

Article

Comparing Crude Oils with Different API Gravities on a Molecular Level Using Mass Spectrometric Analysis. Part 1: Whole Crude Oil

Jandyson M. Santos ^{1,2} , Alberto Wisniewski Jr. ³ , Marcos N. Eberlin ^{1,4} and Wolfgang Schrader ^{2,*}

¹ ThoMSon Mass Spectrometry Laboratory, University of Campinas-UNICAMP, Institute of Chemistry, Campinas 13083-970, São Paulo, Brazil; jandyson.machado@gmail.com (J.M.S.); mneberlin@gmail.com (M.N.E.)

² Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

³ Department of Chemistry, Federal University of Sergipe-UFS, São Cristóvão 49100-000, Sergipe, Brazil; albertowj@ufs.br

⁴ Mackenzie Presbyterian University, São Paulo 01302-907, SP, Brazil

* Correspondence: wschrader@mpi-muelheim.mpg.de

Received: 22 May 2018; Accepted: 17 September 2018; Published: 16 October 2018



Abstract: Different ionization techniques based on different principles have been applied for the direct mass spectrometric (MS) analysis of crude oils providing composition profiles. Such profiles have been used to infer a number of crude oil properties. We have tested the ability of two major atmospheric pressure ionization techniques, electrospray ionization (ESI($\pm$)) and atmospheric pressure photoionization (APPI(+)), in conjunction with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The ultrahigh resolution and accuracy measurements of FT-ICR MS allow for the correlation of mass spectrometric (MS) data with crude oil American Petroleum Institute (API) gravities, which is a major quality parameter used to guide crude oil refining, and represents a value of the density of a crude oil. The double bond equivalent (DBE) distribution as a function of the classes of constituents, as well as the carbon numbers as measured by the carbon number distributions, were examined to correlate the API gravities of heavy, medium, and light crude oils with molecular FT-ICR MS data. An aromaticity tendency was found to directly correlate the FT-ICR MS data with API gravities, regardless of the ionization technique used. This means that an analysis on the molecular level can explain the differences between a heavy and a light crude oil on the basis of the aromaticity of the compounds in different classes. This tendency of FT-ICR MS with all three techniques, namely, ESI(+), ESI(−), and APPI(+), indicates that the molecular composition of the constituents of crude oils is directly associated with API gravity.

Keywords: API gravity; crude oil; SARA fractions; ultrahigh resolution mass spectrometry

1. Introduction

Crude oils provide the most important energy source in the world, and consist of a wide assortment of compounds containing mostly hydrocarbons, with and without heteroatoms, such as sulfur, nitrogen, and oxygen, which vary widely in molecular weight (MW), polarity, volatility, specific gravity, and viscosity [1]. Because of this highly complex chemical mixture, a detailed characterization of its constituents is essential in order to understand the underlying chemistry of crude oil refining, and to guide and improve the whole process [2].

The general parameters of crude oil quality are assessed by measuring its basic physical properties, such as boiling-point distribution, American Petroleum Institute (API) gravity, density, and viscosity [1].

API gravity is perhaps the most useful parameter, giving a broad general picture of the quality of the oil, and determining its market price [1].

The measurement of API gravity is considered, however, a preliminary assay, and in order to more comprehensively understand and characterize the many thousands of components that form the complex mixture of crude oils and their derivatives, a number of analytical techniques have been used, such as elemental analysis, gas chromatography/mass spectrometry (GC/MS), gas chromatography-flame ionization detector (GC-FID), comprehensive two-dimensional gas chromatography (GC $\times$ GC), infrared spectroscopy (IR), ultraviolet spectroscopy (UV), and thermogravimetry (TG). In particular, GC/MS and GC $\times$ GC [3,4] have been extensively used to obtain geochemical information, particularly from the specific biomarkers present in the non-polar fraction of crude oils [5]. However, these techniques are limited to the more volatile, less polar components with a MW < 400 Da [2].

In the last decade, ultrahigh resolution and accuracy mass spectrometry has offered a new tool to characterize crude oils and its derivatives, and its data has been found to directly correlate with the chemical composition of fossil fuels, as well as with their properties and reactivities [2,6]. Fourier transform mass spectrometry (FT-MS), performed either in ion cyclotron resonance (ICR) [7] or orbitrap mass spectrometers [8,9], and even additional non-Fourier transform (FT) techniques, such as high resolution time-of-flight mass spectrometry (TOF-MS) [10], have been used. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been the most common, as it offers the highest available resolution and accuracy [2]. The FT-MS data for crude oils are translated to molecular formulas, generally represented by $C_cH_hN_nO_oS_s$. The most common ionization technique that has been used is electrospray ionization (ESI), both in its negative and positive ion modes, which is particularly suitable for the gentle ionization of the polar (acidic and basic) components. ESI($\pm$) FT-MS has been used in different applications, such as to characterize polar heteroatomic species before and after hydro-treatments [11], naphthenic acids [12], and heavy oil distillation cuts [13]. In addition, it has also been used for the evaluation of the biodegradation level in crude oils [14], and for the measurement of non-polar polyaromatic hydrocarbons and polyaromatic heterocycles in heavy crude oil asphaltenes [15].

But other atmospheric pressure techniques have also been used, and have been found to provide complementary information on the less polar or more volatile constituents, which may escape detection by ESI($\pm$). For instance, atmospheric pressure photoionization (APPI) has been used to evaluate the aromaticity of asphaltenes [16], and atmospheric pressure chemical ionization (APCI) has shown to improve sensitivity [17], whereas both atmospheric pressure laser ionization (APLI) [18,19] and laser desorption ionization (LDI) [20] have been used to better characterize the aromatic hydrocarbons. Sometimes, the FT-ICR MS data obtained from two or more ionization techniques have been combined to give a more comprehensive composition profile. For instance, Cho et al. [21] have obtained an improved detection of highly unsaturated nitrogen compounds using LDI plus the APPI FT-MS data from shale oils. Gaspar et al. [22] have also compared the ability of several techniques (ESI, APCI, APPI, and APLI) to reveal the heteroatomic and non-heteroatomic content, as well as their double bond equivalent (DBE) trends for a heavy crude oil. Double bond equivalents indicate the number of double bonds and ring closing bonds in a molecule, and therefore are a value of hydrogen deficiency.

The FT-MS data obtained with techniques other than ESI($\pm$) have also been found to directly correlate with the important physical and chemical properties of crude oils. For example, Hur et al. [23] found correlations of APPI(+) FT-ICR MS data with the elemental sulfur, nitrogen, nickel, and vanadium contents, as well as with the total acidity number (TAN) and API gravity for 20 crude oils. A correlation between the API gravity and sulfur content of crude oils from different origins, and the APPI(+) FT-ICR MS data, has also been found [24]. But, a comprehensive study correlating industrial bulk properties, like API gravity, with the molecular information obtained by ultrahigh resolution mass spectrometry using multiple ionization methods has not yet been reported.

In this work, the FT-ICR MS data obtained using two complementary atmospheric pressure ionization techniques were processed in terms of class, DBE, and carbon number, so as to try and find the parameters that would directly correlated to the API gravities of three crude oils. The main goal was to evaluate the capability of the FT-ICR MS analysis to understand, on a molecular level, the compounds that are associated with the level of aromaticity of crude oils in terms of different API gravities. ESI(+) was selected, as it should provide a broad profile of the more polar and basic components, such as the N and NO classes. Similarly, ESI(−) was selected in order to focus on the more acidic components, such as the N and O₂ classes. Finally, APPI(+) was selected, as it has been shown to provide a quite broad description of the less polar components, particularly the aromatic hydrocarbons compounds. APPI(−) was not tested as it is known to provide a similar composition of polar components to that obtained by ESI(±) [16]. Three well-characterized crude oils with different API gravities, all from the Sergipe-Alagoas basin, were chosen [25,26]. In this case, emphasis was placed on the fact that the three crude oils originated from the same field and had the same geological history, but showed different API gravities. This meant that only three different oils could be compared.

2. Results and Discussion

2.1. Crude Oil Properties and Elemental Analysis

Table 1 lists the major physical and chemical properties, classification, and the elemental analysis ratio for the three crude oil samples studied. The API gravity classified the samples as light (API30), medium (API23), and heavy (API16) crude oils [27]. Note that, as expected [1], density inversely correlates to the API gravities. Table 1 also shows an interesting trend between API gravity and H/C ratios. Lower H/C ratios indicate higher aromaticity levels for crude oils. The same is true for the direct tendency between the N/C ratios and API gravities, whereas no tendency was found for the O/C and S/C ratios.

Table 1. Major physical properties and elemental analyses ratios for the three crude oil samples.

Data	Sample		
	Sample 1 API30	Sample 2 API23	Sample 3 API16
API gravity	30.0	23.5	16.4
Density (g·cm ^{−3})	0.8735	0.9089	0.9530
Classification *	Light	Medium	Heavy
H/C	1.6686	1.5829	1.5588
N/C	0.0060	0.0042	0.0026
O/C	0.0291	0.0188	0.0363
S/C	0.0013	0.0017	0.0010

* Source: American Petroleum Institute (API) (1997) [27].

2.2. ESI(+) FT-ICR MS

Figure 1A illustrates the class distribution as determined from all of the ions with an assigned molecular formula, as detected by ESI(+) FT-ICR MS for the three crude oils (for an overview of the spectrum see Figure S1). From such a plot, it is clear that fairly similar class distributions of the most basic/polar components detected via ESI(+) are observed, regardless of the different API gravities. In this context, a class indicates the number of different heteroatoms within one molecular assignment. If, for example, one nitrogen atom is present in the elemental composition, this compound belongs to the N₁-class. The assignments that contain only carbon and hydrogen belong to the HC-class.

This lack of correlation between the class distribution and API gravity has also been observed for the APPI(+) FT-ICR MS data [16,24]. But, when looking at the average DBE (Figure 1B), a direct trend was found using the most abundant N[H]-class, which varies from a DBE of 4 to 28. From the average DBE calculation that was described by Cho et al. [28], we found that the average DBE inversely

correlates with the API gravities, and the following tendency was obtained: API16 > API23 > API30. Therefore, since the higher the DBE the higher the aromaticity, lower API gravities also indicate an inverse tendency with an aromaticity tendency order for the three crude oils analyzed. The intention here was to compare three crude oils from the same field with different API gravities. Despite some overall similarities, the differences in the data shown here are obvious, and a direct tendency to the bulk properties can be found.

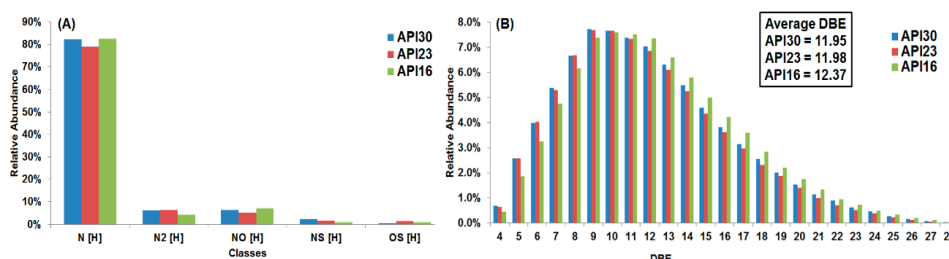


Figure 1. (A) Class distribution and (B) double bond equivalent (DBE) distribution for the N[H]-class. The insert shows the average DBE calculated from (B).

The data obtained from ultrahigh resolution mass spectrometry can be of a high complexity. There are different ways to compare the depth of information that is hidden in all of the numbers and elemental compositions. Kim et al. demonstrated a nice way of comparing different data sets by introducing the planar limit model [29], which is calculated from the linear regression of the line constructed by taking the points of the highest DBE values for each class. It has been demonstrated that the slope increases and the intercept of such a linear regression defines the planar limit and decreases as a function of higher aromaticity [29]. In Figure 2, the data from the N[H]-class from each of the three crudes are compared and, indeed, the slopes increase and the intercepts decrease in either an inverse or direct trend with the API gravity, respectively. Hence, the aromaticity tendency order revealed from the average DBE is also confirmed by the slope and intercept trends obtained using the planar limit concept.

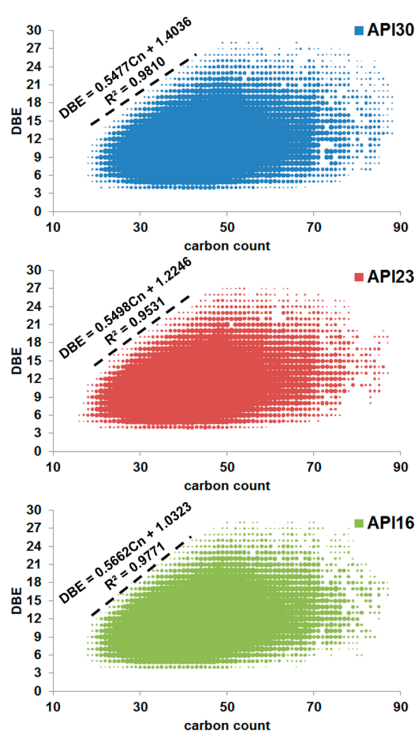


Figure 2. DBE versus carbon count plots for the N[H]-class and the planar limit equations for each plot.

2.3. ESI(−) FT-ICR MS

Figure 3A illustrates class distribution from the ESI(−) FT-ICR MS data for the three crude oils (for the full spectrum see Figure S2). From such a plot that represents the most acid/polar components, no correlation with the API gravity is observed for the N[H]-class, but an inverse tendency is seen for the abundance of the O₂[H]-class, whereas the abundance of the NO[H] and O[H] classes directly correlate with the API gravities.

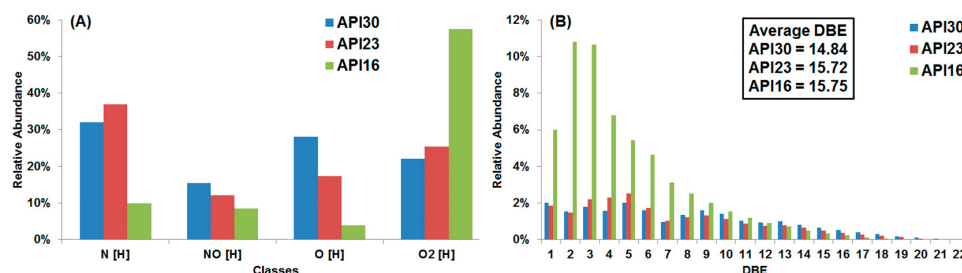


Figure 3. (A) Class distribution and (B) DBE distribution for the O₂[H]-class. The insert shows the average DBE calculated from (B).

The O₂[H]-class, which represents mostly naphthenic acids, is known to have the abundance of heavy crude oils [30,31], with consequently lower API gravities, due to high biodegradation [14]. Here, as demonstrated in Figure 3B, the same inverse trend of the API gravity with the average DBE is seen, as has been observed in Figure 1B.

The concept of planar limit was also applied to the ESI(−) FT-ICR MS data, more specifically to the most abundant O₂[H]-class. The data from the O₂-class, displayed in Figure 4, show that the slope inversely and the intercept directly correlate with API gravity, respectively. From the average DBE and planar limit data, the same tendency to a higher aromaticity in the order of API16 > API23 > API30 was found, as obtained from the ESI(+) and ESI(−) data.

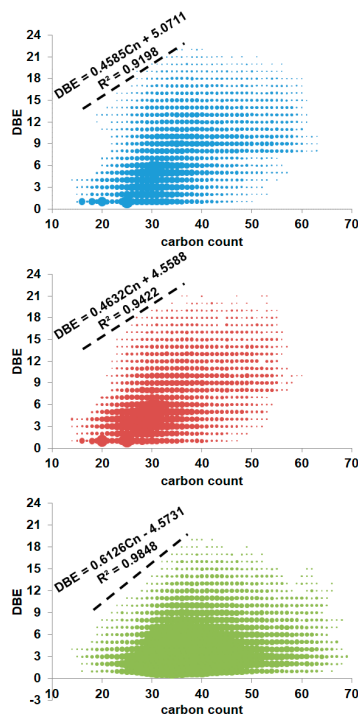


Figure 4. DBE versus carbon count plots for the O₂[H]-class and the planar limit equations for each plot.

2.4. APPI(+) FT-ICR MS

The APPI(+) favors non-polar compounds such as cycloalkane, hydrocarbon, and aromatic species with free electron pairs [16], and produces either protonated molecules $[M + H]^+$ or radical molecular ions M^+ , or both [19]. APPI is often used with a dopant, which facilitates the ionization process and usually forms protonated molecules. Here, toluene and acetone have shown good results for different types of analytes [32].

For APPI(+) (full spectrum shown in Figure S3), as for ESI(+), no direct tendency with class distribution is noted (Figure 5A), which is in accordance with reports from Hur et al. [23], who were also unable to find a correlation between the class distribution and API gravities from the APPI(+) FT-ICR MS data. However, from the average DBE, the same inverse trend with the API gravity was found for the most abundant HC-class (Figure 5B).

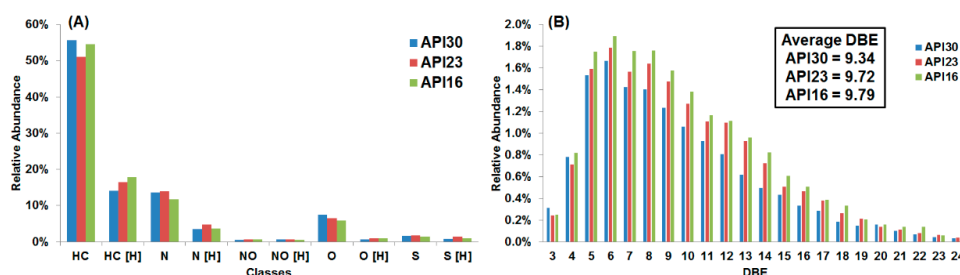


Figure 5. (A) Class distribution and (B) DBE distribution for the HC-class. The insert shows the average DBE calculated from (B).

Again, the planar limit concept was applied to the APPI(+) data (Figure 6), and both the slope and the intercept were found to either inversely or directly correlate with the API gravity, respectively, as was found from the ESI(+) and ESI(−) data. Here, the same tendency to higher aromaticity in the order of $API_{16} > API_{23} > API_{30}$ was found, which means that the aromaticity level increases with a lower API gravity.

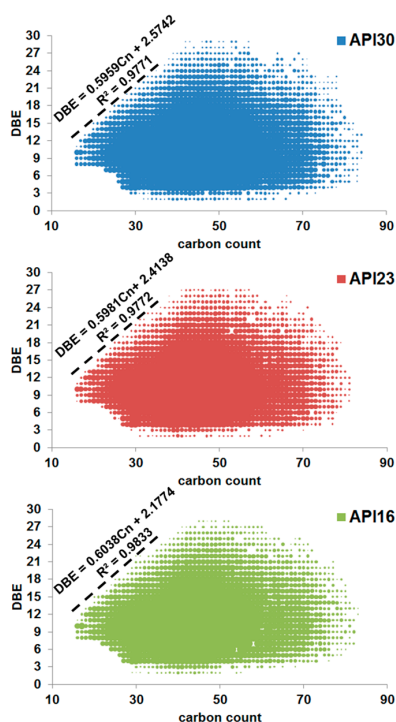


Figure 6. DBE versus carbon count plots for the HC-class and the planar limit equations for each plot.

2.5. Combining ESI($\pm$) and APPI(+)

To show how comprehensively and complementarily the ESI($\pm$) and APPI(+) FT-ICR MS data capture the actual composition of the samples, we constructed Venn diagrams, as illustrated in Figure 7, for the heavy crude oil sample (API16). The number within each circle represents the amount of molecular formulas assigned for each technique, whereas the number within the overlap regions represents the amount of molecular formulas that have been co-assigned. Note that the majority of ion formulas (83%—6887 molecular formulas) were assigned individually and just a small fraction (17%—1451 molecular formulas) were co-assigned. This is in accordance with previous results [22]. Even though the co-assigned formulas were found using different ionization methods, this does not mean that the same compound was ionized. It is not possible to differentiate the different isomeric compounds by MS alone, and it has been shown that different ionization methods ionize different isomers [33]. APPI(+) also greatly surpassed both ESI(+) and ESI(−) in terms of comprehensiveness. This plot shows that the combination of ESI($\pm$) plus APPI(+) provides a fairly broad coverage of the more polar (from medium to high) composition of crude oils, and should therefore provide the best means to look for correlations of chemical composition with physical chemical properties, such as the one we investigated herein.

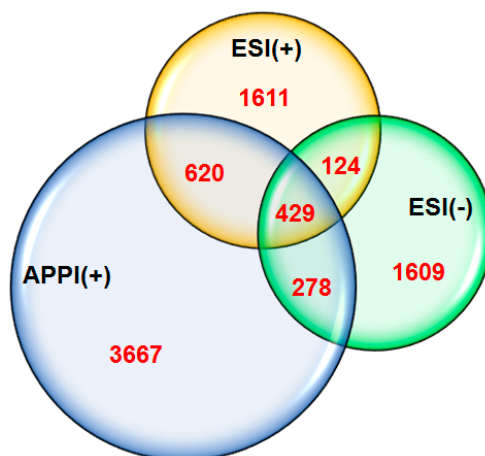


Figure 7. Venn diagrams showing the total amount of assigned molecular formulas obtained from electrospray ionization (ESI(+)), ESI(−), and atmospheric pressure photoionization (APPI(+)) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) data for the heavy crude oil (API16) sample.

A direct comparison of the different classes measured with the different ionization methods ESI($\pm$) and APPI(+) is shown in Figure 8. Figure 8A shows that ESI(+) displays by far the best sensitivity for the N[H]-class, as well as the broadest DBE distribution. For the NO-class, however, as Figure 8B shows, the best abundances have been obtained by ESI(−), whereas the broadest DBE distribution is provided by ESI(+). For the O[H] (or O) class, ESI(−) is found to offer the highest abundances in the low DBE range, but the broadest DBE distribution associated with high abundances is provided by the APPI(+) data (Figure 8C). For the HC (or HC[H]) class, which represents the less polar aromatic hydrocarbons, APPI(+) far surpasses the others (Figure 8D), as is expected from its gas phase ionization mechanism [34]. In this section, we conclude the best ionization technique is attributed to the higher abundances or broadest DBE distribution for the N, N[H], NO, NO[H], O, O[H], HC, and HC [H] classes from the API16 analysis.

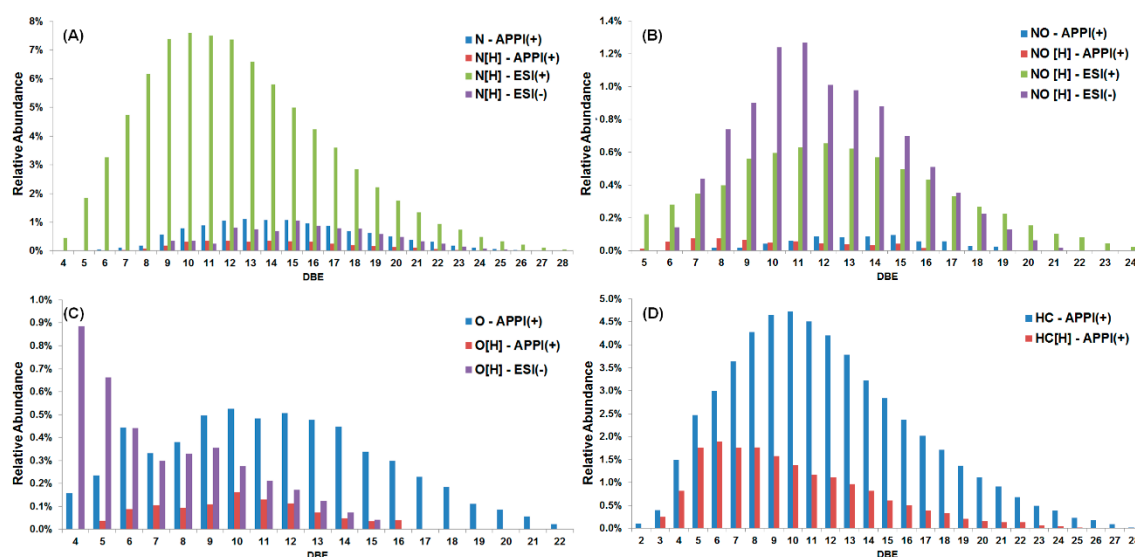


Figure 8. DBE distribution plot for the (A) N and N[H] classes, (B) NO and NO[H] classes, (C) O and O[H] classes, and (D) HC and HC[H] classes, obtained from the ESI(+), ESI(−), and APPI(+) data for the heavy crude oil (API16).

3. Materials and Methods

3.1. Chemicals and Samples

The three crude oil samples collected from the Sergipe-Alagoas basin were provided by Petrobras (Petróleo Brasileiro S/A, Brazil). Toluene (Merck S.A, Germany,) and methanol (J.T. Baker) were used as solvents with an HPLC quality and analytical grade (>99%), and were used without further purification. The crude oil analysis was performed by dissolving 1 mg of the samples in toluene in order to obtain a stock solution of $1 \text{ mg} \cdot \text{mL}^{-1}$, then the stock solution was diluted in methanol, obtaining a final solution of $0.3 \text{ mg} \cdot \text{mL}^{-1}$ in toluene:methanol (1:1 *v/v*). For ESI(+), formic acid was added to facilitate protonation of the basic compounds, hence to favor $[\text{M} + \text{H}]^+$ ions. For ESI(−), methanolic ammonium hydroxide was added so as to facilitate the deprotonation of the more acidic components, in order to favor $[\text{M} - \text{H}]^-$ ions. For APPI(+), no additives were added, as the solvent toluene can act as a dopant for dopant assisted APPI.

3.2. Elemental Analysis

The analysis of the C, H, N, and S contents of the whole crude oil samples were performed using a Vario Elementar CHN-Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany), and the O content was calculated using the difference.

3.3. FT-ICR MS Analysis

FT-ICR MS was performed using a 7 T linear trap quadrupole (LTQ) FT-ICR mass spectrometer (Thermo Fisher, Bremen, Germany) equipped with an ESI source operating in either the positive or negative ion modes, or an APPI(+) source. For ESI($\pm$) FT-ICR MS, the following conditions were used: capillary voltage of +4.0 or −3.5 kV, tube lens +100 or −140 V, capillary temperature 275 °C and capillary voltage +35 or −40 V. Nitrogen was used as a nebulization gas with a sheath gas flow of 4 (arbitrary units), auxiliary gas flow and sweep gas flow of 1 (arbitrary unit) for both. The sample solutions were directly infused at a flow rate of $5 \mu\text{L} \cdot \text{min}^{-1}$. For APPI(+) FT-ICR MS, the following conditions were used: a vaporizer temperature of 350 °C, capillary temperature of 275 °C, tube lens of +75 V, and a Krypton photoionization lamp. Nitrogen was used as a nebulization gas with a sheath gas flow in a range of 5–20 (arbitrary units), and an auxiliary gas flow and sweep gas flow of 5 (arbitrary

unit). The flow rate of $10 \mu\text{L}\cdot\text{min}^{-1}$ was used for the direct infusion of the sample solutions. The data were acquired using a 3 s transient, resulting in a mass resolving power of $m/\Delta m_{50\%} = 400,000$ at m/z 400, and 100 scans were averaged in each run. The data acquisitions were performed in the range of m/z 150–1400. The FT-ICR MS data were collected using the LTQ FT Ultra 2.2 (Thermo Fisher, Bremen, Germany) software.

3.4. Data Analysis

The unprocessed FT-ICR MS data obtained were processed and analyzed by Xcalibur 2.2 software (Thermo Fischer Scientific, Bremen, Germany), as described previously [15]. From the MS data, the peak lists were imported and converted to molecular formulas using Composer V1.5.0 software (Sierra Analytics, Modesto, CA, USA). To process and assign formulas in the MS data, the following parameters were applied: $0 \leq H \leq 1000$, $0 \leq C \leq 200$, $0 \leq N \leq 3$, $0 \leq O \leq 3$, $0 \leq S \leq 3$, and $0 \leq \text{DBE} \leq 40$, with a maximum mass error of 1 ppm, where the protonated, deprotonated molecules, or radical species were distinguished and assigned separately. Then, the list of molecular formulas processed was generated and transferred into Excel software (Microsoft Office Professional Plus 2010, Microsoft Excel 2010) using a lab-written tool, for further data evaluation.

4. Conclusions

We have performed a detailed characterization of crude oils with different API gravities on a molecular level from FT-ICR MS data, using different ionization techniques. Different data interpretations such as the average DBE from the DBE distribution plots, and the concept of planar limit from the DBE versus carbon count plots, demonstrated the existence of a trend between the molecular composition and API gravity. The molecular composition was obtained based on the most acidic (ESI(−)) and basic (ESI(+)) polar constituents of crude oils, as well as the less polar components, namely the aromatic hydrocarbons (APPI(+)), which shows the broadest composition of the crudes using FT-ICR MS analysis. An aromaticity tendency order was established in the following order, that is, $\text{API16} > \text{API23} > \text{API30}$, showing that the heavy crude oil presents a higher aromaticity level when compared with the medium and light crude oils, and that this trend can be properly revealed by applying direct FT-ICR MS analysis and a comprehensive set of ionization techniques. These results show that it is possible to correlate molecular information from mass spectrometric data sets with bulk parameters from a crude oil, such as the API gravity. Although the data obtained from ultrahigh resolution MS studies are extremely complex, they allow for a detailed characterization of such complex mixtures.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/11/10/2766/s1>, Figure S1: ESI(+) FT-ICR MS for the crude oils with different API gravities; Figure S2: ESI(−) FT-ICR MS for the crude oils with different API gravities; Figure S3: APPI(+) FT-ICR MS for the crude oils with different API gravities; Figure S4: ESI(+), ESI(−), and APPI(+) FT-ICR MS for the heavy crude oil with API gravity of 16 (API16).

Author Contributions: W.S. and M.N.E. conceived research; J.M.S. performed the experiments and analyzed the data; A.W.J. contributed reagents, materials, and analysis tools; J.M.S. and W.S. wrote the paper.

Funding: São Paulo Research Foundation (FAPESP) and Petróleo Brasileiro S/A (Petrobras)

Acknowledgments: The authors are grateful to FAPESP (process numbers 2013/19161-4 and 2015/05818-7) for the fellowships, and to Petrobras (Petróleo Brasileiro S/A) for financial support. Additionally, the authors thank David Stranz (Sierra Analytics, Modesto, CA, USA) for assistance in MS-data evaluation.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Speight, J.G. *The Chemistry and Technology of Petroleum*, 4th ed.; CRC Press: New York, NY, USA, 2006.
2. Cho, Y.; Ahmed, A.; Islam, A.; Kim, S. Developments in FT-ICR MS instrumentation, ionization techniques, and data interpretation methods for petroleomics. *Mass Spectrom. Rev.* **2015**, *34*, 248–263. [[CrossRef](#)] [[PubMed](#)]
3. Casilli, A.; Silva, R.C.; Laakia, J.; Oliveira, C.J.F.; Ferreira, A.A.; Loureiro, M.R.B.; Azevedo, D.A.; Aquino Neto, F.R. High resolution molecular organic geochemistry assessment of Brazilian lacustrine crude oils. *Org. Geochem.* **2014**, *68*, 61–70. [[CrossRef](#)]
4. Li, S.; Cao, J.; Hu, S.; Zhang, D.; Fan, R. Analysis of terpanes in biodegraded oils from China using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. *Fuel* **2014**, *133*, 153–162. [[CrossRef](#)]
5. Duan, Y. Geochemical characteristics of crude oil in fluvial deposits from maling oilfield of ordos basin, China. *Org. Geochem.* **2012**, *52*, 35–43. [[CrossRef](#)]
6. Chacon-Patino, M.L.; Vesga-Martinez, S.J.; Blanco-Tirado, C.; Orrego-Ruiz, J.A.; Gomez-Escudero, A.; Combariza, M.Y. Exploring Occluded Compounds and Their Interactions with Asphaltene Networks Using High-Resolution Mass Spectrometry. *Energy Fuels* **2016**, *30*, 4550–4561. [[CrossRef](#)]
7. Corilo, Y.E.; Vaz, B.G.; Simas, R.C.; Lopes Nascimento, H.D.; Klitzke, C.F.; Pereira, R.C.L.; Bastos, W.L.; Santos Neto, E.V.; Rodgers, R.P.; Eberlin, M.N. Petroleomics by EASI($\pm$) FT-ICR MS. *Anal. Chem.* **2010**, *82*, 3990–3996. [[CrossRef](#)] [[PubMed](#)]
8. Zhurov, K.O.; Kozhinov, A.N.; Tsybin, Y.O. Evaluation of high-field orbitrap fourier transform mass spectrometer for petroleomics. *Energy Fuels* **2013**, *27*, 2974–2983. [[CrossRef](#)]
9. Vetere, A.; Schrader, W. Mass Spectrometric Coverage of Complex Mixtures: Exploring the Carbon Space of Crude oil. *Chem. Sel.* **2017**, *2*, 849–853. [[CrossRef](#)]
10. Klitzke, C.F.; Corilo, Y.E.; Siek, K.; Binkley, J.; Patrick, J.; Eberlin, M.N. Petroleomics by ultrahigh-resolution time-of-flight mass spectrometry. *Energy Fuels* **2012**, *26*, 5787–5794. [[CrossRef](#)]
11. Wu, Z.; Rodgers, R.P.; Marshall, A.G.; Strohm, J.J.; Song, C. Comparative compositional analysis of untreated and hydrotreated oil by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2005**, *19*, 1072–1077. [[CrossRef](#)]
12. Headley, J.V.; Barrow, M.P.; Peru, K.M.; Fahlman, B.; Frank, R.A.; Bickerton, G.; McMaster, M.E.; Parrott, J.; Hewitt, L.M. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 1899–1909. [[CrossRef](#)] [[PubMed](#)]
13. Freitas, S.; Malacarne, M.M.; Romão, W.; Dalmaschio, G.P.; Castro, E.V.R.; Celante, V.G.; Freitas, M.B.J.G. Analysis of the heavy oil distillation cuts corrosion by electrospray ionization FT-ICR mass spectrometry, electrochemical impedance spectroscopy, and scanning electron microscopy. *Fuel* **2013**, *104*, 656–663. [[CrossRef](#)]
14. Vaz, B.G.; Silva, R.C.; Klitzke, C.F.; Simas, R.C.; Lopes Nascimento, H.D.; Pereira, R.C.L.; Garcia, D.F.; Eberlin, M.N.; Azevedo, D.A. Assessing biodegradation in the llanos orientales crude oils by electrospray ionization ultrahigh resolution and accuracy fourier transform mass spectrometry and chemometric analysis. *Energy Fuels* **2013**, *27*, 1277–1284. [[CrossRef](#)]
15. Molnárné Guricza, L.; Schrader, W. Electrospray ionization for determination of non-polar polyaromatic hydrocarbons and polyaromatic heterocycles in heavy crude oil asphaltenes. *J. Mass Spectrom.* **2015**, *50*, 549–557. [[CrossRef](#)] [[PubMed](#)]
16. Pereira, T.M.C.; Vanini, G.; Oliveira, E.C.S.; Cardoso, F.M.R.; Fleming, F.P.; Neto, A.C.; Lacerda, V., Jr.; Castro, E.V.R.; Vaz, B.G.; Romão, W. An evaluation of the aromaticity of asphaltenes using atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry—APPI($\pm$) FT-ICR MS. *Fuel* **2014**, *118*, 348–357. [[CrossRef](#)]
17. Kim, Y.H.; Kim, S. Improved Abundance Sensitivity of Molecular Ions in Positive-Ion APCI MS Analysis of Petroleum in Toluene. *J. Am. Soc. Mass Spectrom.* **2010**, *21*, 386–392. [[CrossRef](#)] [[PubMed](#)]
18. Panda, S.K.; Andersson, J.T.; Schrader, W. Characterization of Supercomplex Crude Oil Mixtures: What Is Really in There? *Angew. Chem. Int. Ed.* **2009**, *48*, 1788–1791. [[CrossRef](#)] [[PubMed](#)]

19. Schrader, W.; Panda, S.K.; Brockmann, K.J.; Benter, T. Characterization of non-polar aromatic hydrocarbons in crude oil using atmospheric pressure laser ionization and Fourier transform ion cyclotron resonance mass spectrometry (APLI FT-ICR MS). *Analyst* **2008**, *133*, 867–869. [[CrossRef](#)] [[PubMed](#)]
20. Palacio Lozano, D.C.; Orrego-Ruiz, J.A.; Barrow, M.P.; Cabanzo Hernandez, R.; Mejía-Ospino, E. Analysis of the molecular weight distribution of vacuum residues and their molecular distillation fractions by laser desorption ionization mass spectrometry. *Fuel* **2016**, *171*, 247–252. [[CrossRef](#)]
21. Cho, Y.; Jin, J.M.; Witt, M.; Birdwell, J.E.; Na, J.G.; Roh, N.S.; Kim, S. Comparing laser desorption ionization and atmospheric pressure photoionization coupled to fourier transform ion cyclotron resonance mass spectrometry to characterize shale oils at the molecular level. *Energy Fuels* **2013**, *27*, 1830–1837. [[CrossRef](#)]
22. Gaspar, A.; Zellermann, E.; Lababidi, S.; Reece, J.; Schrader, W. Impact of different ionization methods on the molecular assignments of asphaltenes by FT-ICR mass spectrometry. *Anal. Chem.* **2012**, *84*, 5257–5267. [[CrossRef](#)] [[PubMed](#)]
23. Hur, M.; Yeo, I.; Kim, E.; No, M.H.; Koh, J.; Cho, Y.J.; Lee, J.W.; Kim, S. Correlation of FT-ICR mass spectra with the chemical and physical properties of associated crude oils. *Energy Fuels* **2010**, *24*, 5524–5532. [[CrossRef](#)]
24. Chiaberge, S.; Fiorani, T.; Savoini, A.; Bionda, A.; Ramello, S.; Pastori, M.; Cesti, P. Classification of crude oil samples through statistical analysis of APPI FTICR mass spectra. *Fuel Process. Technol.* **2013**, *106*, 181–185. [[CrossRef](#)]
25. Maciel, S.T.A.; Wisniewski, A., Jr.; De Souza, M.J.B. Use of micropyrolysis and TG to study the thermal catalytic conversion of onshore crude oil using the zeolite catalysts type y and ferrierite. *J. Therm. Anal. Calorim.* **2015**, *122*, 369–377. [[CrossRef](#)]
26. Santos, J.M.; Santos, F.M.L.; Araujo, R.G.O.; Lessa, A.C.; Souza, J.P.D.; Santos, M.J.D.; Wisniewski, A. Chemical aspects of onshore crude oils from the Carmópolis Field, Sergipe-Alagoas Basin, Brazil: A case study on the industrial process for water-oil separation. *Energy Fuels* **2015**, *29*, 1315–1322. [[CrossRef](#)]
27. Daubert, T.E.; Danner, R.P.E. *API Technical Data Book—Petroleum Refining*; American Petroleum Institute (API): Washington, DC, USA, 1997.
28. Cho, Y.; Na, J.G.; Nho, N.S.; Kim, S.; Kim, S. Application of saturates, aromatics, resins, and asphaltenes crude oil fractionation for detailed chemical characterization of heavy crude oils by fourier transform ion cyclotron resonance mass spectrometry equipped with atmospheric pressure photoionization. *Energy Fuels* **2012**, *26*, 2558–2565. [[CrossRef](#)]
29. Cho, Y.; Kim, Y.H.; Kim, S. Planar limit-assisted structural interpretation of saturates/aromatics/resins/asphaltenes fractionated crude oil compounds observed by fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2011**, *83*, 6068–6073. [[CrossRef](#)] [[PubMed](#)]
30. Rowland, S.M.; Robbins, W.K.; Corilo, Y.E.; Marshall, A.G.; Rodgers, R.P. Solid-phase extraction fractionation to extend the characterization of naphthenic acids in crude oil by electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2014**, *28*, 5043–5048. [[CrossRef](#)]
31. Terra, L.A.; Filgueiras, P.R.; Tose, L.V.; Romão, W.; De Souza, D.D.; De Castro, E.V.R.; De Oliveira, M.S.L.; Dias, J.C.M.; Poppi, R.J. Petroleomics by electrospray ionization FT-ICR mass spectrometry coupled to partial least squares with variable selection methods: Prediction of the total acid number of crude oils. *Analyst* **2014**, *139*, 4908–4916. [[CrossRef](#)] [[PubMed](#)]
32. Klee, S.; Albrecht, S.; Derpmann, V.; Kersten, H.; Benter, T. Generation of ion-bound solvent clusters as reactant ions in dopant-assisted APPI and APLI. *Anal. Bioanal. Chem.* **2013**, *405*, 6933–6951. [[CrossRef](#)] [[PubMed](#)]
33. Vetere, A.; Schrader, W. 1-and 2-Photon Ionization for Online FAIMS-FTMS Coupling Allows New Insights into the Constitution of Crude Oils. *Anal. Chem.* **2015**, *87*, 8874–8879. [[CrossRef](#)] [[PubMed](#)]
34. Kauppila, T.J.; Kuuranne, T.; Meurer, E.C.; Eberlin, M.N.; Kotiaho, T.; Kostinen, R. Atmospheric pressure photoionization mass spectrometry. Ionization mechanism and the effect of solvent on the ionization of naphthalenes. *Anal. Chem.* **2002**, *74*, 5470–5479. [[CrossRef](#)] [[PubMed](#)]

