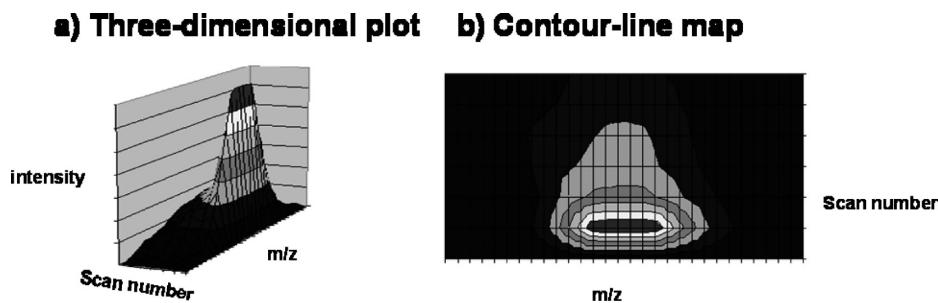


Figure 3. Visualization of DIP-MS data: (a) 3D plot and (b) contour-line plot.

single large polycyclic aromatic core (island model),² although the archipelago model with aromatic cores linked by reactive bridges and substituted with alkyl side chains is also widely considered in the literature.^{23–29}

Their analysis is always difficult and conventionally requires the combination of several techniques or very complex and time-consuming pretreatment or separation procedures. In this work, the application of the DIP-MS technique to the analysis of asphaltenes is proposed and described. They can be detected by the DIP-MS technique without any previous separation, as a function of their boiling point and volatility, by programming a suitable probe temperature ramp that behaves as a fractional distillation. Similar to this, DIP-MS becomes suitable for a detailed investigation, because it allows for the separation and identification of some classes of chemical compounds in complex mixtures, giving more information than a simple routine analysis.

2. Principle and Potential Applications of DIP-MS

2.1. Principles of the Technique. The DIP-MS technique is based on the direct sample introduction and vaporization into the vacuum chamber and eventual ionization by electronic impact.

The sample, liquid or solid, is introduced into a quartz cup located into the tip of the probe (Figure 1) that enters the vacuum chamber through an inlet. When the probe is located near the source, the heat of the filament under vacuum conditions is enough to vaporize the light samples or the light components of the sample and the detection of the signal begins immediately. To avoid the “bumping out” of the liquid (solvent or liquid volatile sample) in the chamber, the sample is equilibrated under vacuum before inserting into the ionization chamber. In any case, only a minimum amount of material has to be added, otherwise the ionization source

may be contaminated and the spectra produced will be saturated, leading to possible distortion of the isotope patterns.

The high-boiling components, such as asphaltenes, need more heat to vaporize than that furnished by the sole source, and the tip of the probe must be heated in a temperature-programmed mode to make the different components of the sample available to be detected, with a similar procedure to the fractional distillation, favored by the combined effect of vacuum and heat.

It is important to note that vacuum dramatically decreases the boiling temperature of the compounds, allowing for the vaporization of high-boiling-point species even when not very high temperatures are applied. By thermodynamic calculations, the change of the boiling point of some representative polycyclic aromatic hydrocarbons from atmospheric to the pressure value of 7×10^{-5} mbar (i.e., the maximum vacuum level present in the mass spectrometer) was determined; e.g., the boiling point of benzocoronene is 566 °C at atmospheric pressure and decreases to 303 °C at 10 mbar and 48 °C at 7×10^{-5} mbar, similarly the boiling point of coronene decreases from 525 to 288 to 46 °C, respectively, or the boiling point of picene decreases from 518 to 292 to 53 °C, respectively.

2.2. Data Processing. When a series of samples is analyzed by DIP-MS and compared, the amount of each sample should be approximately the same, to obtain comparable maps of the raw mass data, graphically displayed and analyzed with different approaches.

The total ion current (TIC) profile plots the sum of the intensity of all masses versus the time of analysis. It does not allow for the identification of the single compounds present in the sample, although it gives some information about their vaporization process; low- and intermediate-temperature range and the final isotherm at 340 °C can be defined overlapping the temperature profile to the time axis of the analysis (top of Figure 2). The relative intensity of the different areas can be used as a sort of fingerprint of the sample and its partition into light–medium–heavy species. In Figure 2, the TIC profile of asphaltene A is depicted and the three main regions are well-defined, with the contribution of the very high-boiling-point compounds that cover the whole region at 340 °C and the two steps at lower temperature equally present.

At each point of the TIC profile (i.e., at a chosen temperature of the probe), a conventional mass spectrum is registered that describes the species able to vaporize at that temperature. The melted asphaltenic mixture creates at every single instant (i.e., temperature) a “vapor” phase, and the presence of dynamic vacuum prevents secondary reactions among the different components.

This mass spectrum does not correspond to the fragmentation pattern of a single compound and, consequently,

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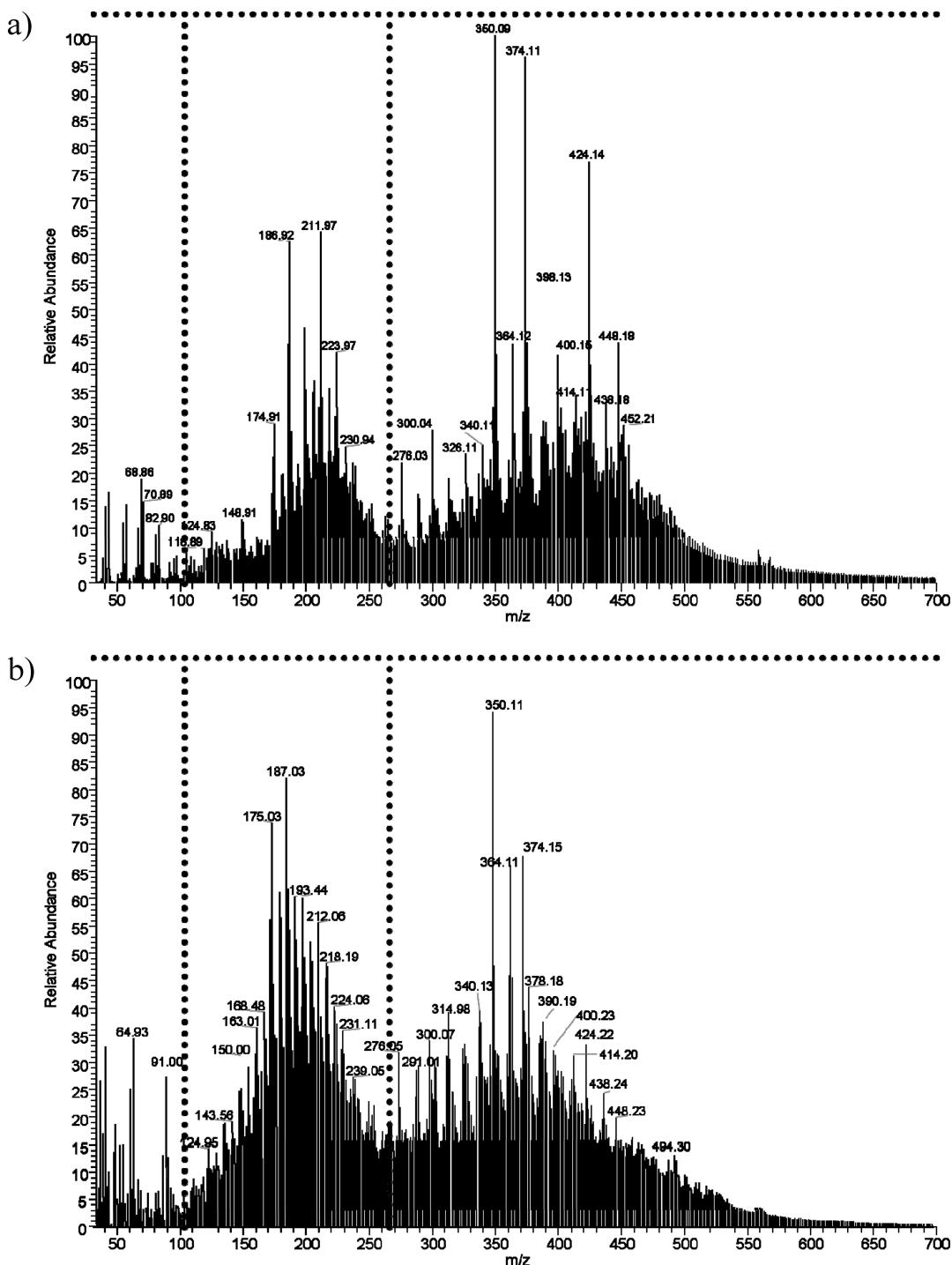


Figure 4. Average mass spectrum of asphaltenes A (top) and B (bottom).

cannot be used to accurately identify the compound, but it represents the sum of the fragmentation pattern of all of the species vaporized at that moment (bottom of Figure 2). In this way, general information can be obtained on the nature (aliphatic and aromatic) of the species, the presence of homologous sequences, and the molecular ions, when stable polycyclic aromatic compounds are vaporized. Because this approach is not focused on the identification of single compounds, it does not require the application of highly sophisticated and expensive high-resolution mass spectrometers.

A more performing representation of DIP-MS data is obtained by the contour map.

In the mass spectrometer, the magnitude, I (dependent variable), of the ion flux is recorded as a function of the mass/charge ratio, m/z (independent variable). In DIP-MS analysis with a temperature-programmed probe, I can therefore be plotted as a function of m/z and T (temperature of the probe), t (time of the temperature program), or n (scan number linearly related to t) simultaneously. This plot can be displayed as either a three-dimensional (3D) plot (Figure 3a) or a contour-line map (Figure 3b), where m/z and n are assigned to x and y axes, respectively, and I values are shown by contour lines and different colors.

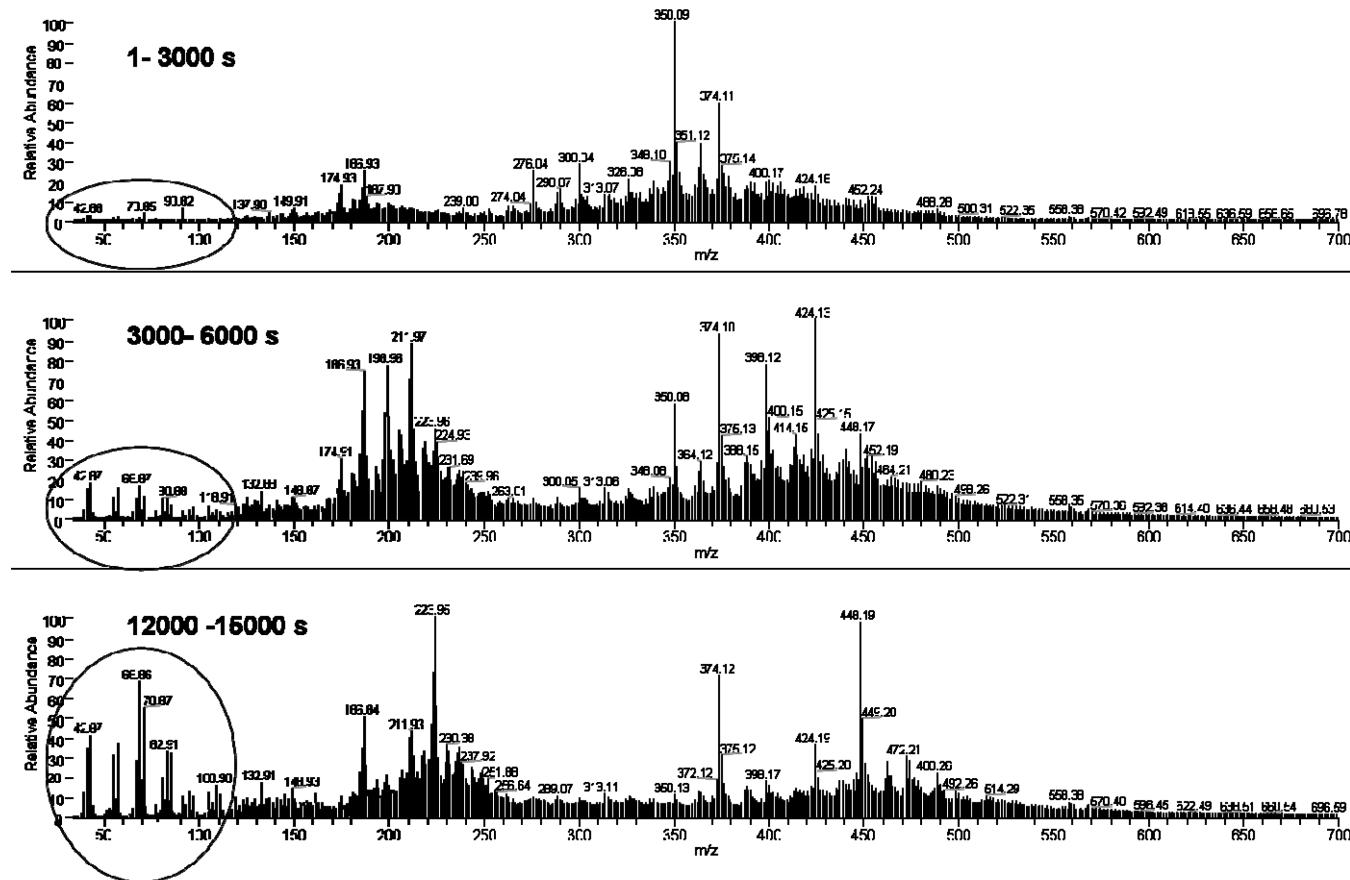


Figure 5. DIP-MS spectra of asphaltene A recorded between 1 and 3000 s, 3000 and 6000 s, and 12 000 and 15 000 s.

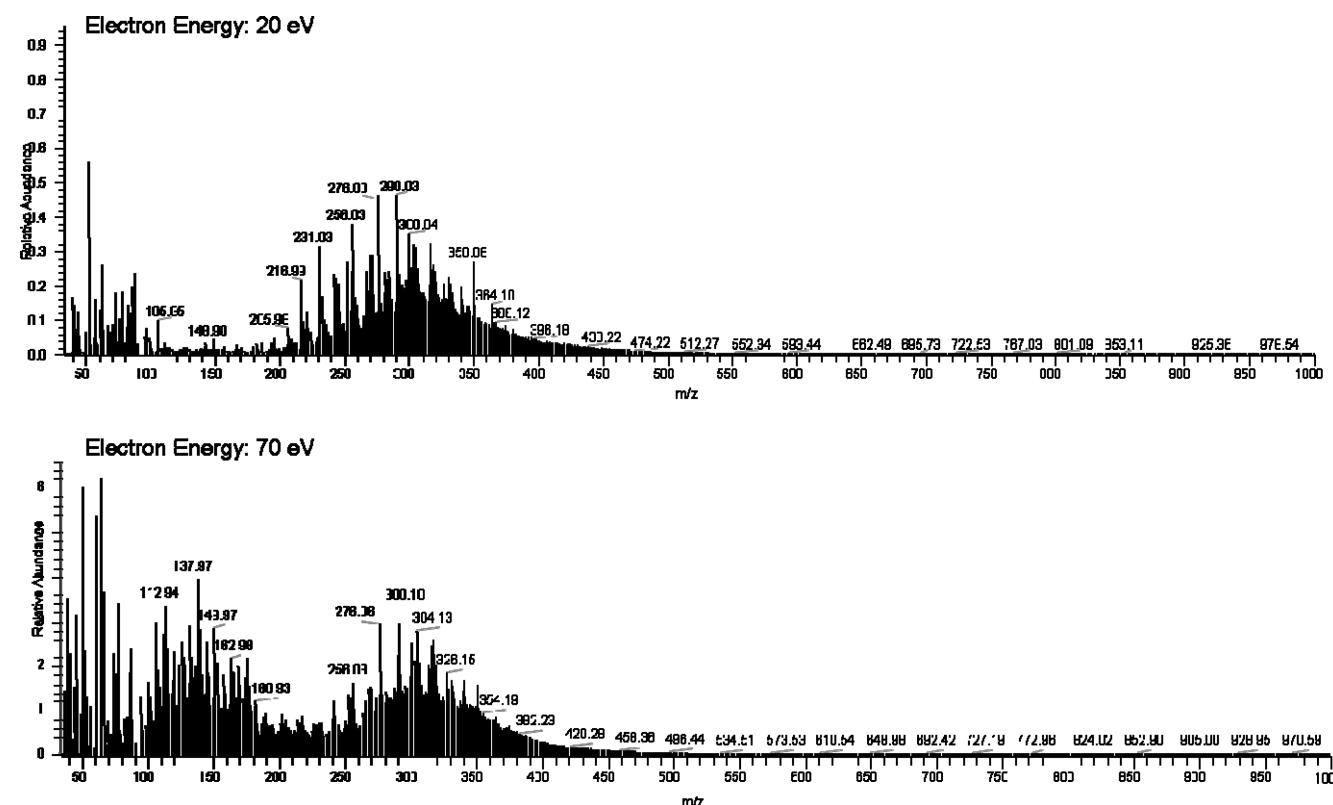
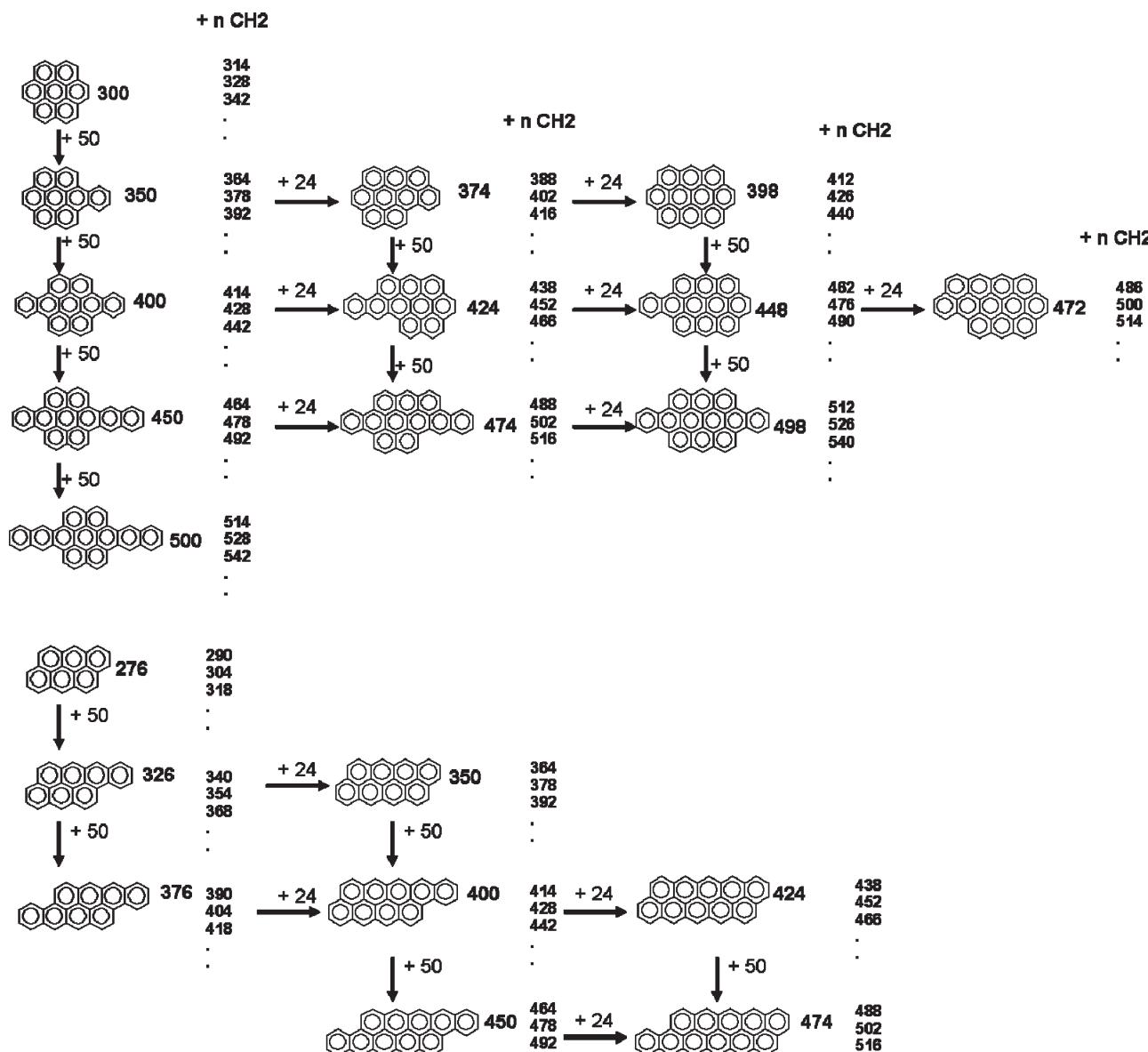


Figure 6. DIP-MS spectra of asphaltene B recorded at (top) 20 eV and (bottom) 70 eV.

Scheme 1. Logical Scheme of Alkyl-polyaromatic Hydrocarbon Evolution (and the Corresponding Molecular Weights) Possibly Present in the Samples Starting from Their Low-Molecular-Weight Building Blocks (Coronene and Dibenzopyrene)



3. Experimental Section

3.1. Samples. Two samples of asphaltenes (named A and B) were analyzed after thermal treatment, coming from two different heavy crude oil derivatives: visbreaking tar and Ural 550+ residues, respectively. They were treated at 420 °C in a thermal industrial plant, according to a procedure described in ref 30, so that they were considered the final product of refinery manipulation. The asphaltenes were precipitated from the corresponding oils according to the following procedure: Toluene (HPLC grade, Sigma-Aldrich) was gently stirred for 30 min at room temperature with the oil samples (volume ratio of 5:1). The mixture was filtered with a 0.5 µm Millipore filter to separate the oil impurities. Toluene was then removed by a rotavapor, and the toluene-free crude oil was mixed with *n*-heptane (volume ratio of 1:50, HPLC grade, Sigma-Aldrich) to precipitate asphaltenes. The mixture was stirred for 2 h and filtered with a 0.5 µm Millipore filter. The asphaltenes collected on the filter

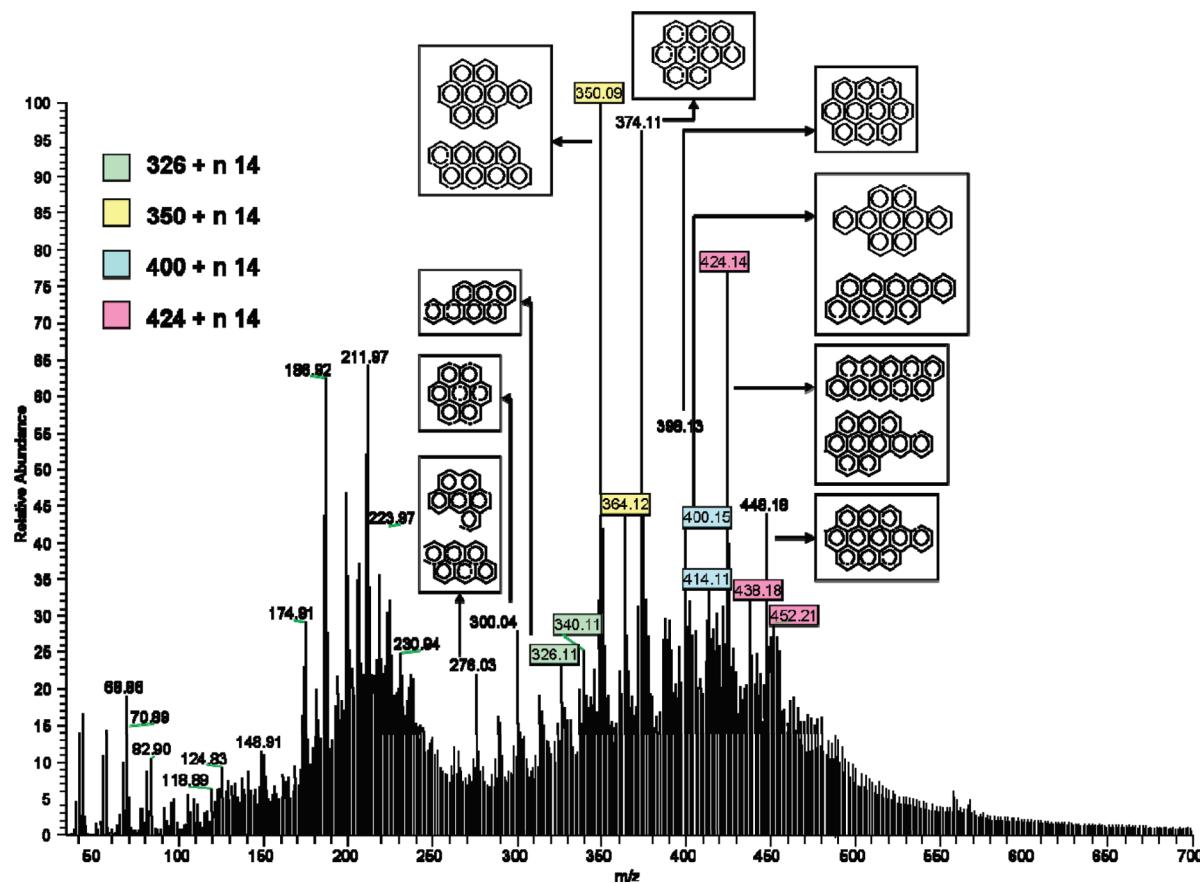
were washed several times with *n*-heptane until the filtrate became colorless. The solid asphaltenes were dried in vacuum at room temperature with an oil-free pump to evaporate the solvent. The elemental composition of sample A is C, 91.3; H, 5.07; N, 0.98; S, 2.23 (wt %), and the elemental composition of sample B is C, 90.0; H, 5.36; N, 2.18; S, 2.31 (wt %).

3.2. Apparatus. DIP-MS analyses were performed by direct introduction of the probe into a system equipped with a detector MS Trace DSQ Thermo with electron-impact ionization and a DIP module. The probe temperature program was the following: 120 °C for 10 s, 60 °C/min up to 200 °C, 50 °C/min up to 340 °C, and 340 °C for 15 min, prolonged up to 240 min for cognitive purposes. The analyses were performed with an ionization voltage of 20 and 70 eV, a source temperature of 250 °C, a mass range between *m/z* 33 and 1000, a scan rate of 2.14 scan/s, and a vacuum better than 7×10^{-5} mbar.

4. Results and Discussion

The DIP mass spectra of the asphaltenes A and B are shown in Figure 4, resulting from the sum of all of the spectra scanned

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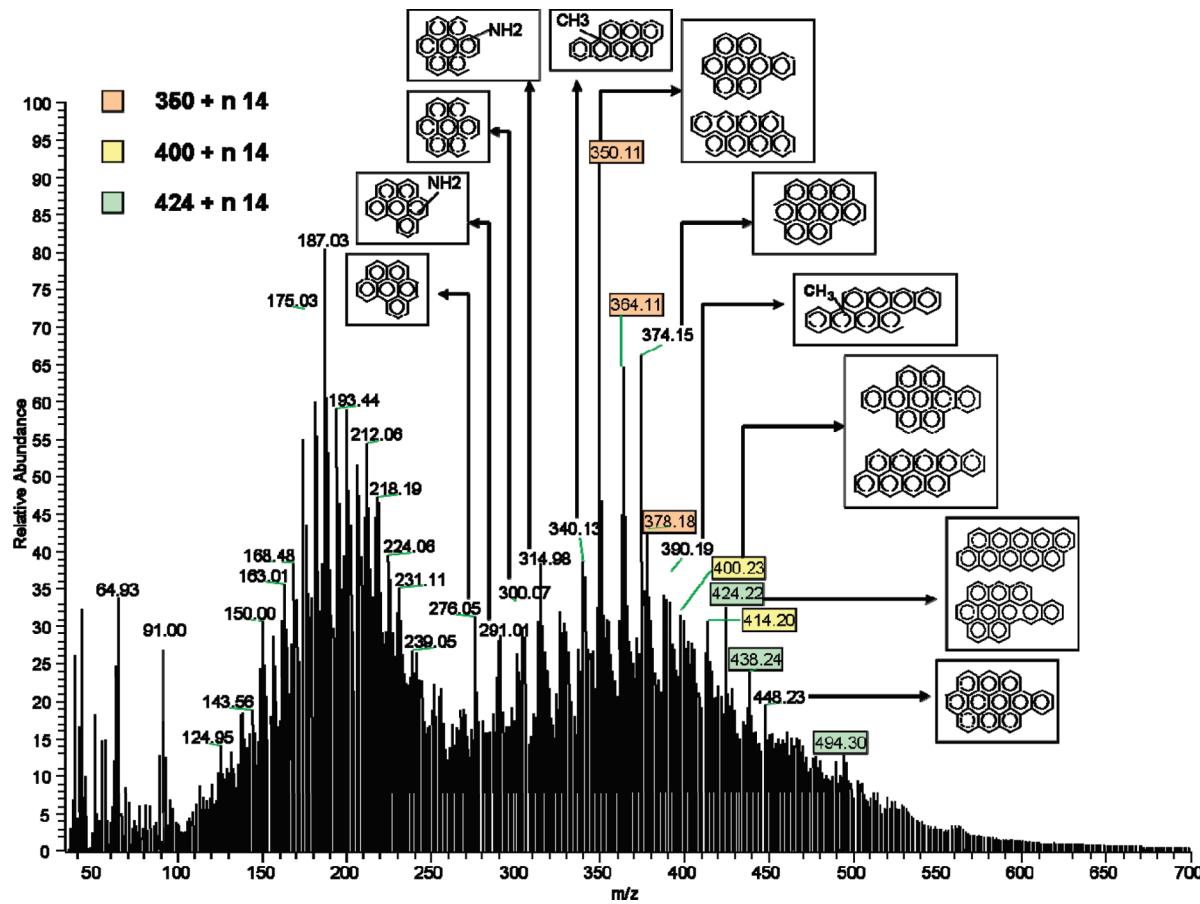


Figure 9. Average DIP–MS spectrum of asphaltene B (polyaromatics labeled by indicative structures and alkyl-aromatics labeled by colored boxes).

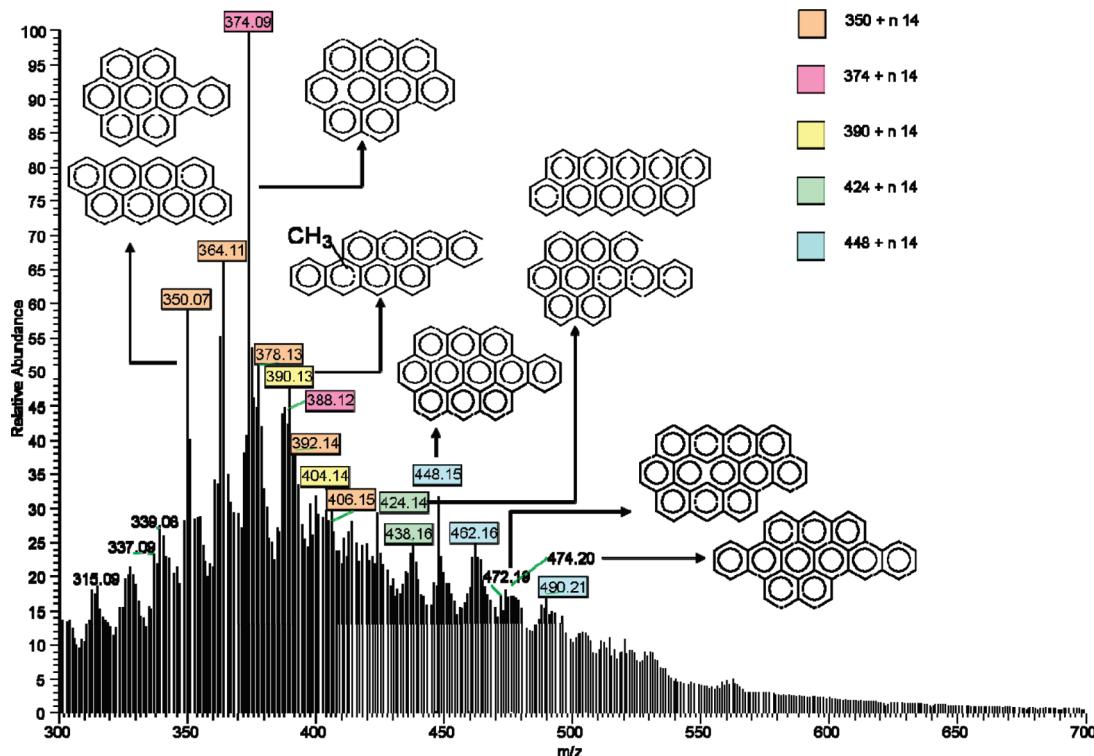


Figure 10. DIP–MS spectrum of asphaltene B after 200 min at 340 °C (polyaromatics labeled by indicative structures and alkyl-aromatics labeled by colored boxes).

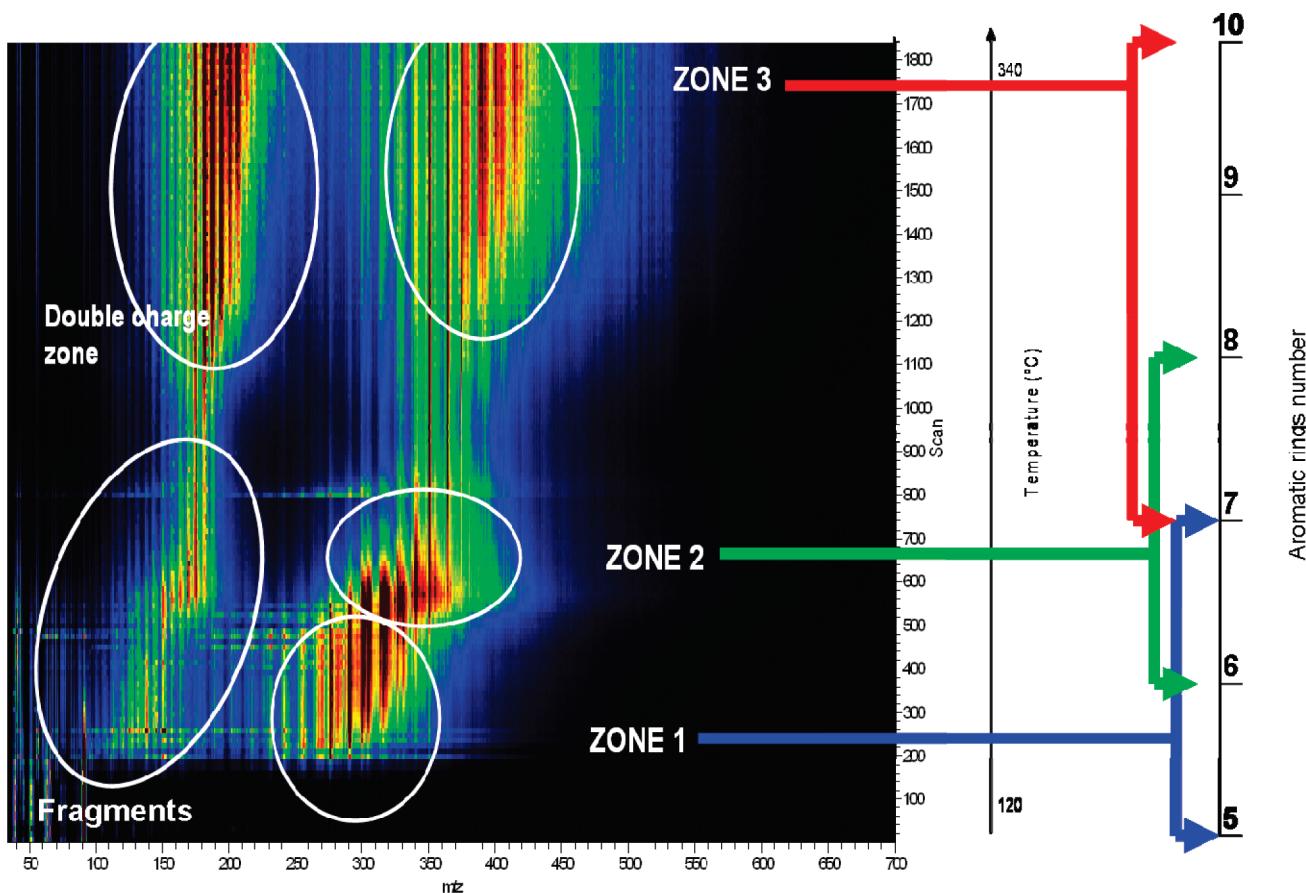


Figure 11. Contour map of asphaltene B.

4.1. m/z 33–100 Region. In this mass range, aliphatic signals are mainly collected. In this range, the spectra of the two asphaltenes show low-intensity aliphatic fragments (homologous series of m/z 41–55–69–83–97 and 43–57–71–85–99) and alkyl-monoaromatic species (e.g., m/z 91 of toluene) at a negligible amount in comparison to that of the signals present in the other ranges. At short analysis times (i.e., a relatively low probe temperature), these peaks are hardly detectable and become more intense with an increasing time and temperature of the run. This evolution is clearly shown in Figure 5, where mass spectra of asphaltene A are reported, as a result of the sum of the mass spectra collected at three different time intervals, i.e., corresponding to the temperature range from 120 to 340 °C and two different levels (at the real beginning and at a steady state) of the isotherm at 340 °C, respectively. An explanation of this behavior is that these fragments are more likely due to alkyl chains bonded to polycyclic aromatics with extent substitution degree are able to vaporize only when the temperature of the probe is increased to a suitable value, giving rise to “light” alkyl fragments at high temperature.

Asphaltenes A and B show (Figure 4) a different fingerprint in this region, with the former showing a well-ordered paraffinic pattern and the latter showing few selected fragments (m/z 65 and 91) dominating the area, because of alkyl benzene derivatives.

4.2. m/z 100–260 Region. This area is characterized by a continuum of signals at each single mass value (Figure 4), resulting from a quite complex distribution of a wide number of alkyl-polyaromatics with medium molecular weight and boiling point from 280 to 500 °C at atmospheric pressure (AP). Because the intensity of this area is higher during the isotherm at 340 °C under vacuum conditions (i.e., evaporation conditions more efficient than 500 °C at AP), the vaporization of “light” species appears unusual. Therefore, besides the presence of single-charge fragments, the phenomenon of “double-charge” formation is proposed as a complementary contribution to this area. This phenomenon is more easily present when there are molecules with a high number of condensed aromatic rings that have a greater ability to stabilize the double charge. In Figure 5, it is possible to find a clear correspondence between the main signals at high m/z values (e.g., m/z 276, 300, 350, 374, 424, and 448) and the main signals in this medium m/z range (i.e., m/z 138, 150, 175, 187, 212, and 224).

To verify this attribution, the same experiment was performed applying the ionization energy of 20 eV (instead of the “conventional” 70 eV). The m/z 100–226 area becomes free of peaks, because of either avoided formation of double-charge species or limited fragmentation of the single-charge molecular ions (Figure 6). Another evidence of the presence of single- and double-charge species is reported later (see comments to Figure 11).

Furthermore, these “double-charge” peaks, often considered as a disturbing interference, can be helpfully applied for a correct interpretation of the corresponding “single-charge” signals, when used coupled, as a diagnostic tool to determine

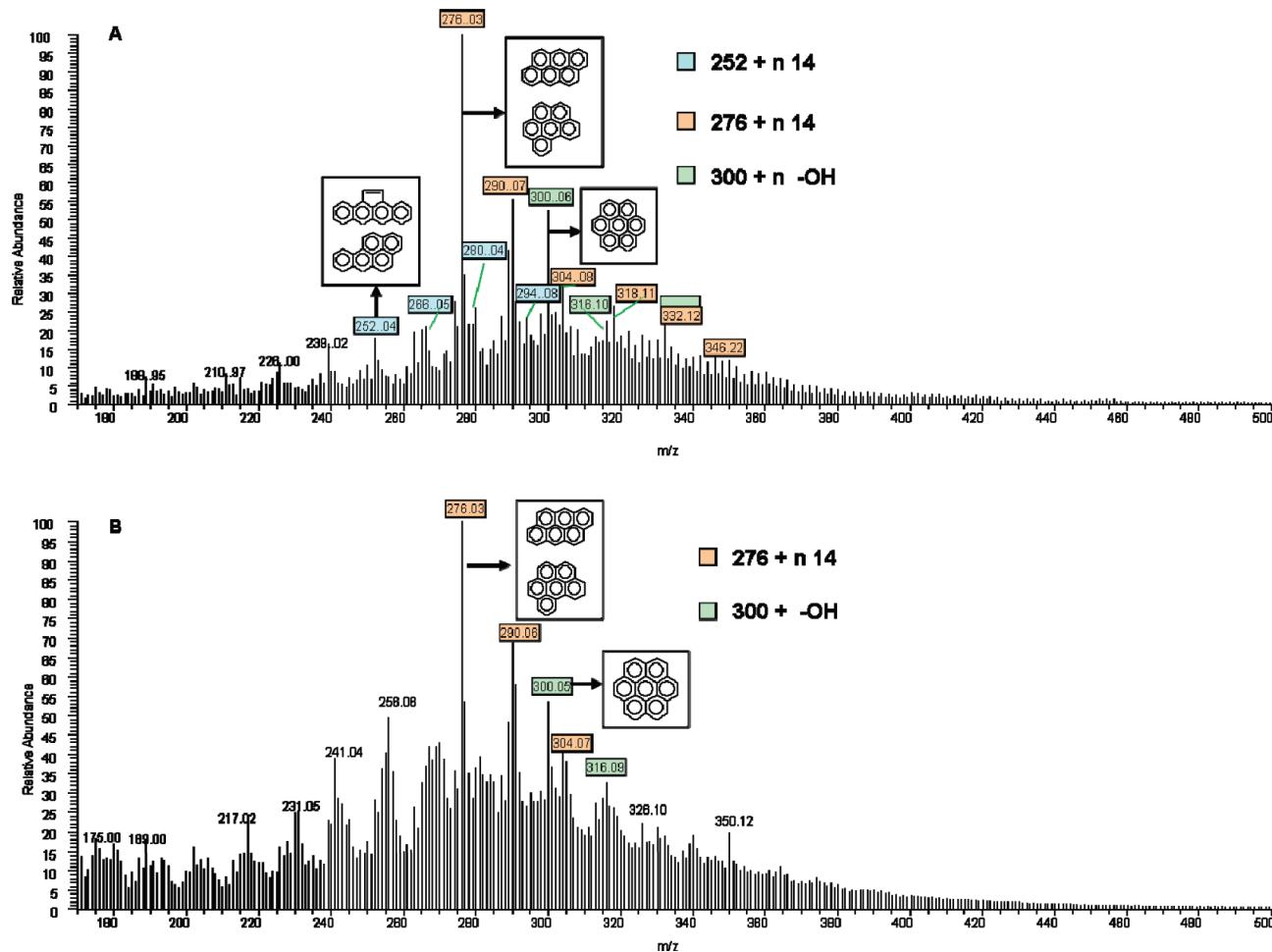


Figure 12. DIP-MS spectra of zone 1 for asphaltenes A and B (polyaromatics labeled by indicative structures and alkyl-aromatics labeled by colored boxes).

the presence of polycyclic aromatic hydrocarbon (PAH) with a high number of aromatic rings.

The two asphaltenes analyzed in this work differentiate in the m/z 100–260 region for both intensity and distribution of the masses. The asphaltene A profile presents weak signals up to m/z 170, and then the intensity increases in a bell-shape mode, with a maximum at around m/z 212. Selected masses attributed to “double-charge” species (m/z 175, 187, 212, 224, and 231) superimpose on the others, representative of few defined building blocks. In asphaltene B, the whole area is covered by a bell-shape population, with dominating peaks at m/z 143, 175, 187, 193, 212, 218, 224, 231, and 239. In this case, the region is more equally crowded than the high-molecular-weight region and not all of these signals can be related to double-charge species. Probably a wide series of aromatic structures is present in this sample.

4.3. m/z 260–700 Region. This area shows the most intense peaks of the whole mass spectrum and is also the most crowded (Figure 4). Selected mass peaks, where PAH molecular weights can be identified, superimpose on the continuum of low-intensity peaks present at each m/z value, more likely representative of molecular ions than fragments. Also, in this region, the peak distribution of asphaltene A differs from that of asphaltene B, with few intense signals well-evident in the m/z 350–450 range, with respect to a wide series of signals present from m/z 290 to 492. Aliphatic fragments are present in small quantity, probably connected to the waxy fraction of these deposits.²⁴

Because of the complexity of the distribution, two different approaches were applied in the attempt to assign the peaks: (a) interpretation of the “traditional” DIP-MS spectrum with attribution of the main peaks [in the effort to give a “realistic” picture to the main m/z values, they are interpreted on the basis of the evolution of polyaromatic and alkyl-polyaromatic species from few certain base building blocks (i.e., coronene and dibenzopyrene) that were identified by additional separated pyrolysis experiments (not shown here)] and (b) creation of the contour map that allows for a more detailed analysis of different zones, created according to the temperature of the probe.

4.3.1. “Traditional” DIP-MS Spectrum. The analysis of the “traditional” DIP-MS spectrum is based on the identification of the homologous series, related to the evolution from low-molecular-weight building blocks (e.g., coronene and dibenzopyrene) by the addition of alkyl side chains (i.e., m/z +14) or addition/condensation of aromatic rings (i.e., m/z +50 and +24, respectively), according to Scheme 1. The real nature of the two low-molecular-weight building blocks was confirmed by separating additional pyrolysis experiments.

The mass spectrum of asphaltene A (Figure 7) shows two homologous series of main peaks (m/z 350, 374, 398, 424, and 448) and minor peaks (m/z 276, 300, 326, 340, 364, 400, 414, 438, 448, and 452), probably originated from two different base structures.

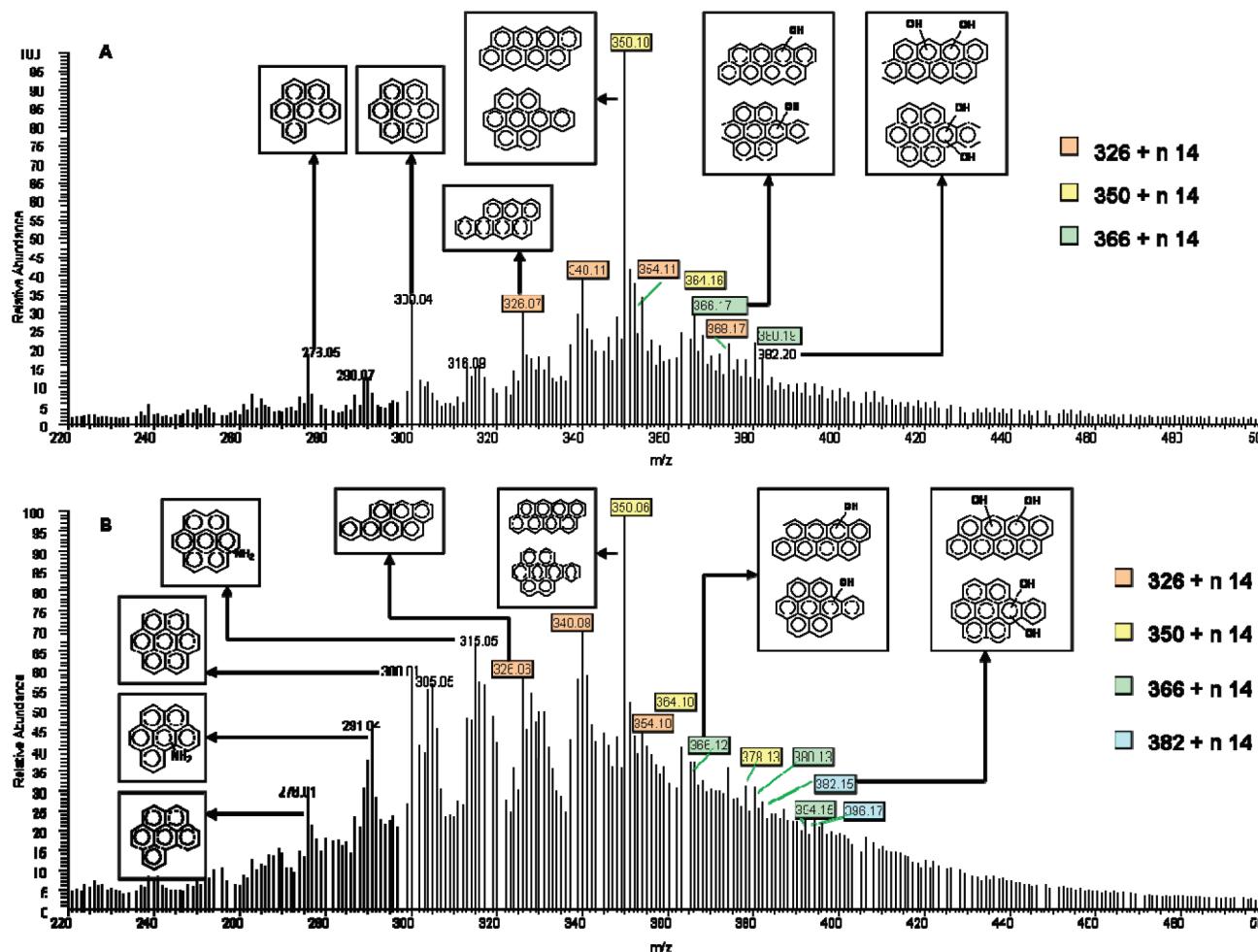


Figure 13. DIP-MS spectra of zone 2 for asphaltenes A and B (polyaromatics labeled by indicative structures and alkyl-aromatics labeled by colored boxes).

The main series (3 times more intense than the top of the bell) starts from mass m/z 350, corresponding to 8 polyaromatic condensed rings (Scheme 1), by following ordered additions of 24 mass unit (peri-condensation) up to 12 condensed rings.

In the second series, the m/z 300 peak may correspond to the molecular weight of coronene (7 condensed aromatic rings). From this attribution, we propose that the m/z 276 peak, which differs of 24 mass unit from coronene, may be associated more likely to benzo[*ghi*]perylene (6 peri-condensed aromatic rings) than to anthanthrene (6 ortho-condensed aromatic rings) by the addition of two carbon atoms. The other peaks of the series are consistent with the addition of C and H atoms, according to Scheme 1, up to the formation of 11 condensed aromatic ring structures. Secondary series are also present, which may be due to alkyl derivatives of these polyaromatics because they each differ by m/z 14 (colored small boxes in Figure 7).

Obviously, the chemical structures related to the mass peaks are representative of a class of molecules, including the isomers, and cannot be ascribed with confidence to one specific structure.

When the probe temperature of 340 °C is prolonged up to 240 min isotherm, the heaviest PAH becomes vaporizable and clearly visible by the DIP-MS technique. This allows for the detection of higher molecular-weight species (m/z 374–514), both polyaromatics (indicated by structures in

Figure 8) and alkyl-polyaromatics (indicated by colored boxes in Figure 8).

The DIP-MS spectrum of asphaltene B is shown in Figure 9. The mass spectrum looks quite different from that of asphaltene A (Figure 7). In particular, only three high-intensity peaks (m/z 350, 364, and 374) are superimposed on a population of medium-intensity peaks, tentatively corresponding to polycondensed species at 8–9 aromatic rings. The proposed attribution for the secondary series of peaks (with masses of m/z 276, 300, 315, 326, 328, 340, 378, 390, 400, 414, 424, 438, and 448) suggests that this sample constituted of a wide distribution of PAHs of 6–11 aromatic rings.

In asphaltene B, the heaviest polyaromatic structures have a mass of m/z 472–494 (corresponding to 11–12 aromatic rings), already visible at the standard temperature program (Figure 9) and particularly evident after 200 min of treatment at 340 °C (Figure 10).

4.3.2. DIP-MS Contour Map. The contour map is obtained by plotting the number of scans (related to the probe temperature during the experiment) against the m/z mass value, according to the procedure previously described. The intensity of the signal (from 2×10^3 to 2×10^7 MS counts) is represented by colors: from the black of the background to the top of the most intense peaks in the blue–pale green–yellow–orange–red–dark blue color range. Figure 11 shows the contour map of asphaltene B. The three main regions described up to now are clearly separated along the x axis

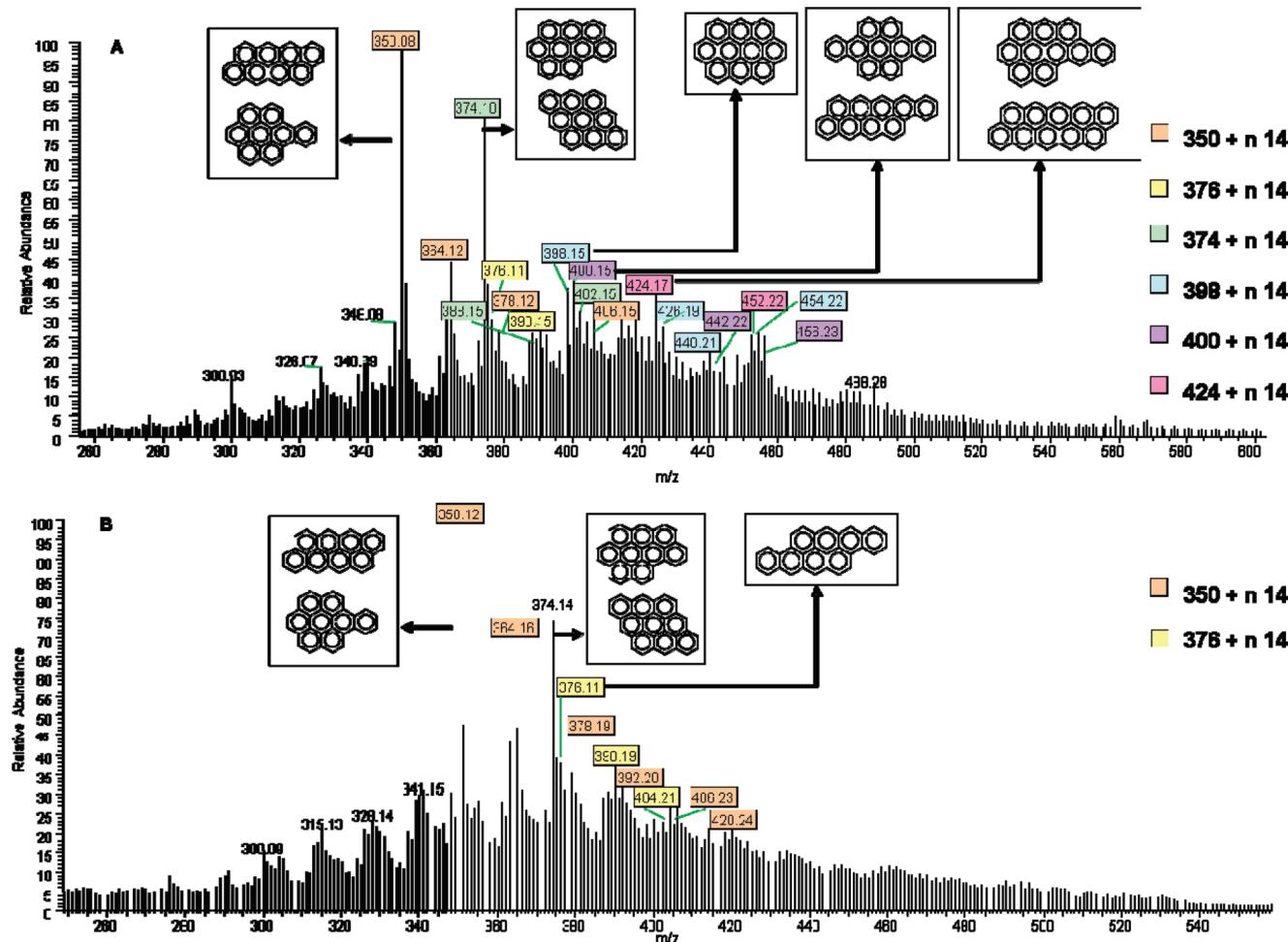


Figure 14. DIP-MS spectra of zone 3 for asphaltenes A and B (polyaromatics labeled by indicative structures and alkyl-aromatics labeled by colored boxes).

(m/z): light–medium- and heavy-molecular-weight species are visible at all of the temperatures applied during the experiment. The low m/z region appears at the temperature range from 120 to 340 °C, with the most intense development at the beginning of the isotherm at 340 °C.

The intermediate m/z range evolves only during the isotherm at 340 °C and forms separated blobs in correspondence with the most intense blobs of the high m/z region. The point-by-point mass analysis identifies single-charge fragments at low temperature and double-charge species at high temperature, which clearly correspond to single-charge peaks in the highest mass region.

The mass distribution in the m/z 260–700 region is characterized by three main areas. When the mass spectrum of each area is analyzed, it is possible to individuate signals not clearly identified in the comprehensive spectra of Figures 7 and 9, which appear too crowded to allow for a detailed investigation of their chemical species.

The DIP-MS spectrum of zone 1 (analysis time of 1–4 min, i.e., 120–340 °C), reported in Figure 12, shows a mass range from m/z 180 to 420, with main peaks reasonably attributed to low-boiling PAHs (i.e., 5–7 aromatic rings). The structures of the bare polyaromatics, corresponding to the main masses, are drawn in Figure 12, whereas the masses indicated by colored boxes correspond to alkyl derivatives that constitute the homologous series of the m/z 14 unit (CH_2 group) from each “bare” polyaromatic.

Asphaltene A is characterized by benzo[*a*]pyrene-like compounds of mass m/z 252 and branched derivatives not present in asphaltene B and by parent molecular structures of m/z 276 and 300 masses, with substituents such as aliphatic chains or –OH groups, with the related mass peaks clearly visible in this spectrum.

Zone 2 of the DIP-MS spectrum (analysis time, 8–12 min; first part of the isotherm at 340 °C) includes masses from m/z 240 to 460, characterized by PAHs with 6–8 aromatic rings and amino groups (Figure 13). In particular, the spectra clearly show one peak at m/z 326 (e.g., benzo[*k*]anthanthrene) and the homologous CH_2 series and another dominating peak at m/z 350 (e.g., benzocoronene), followed by others that can be related to the presence of –OH and aliphatic substitutes of the parent structure.

The analysis of this area provides evidence of the presence of odd m/z values in asphaltene B. Because the fragmentation of the species is scarcely feasible for condensed high-molecular-weight polyaromatic compounds, these masses are proposed to correspond to single N-containing compounds that are found to greatly out number those with multiple N atoms.¹⁸

In zone 3 (analysis time, 12–15 min; second part of the isotherm at 340 °C), masses in the m/z 280–560 range develop (Figure 14). In both samples, the main peaks have masses of m/z 350 (e.g., benzocoronene) and m/z 374 (e.g., dibenzo[*m,k,j*]coronene), i.e., PAHs with 7–12 aromatic

rings. In asphaltene A, besides these species (and their homologous aliphatic series), other peaks are obtained, whose masses agree with more complex polycyclic aromatic and alkyl-polycyclic aromatic compounds. By reverse, in asphaltene B, the main peaks represent the starting point of the homologous series ($m/z +14$).

This plotting procedure indicates that the species in the vapor phase tend to have an increasing number of aromatic rings, analysis time, and probe temperature.

The evidence found here agrees well for sample A, with the asphaltene molecular architecture proposed in the modified Yen model, with a single PAH ring system with peripheral cycloalkane-, branched-, and straight-chain substituents.² On the contrary, the overview of sample B obtained with DIP–MS agrees better with an archipelago structure,^{31,32} i.e., aromatic cores linked by reactive bridges and substituents with side chains.

5. Conclusions

The application of the DIP–MS technique to the analysis of asphaltenes is proposed and described. On the basis of introduction and vaporization under vacuum at a controlled temperature of the solid samples directly into the ionization chamber, DIP–MS allows for separation of the asphaltene components according to their boiling points up to masses of m/z 560. In fact, the melted asphaltene mixture creates a vapor

phase from different components at every single instant (i.e., temperature), and the presence of a dynamic vacuum prevents secondary reactions among them in the gas phase.

Asphaltenes, obtained by thermal treatment from two heavy crude oil derivatives, were analyzed with this technique, and clear evidence on the nature of their components is obtained that allows for the proposal of the following conclusions.

Asphaltene A is characterized by species with a compact polycyclic aromatic core, such as benzo[*a*]pyrene-, benzo[*k*]-anthanthrene-, coronene-, benzocoronene-, and dibenzo[*m,kj*]-coronene-like structures, and paraffinic (and hydroxyl) side chains, in agreement with the asphaltene model proposed by Yen.² The low m/z peaks are due to paraffin fragmentation and “double-charge” species (e.g., m/z 175, 187, 212, 224, and 231), while the real “building blocks” are related to masses in the m/z 350–450 range.

Conversely, asphaltene B shows a wide distribution of species with m/z 276–492 molecular weight, because of growing polycondensed species at 6–12 aromatic rings with alkylbenzenes and aliphatic and heteroatom (O and N) chains. In this case, the different distribution of main peaks between medium and high m/z regions is explained with the presence of “single-charge” species also in the m/z 175–239 region. These data agree with a more complex “archipelago” structure.³²

From this evidence, DIP–MS is a suitable technique to provide a fast and easy way to characterize the fingerprints of heavy derivatives of the crude oil and refinery industry.

(31) Yang, X.; Kilpatrick, P. *Energy Fuels* 2005, 19, 1360–1375.

(32) Wiehe, I. A. *Energy Fuels* 1994, 8, 536–544.