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Petroleomics by Direct Analysis in Real Time-Mass Spectrometry

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Abstract

The analysis of crude oil and its fractions applying ambient ionization techniques is yet under explored in mass spectrometry (MS). Direct Analysis in Real Time (DART) in positive ion mode detection was coupled to linear ion trap quadrupole (LTQ) and Orbitrap mass spectrometer and optimized to analyze crude oil and paraffin samples. The ionization and acquisition parameters of the DART-MS such as the template substrates (paper, TLC plate and glass), temperature (from 100 up to 400 ^{o}C), carrier gas (helium and nitrogen), concentration of analyte (from 0.33 to 6 mg mL^{-1}) and acquisition time (from 1 to 10 μscans) were optimized for crude oil analyzes. DART-MS rendered the optimum conditions of operation using paper as a substrate, T = 400 ^{o}C, helium as a carrier gas, sample concentration ≥ 6 mg mL^{-1}, and acquisition time < 2 μscans. For crude oils analyzes, DART(+)-Orbitrap mass spectra detected nitrogen-containing protonated species, whereas for paraffin samples, hydroxylated HCs species (O_x classes, where x = 1-4) with DBEs of 1-4 were detected, being their structures and connectivity confirmed by CID experiments (MS^2). The DART(+)-MS and CID experiments (MS^2 and MS^3) were also able to identify porphyrin standard compounds as $[M + H]^+$ ions of *m/z* 615.2502 and 680.1763, where M = $C_{44}H_{30}N_4$ and $C_{44}H_{28}N_4OV$, respectively.

Key-words: ambient mass spectrometry, DART-MS, crude oil, paraffin, porphyrin.

1. Introduction

A paragraph on interest of what you have done

A paragraphe on other analytical techniques thatwre applied to what you have done and their limitations.

The objective of this work was to investigate the application of a direct analysis in rReal time (0DART) for this purpose. DART developed by Cody and Laramée,[1] is a type of ambient pressure ionization technique. Its coupling with mass spectrometry has allowed many applications in different fields such as forensic,[2-6] pharmaceutical,[7-9] food,[10-14] analysis, in biology,[15-17] chemistry,[18-20] In crude oil analysis [21] there are no application of DART except the work of Rummel et al.,[22] where it was coupled to Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer . Here, the DART source was coupled to a hybrid mass analyzer (LTQ Orbitrap Velos Pro™) and the ionization and acquisition parameters (substrates, temperature and type of gas heater, concentration of analyte and acquisition time) were optimized for crude oil analyzes. The ability of DART source in paraffin and porphyrin compounds ionization was also evaluated.

2. Procedure

2.1 Reagents and samples

Dichloromethane, heptane, and tetrahydrofuran, THF, (analytical grades with purity higher than 99.5%) were supplied by Sigma–Aldrich Chemicals USA and were used to prepare solutions of crude oil, paraffin and porphyrin standard compounds.

Seven crude oil samples, named samples A to G, were supplied by PETROBRAS and characterized to determine the API degree (ASTM D1298-99) and saturates, aromatics, resins, and asphaltenes (SARA) content. For all the crude oils evaluated, API degree values

ranged from 26 to 30, classifying them as medium crude oils (API degree = 22-30). Saturates content ranged from 51 to 65 wt %. To evaluate the detection sensibility of DART technique, samples were diluted in dichloromethane in five different concentrations: 0.33; 1.0; 1.6; 3.3 and 6 mg mL^{-1}. A volume of 10μL was spotted on the paper surface and analysed by DART-MS. Two other surfaces were tested as substrates: glass and a thin layer chromatography (TLC) plate. The stationary phase of TLC is composed of silica gel.

Three saturated hydrocarbon samples were also studied in this work, named paraffin A, B and C. The first two samples, paraffins A and B, were purchased from Sigma–Aldrich Chemicals USA and Vetec Química Fina Ltda, respectively, whereas the paraffin C was obtained from a food grade process. The organic solutions were prepared in heptane at ≈ 10 mg mL^{-1} and a volume of 10μL was spotted on the TLC plate.

The porphyrin standard compounds such as 5,10,15,20-tetraphenyl-21H,23H-porphine and 5,10,15,20-tetraphenyl-21H,23H-porphine vanadium(IV) oxide, with molecular formula (M) equal to $C_{44}H_{30}N_4$ and $C_{44}H_{28}N_4OV$ and molecular weight of 614.2471 and 679.1703, respectively, were also studied. Both porphyrin standard compounds were purchased from Sigma–Aldrich Chemicals USA. Solutions were prepared at 100 mg L^{-1} in THF and after, a volume of 10μL was spotted on paper substrate and analysed by DART(+)-MS.

2.2 DART(+)-MS

For the experiments, DART–MS system consisting of a DART ion source (IonSense, Saugus, MA, USA) was coupled with a hybrid mass spectrometer: LTQ Orbitrap Velos Pro™ (Thermo Fisher Scientific, Bremen, Germany). The operating conditions of the DART ion

source were as follows: positive ion mode; helium flow: 4.0 L min^{-1}; discharge needle voltage: 3.0 kV; perforated and grid electrode potentials: +150 and +350 V, respectively. The distance between the DART gun exit and mass spectrometer inlet was about 5-10 mm. For glasses and paper surfaces, the sample introductions were carried out manually, whereas for TLC plate substrate it was automatically performed using Dip-it holder samplers. To assess the influence of the gas beam temperature on the signal intensity, crude oil spots were analyzed at different temperatures ranging from 100 to 400 ^{o}C using helium and nitrogen as the gas beam.

DART(+) mass spectra were acquired using both a LTQ and an Orbitrap mass analyzers. For high resolution experiments using Orbitrap mass analyzer, a mass resolving power of 100,000 (FWHM, at *m/z* 400; 0.5 s scan cycle time) was reached. As consequence, a mass error about 3 to 5 ppm was measured, where the mass accuracy is determined from Error (ppm) = $((m/z_{measured} - m/z_{theoretical})/m/z_{theoretical}) \times 10^6$.

The maximum ion injection time was about 10 and 300 ms for LTQ and Orbitrap, respectively, with the automatic gain control (AGC, corresponding to the number of changes transferred from the front-stage ion trap to the orbitrap analyzer) target set at 1×10^5. The full scan mass spectra were acquired over the range of *m/z* 150–1000. Tandem mass spectrometry (DART-MS/MS) was also performed by collision-induced dissociation with a collision energy of 15–30% (manufacturer's unit) using LTQ as mass analyzer.

For crude oil samples, the DART(+)-Orbitrap mass spectra were acquired and processed using Composer software (Sierra Analytics, Pasadena, CA, USA). The MS data were processed and the elemental composition of the sample was determined by measuring the

m/z values. Class and DBE distributions, and carbon number (CN) *versus* DBE graphs were plotted to better analyze the results. DBE is defined as the number of rings added and the number of double bonds in each molecular structure. The unsaturation level of each compound can be deduced directly from its DBE value according to equation 1:[23,24,25]

$$DBE = c - h/2 + n/2 + 1 \quad (\textbf{equation 1})$$

Where c, h, and n are the numbers of carbon, hydrogen, and nitrogen atoms, respectively, in the molecular formula.

3. Results

3.1 DART(+)MS Optimization

The sensibility of DART(+)-MS technique for crude oil analyzes as function of some parameters were evaluated such as: substrate (TLC plate, glass and paper, **Figure 2**); temperature (from 100 to 400 ^{o}C, **Figure 3**); type of gas heater (He and N_2, **Figure 4**); concentration of analyte (from 0.33 to 6 mg mL^{-1}, **Figure 5**); and acquisition time for Orbitrap experiments (number of microscans, **Figure 8).**

Figures 2a-c show DART(+)LTQ mass spectra (using Helium as heater at 400 ^{o}C) of a typical Brazilian crude oil (sample A at 10 mg mL^{-1}) as a function of different substrates: **(a)** TLC; **(b)** glass; and **(c)** paper. A higher amplitude and distribution of signals with profiles ranging from *m/z* 200-800 was observed when paper substrate was applied. The sensibility of DART(+) source increased in the following order: TLC < glass < paper. As consequence,

the average molar mass distribution (M_w) was shifted for higher values of *m/z* (from *m/z* 280 to 360). A lower chemical interaction between polar organic compounds and the cellulose ($(C_6H_{10}O_5)_n$) was the key contributor to have a better ionization efficiency using paper as substrate.

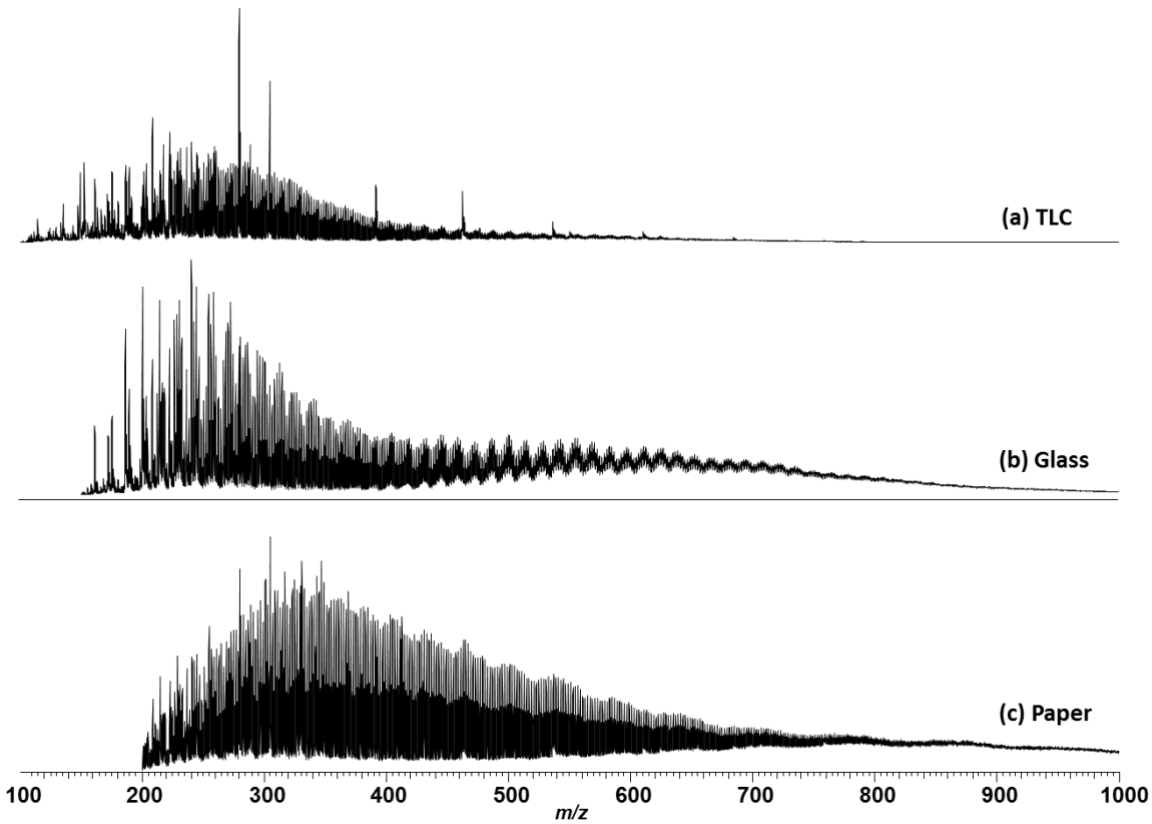

Figure 2. DART(+)-LTQ MS for a typical Brazilian crude oil sample on the **(a)** TLC plate, **(b)** glass and **(c)** paper substrates.

The ionization efficiency of DART source was also tested as a function of temperature, **Figure 3**, and the type of the gas heater (Helium or N_2), **Figure 4**. **Figure 3** shows the DART(+)-LTQ mass spectra as a function of temperature using Helium at **(3a)** 100ºC, **(3b)** 200ºC, **(3c)** 300 ºC, and (**3d**) 400 ºC. It is possible to note that a higher sensibility and a higher amplitude of signals with *m/z* from 200-1000 and M_w = 400 Da was observed

with 400 ºC as the optimum temperature, **Figure 3d**. Changing the He gas heater to N_2 (**Figures 4a-b)**, the DART(+)-LTQ mass spectrum at 400 ºC, **Figure 4b**, showed a similar performance to that one with He at 300 ºC, **Figure 4c**, thus proving the better efficiency of molecules ionization in presence of He due to its higher internal energy of ionization (He = 19.8 eV *versus* N_2 = 15.6 eV).

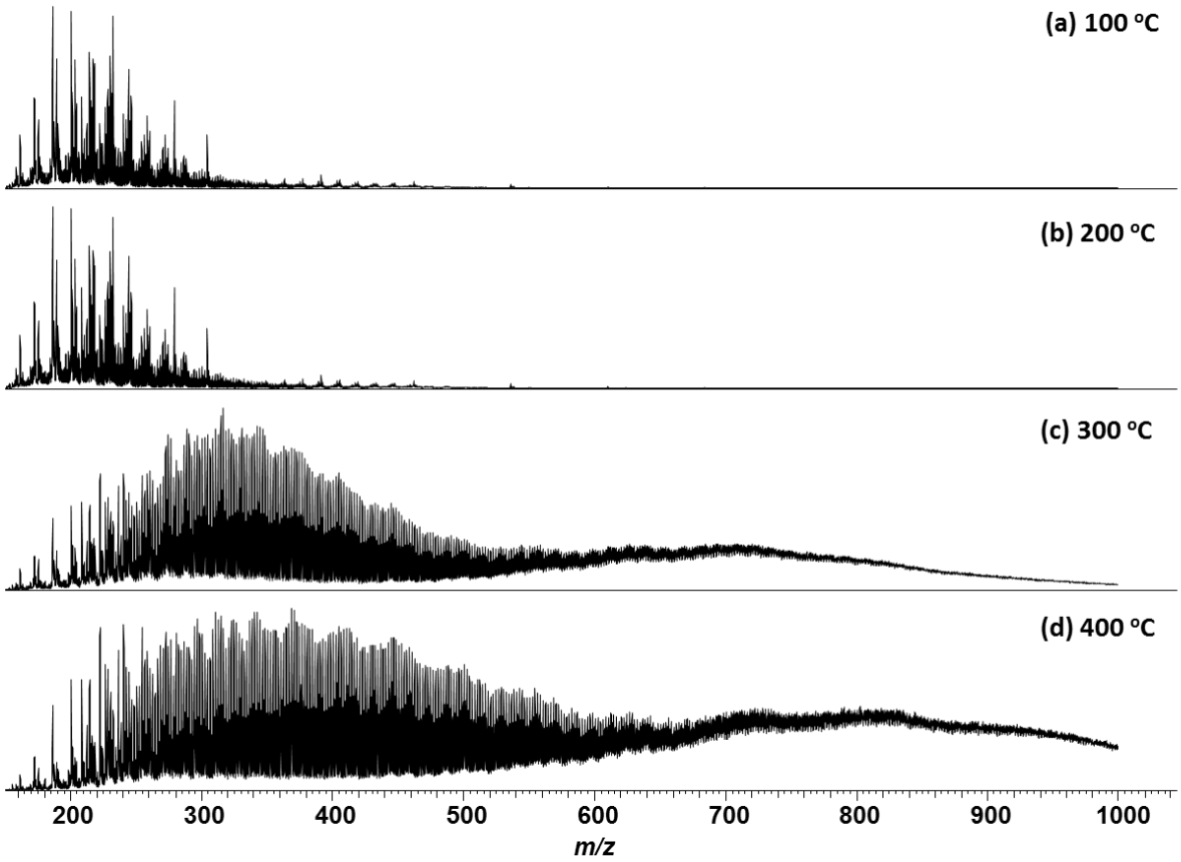

Figure 3. DART(+)-LTQ MS on a Brazilian crude oil solution spot (concentration of 10 mg mL^{-1}) as a function of temperature using He as gas heater at **(a)** 100, **(b)** 200, **(c)** 300 and **(d)** 400 ºC.

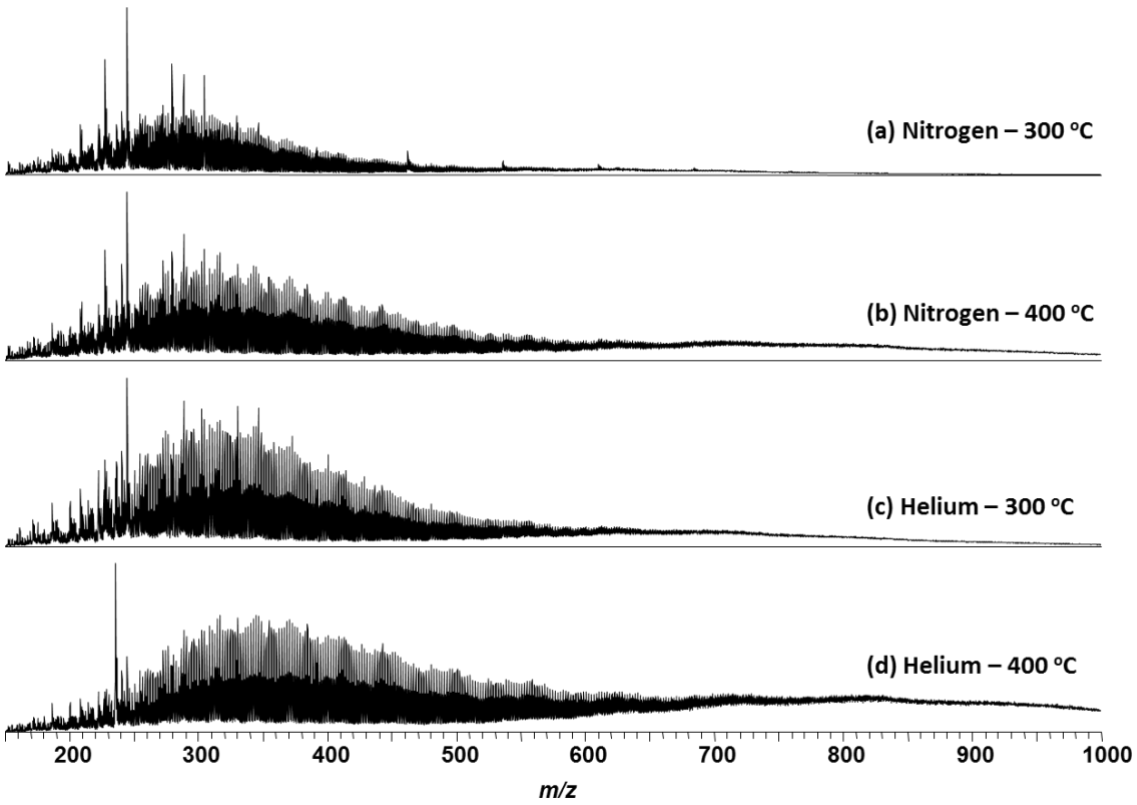

Figure 4. DART(+)-LTQ MS for a crude oil solution spot as a function of gas heater: nitrogen and helium at 300 (**a** and **c**) and 400 ºC (**b** and **d**), respectively.

The sensibility of DART(+)-MS technique was also evaluated as a function of concentration of crude oil (from 0.33 to 6 mg mL^{-1}). As consequence of increasing crude oil concentration, a higher signal-to-noise ratio and amplitude of signals were easily observed (see the decreasing of relative intensity of ions of *m/z* 279, 329, 346 and 411 formed from the paper substrate). Therefore, it is suggested that concentrations higher than 6 mg mL^{-1} must be used for crude oil analysis.

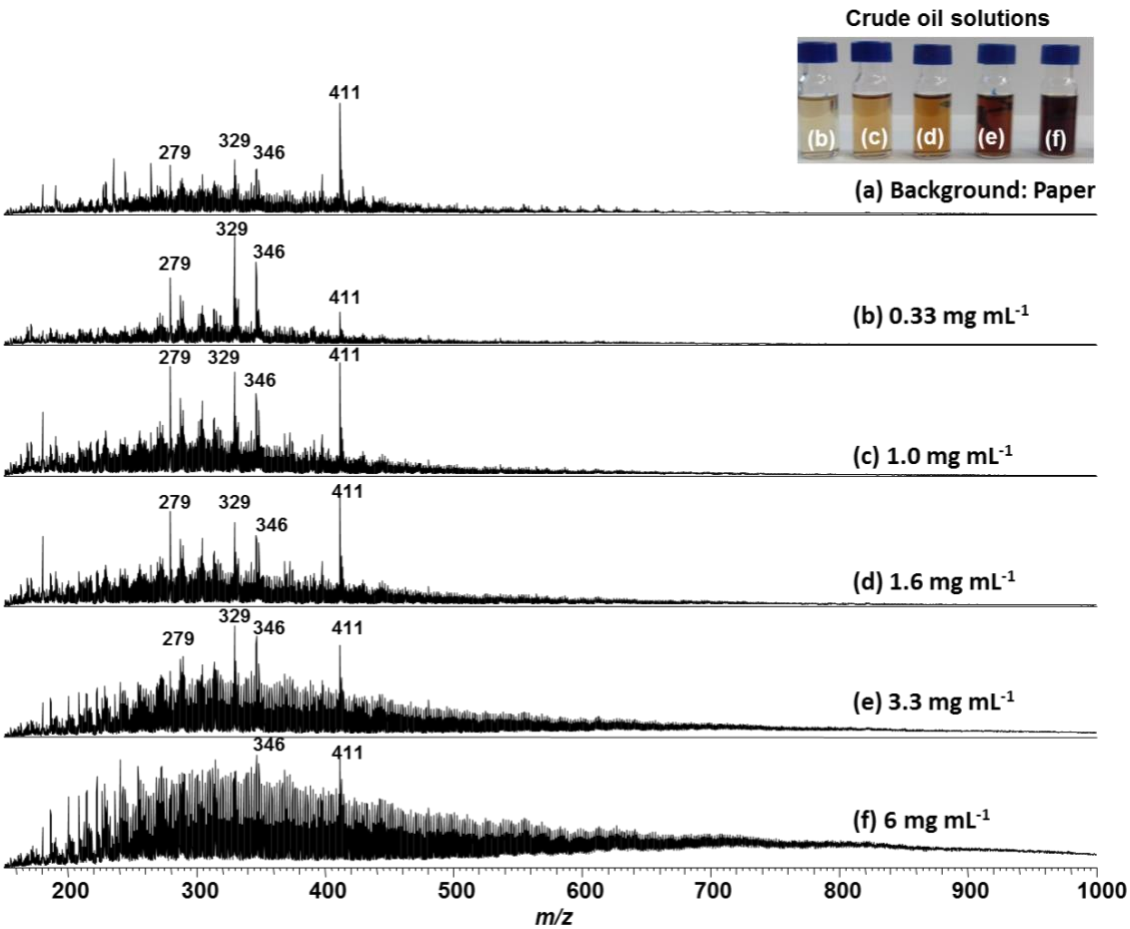

Figure 5. DART(+)-LTQ MS as a function of crude oil concentration: **(a)** 0, **(b)** 0.33 **(c)** 1.0, **(d)** 1.6, **(e)** 3.3 and **(f)** 6 mg mL^{-1}. He at 400 ^{o}C was used as gas heater.

3.2 Crude oil analyzes

After optimization of DART source ionization conditions as following: substrate (paper), temperature (T = 400 ^{o}C), gas heater (Helium) and concentration (≥ 6 mg mL^{-1}), DART(+) mass spectra at high resolution (FWHM ≈ 100,000 at *m/z* 400) were acquired for seven crude oil samples (samples A-G), using Orbitrap mass analyzer, **Figure 6**.

Figures 6a-g show the DART(+)-Orbitrap mass spectra of seven typical Brazilian crude oil samples, showing peaks profile from *m/z* 200-700 with M_w centered from *m/z* 374 to 453. Nitrogen-containing species were detected as protonated molecules, that is, $[M-H]^+$ cations, according to the proposed mechanism of **equation 3**. The magnified region near *m/z* 310-312 indicates that DART(+) detected pyridine analogous compounds (N class): $[C_{23}H_{21}N + H]^+$, $[C_{22}H_{31}N + H]^+$, $[C_{23}H_{21}N + H]^+$ and $[C_{22}H_{33}N + H]^+$ ions with *m/z* 310.1577, 310.2517, 312.1734 and 312.2674, and DBEs of 15, 8, 13 and 7, respectively. The theoretical *m/z* values for these ions are 310.1590, 310.2529, 312.1734 and 312.2674, thus providing a medium mass error of about -4.02 ppm. In Petroleomic, ultra-high resolution and accuracy mass spectrometry with FWHM > 400,000 and exact mass < 1 ppm is required for the identification of complex organic mixtures, thus ensuring an excellent recalibration data from Composer *software*. Accurate mass measurements define the unique elemental composition ($C_cH_hN_nO_oS_s$) and DBE from singly charged ions.[26,27] To correct the mass deviation (Error > 1 ppm), DART(+)-Orbitrap mass spectra were further processed with the Composer *software*, especially designed for formula attribution via automatic recalibration for known homologous series from the measured *m/z* values of polar crude oil markers.[28,29] A medium of approximately 350 molecular formula (where n = 7) were assigned from monoisotopic components for the Orbitrap mass spectra, corresponding to a medium percentage of 70 % of all assignments.

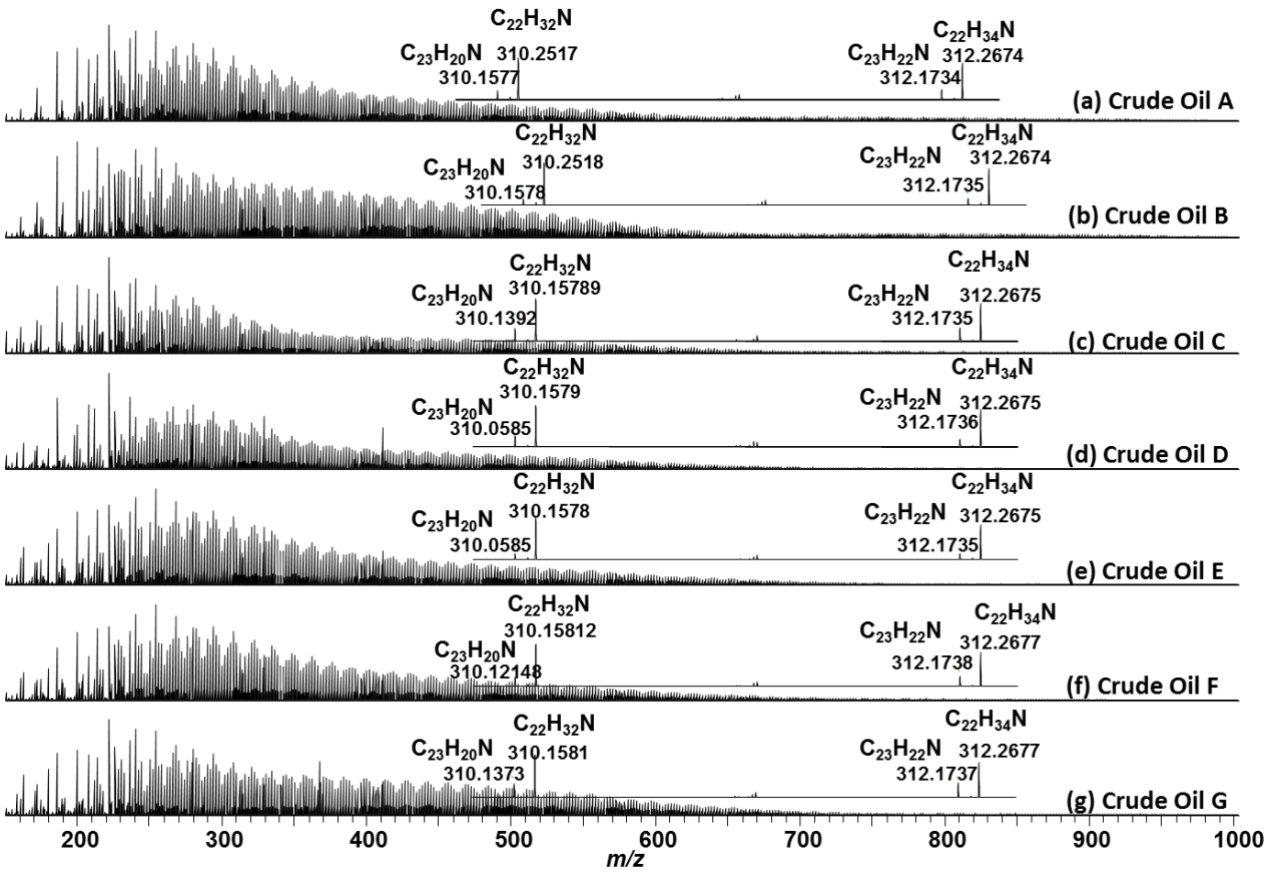

Figure 6. DART(+)-Orbitrap MS for seven crude oil samples (A-G). He was used as gas heater at 400 ºC. Acquisition time of 1 microscan.

One way to display the similarities or differences between the signal patterns of crude oil samples is the construction of certain types of plots, such as the plots of the relative abundances of different classes of compounds, DBE *vs* intensity and DBE *vs* CN,[30] **Figure 7a-c**. **Figure 7a** displays the distribution of polar compound classes (NH], NO[H], and O[H]) obtained from DART(+)-Orbitrap MS. In all cases, DART(+) seems to efficiently promoted the ionization of polar compounds, as protonated cations ($[M + H]^+$), with their magnitude following the order: N[H] > O[H] > NO[H]. The DBE relative abundance distributions of

N[H] class for samples A-G were also evaluated, **Figure 7b**, in which a distribution ranging from 4 to 20 was observed. **Figure 7c** presents the DBE *versus* CN for the majority class, N[H] class, for the sample F. Carbon numbers ranged from C_{12} to C_{45} for pyridine compound species (DBEs = 4-20), with maximum abundance around C_{16} and DBE = 8 were observed.

An attempt to improve the exact mass and consequently the signal-to-noise ratio in an Orbitrap analyzer was made by increasing its acquisition time. **Figure 8** shows the DART(+)Orbitrap mass spectra as a function of the acquisition time (number of microscans) for sample F. The M_w decreased as the number of microscan increased (1 → 10) as well as the population of nitrogen compounds assignments, depicted by the DBE *vs* CN plot (see the insert of **Figure 8**). The number of assigned molecular formulas decreases from 288 (for 1 μscan) to 199 (for 10 μscans). Probably, the ions transmission from the LTQ to Orbitrap was affected by fact that desorption and ionization mechanism of DART acts only in a specific point. Hence, the ionic population was reduced as function of time.

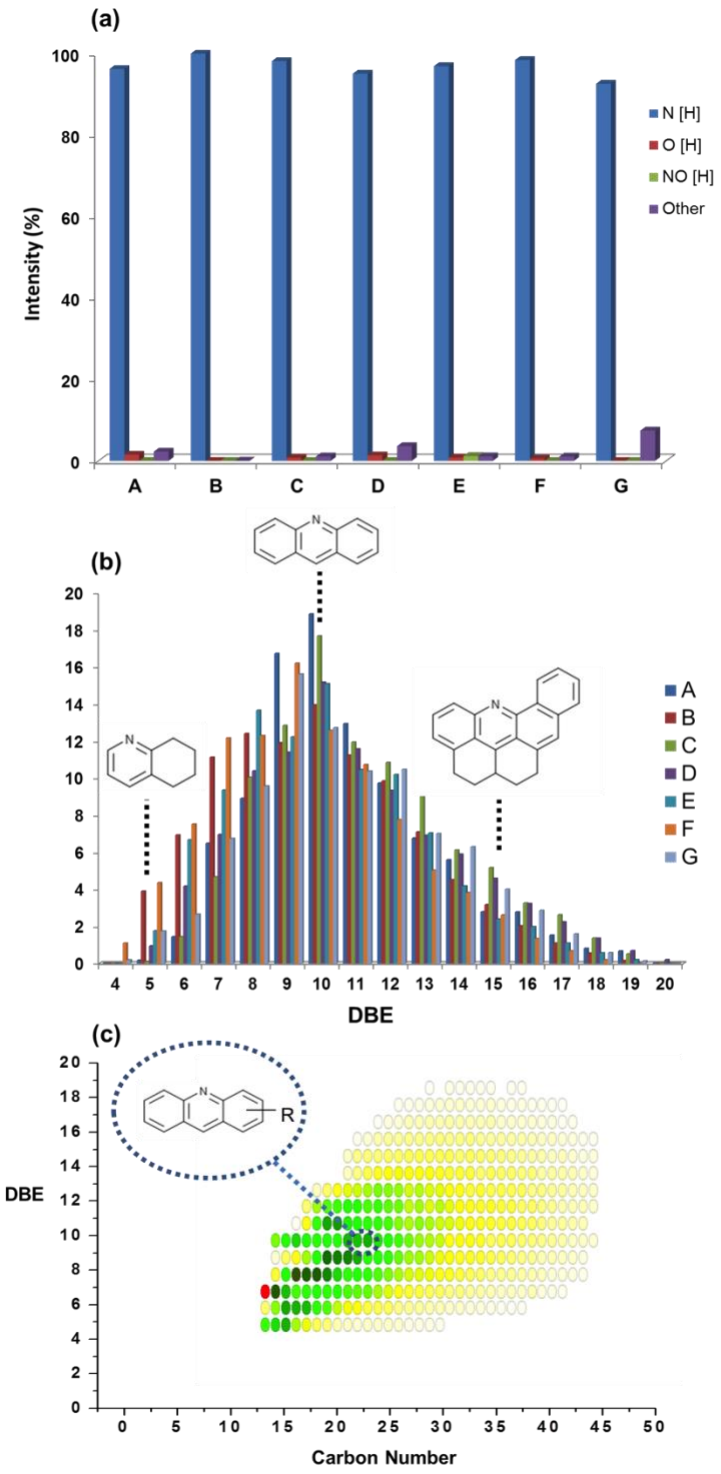

Figure 7. Class distribution, DBE *versus* intensity of seven crude oil samples (A-G) and DBE *versus* CN plots of sample F generated from DART(+)Orbitrap data.

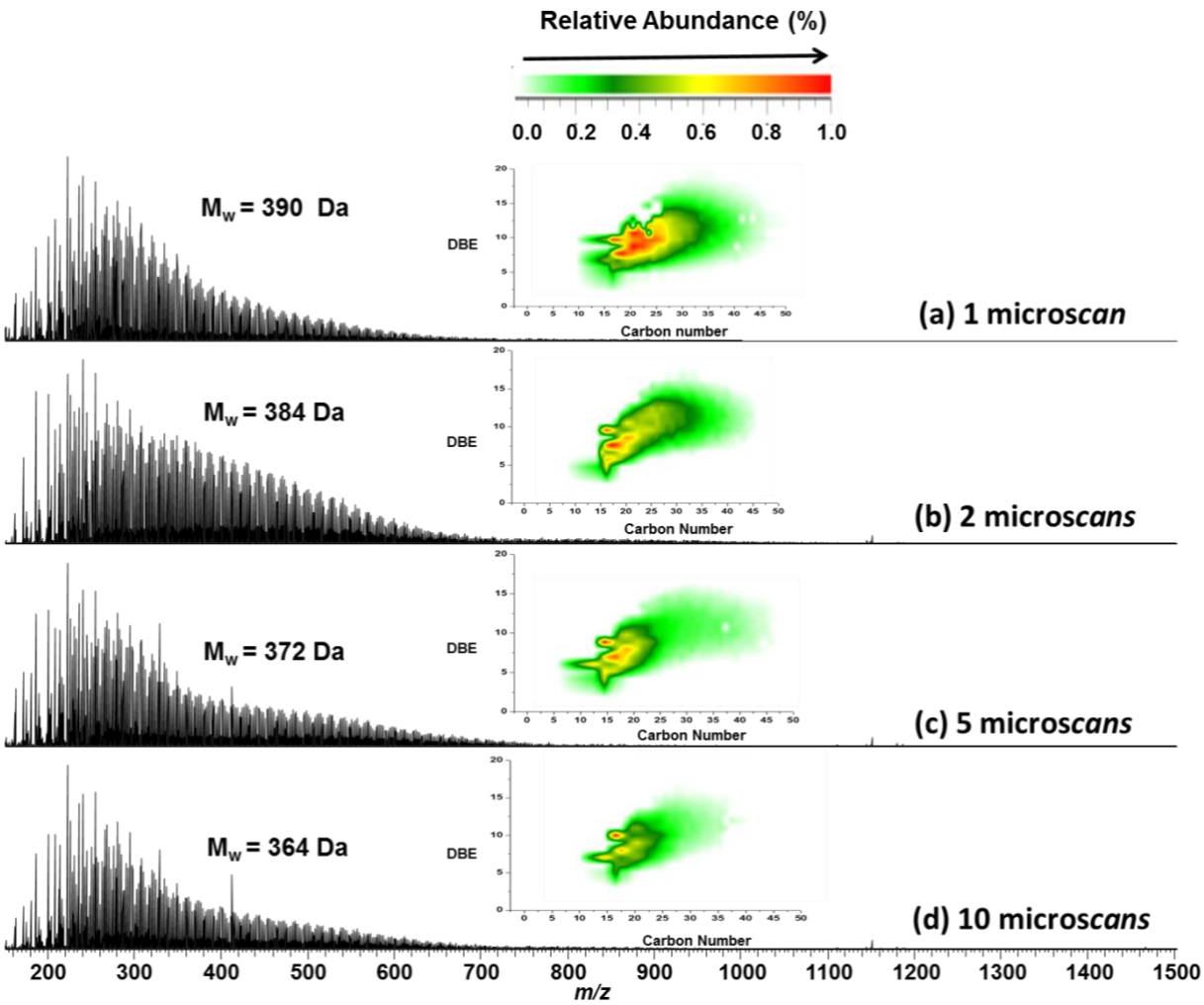

Figure 8. DART(+)Orbitrap mass spectra as a function of acquisition time (number of microscans) for crude oil sample A. Note that M_w decreases as the number of microscan increases as well as the nitrogen compounds assignments decreases as showed by DBE *vs* CN plot (see the insert of **Figure 8**).

3.3 Paraffin Analyzes

The analysis of hydrocarbons (HCs) using atmospheric or ambient ionization techniques still remain a challenge in mass spectrometry.[31] **Figure 9** shows DART(+)-Orbitrap mass spectra for the three paraffin samples evaluated. The right side inserts show

paraffin detection as oxygenated HCs species (O_x classes, where x = 1-4) with DBEs of 1-4 and a mass error of - 3-4 ppm. In all cases, a similar Gaussian profile from *m/z* 250-600 was observed. The oxidized HCs species were generated at high temperature and atmospheric pressure from short-life time oxygen-based species such as OH and OOH radicals and also H_3O^+ ion in contact with HCs compound species, producing oxidized HCs (Ox classes).[31,32]

In 2009, Cooks et al.[33] has also analyzed saturated hydrocarbons ($C_{15}H_{32}$ to $C_{30}H_{62}$) using discharge-induced oxidation in desorption electrospray ionization. Multiple oxidations and dehydrogenations occurred during the DESI discharge, but no hydrocarbon fragmentation was observed. DESI-Orbitrap mass spectrum of a petroleum distillate containing vacuum gas oil saturates (boiling point > 316 ^oC) showed HCs species containing two oxygen additions in alkanes structures from $C_{21}H_{44}$ to $C_{36}H_{74}$, similar to observed for DART(+)Orbitrap data.

To confirm the structures and the connectivity of some oxygenates HCs compound classes (O_x classes), which were identified using DART(+)-Orbitrap MS, the DART(+)-MS/MS spectra were acquired for the ions with *m/z* 337, 351, 365, 379 and 393. This approach identifies the characteristic neutral loss and confirms the existence of hydroxylated HCs compounds such as alcohols from successive eliminations of 18 Da (H_2O), and 28 Da (CH_2=CH_2) along the molecule, **Figure 10**.

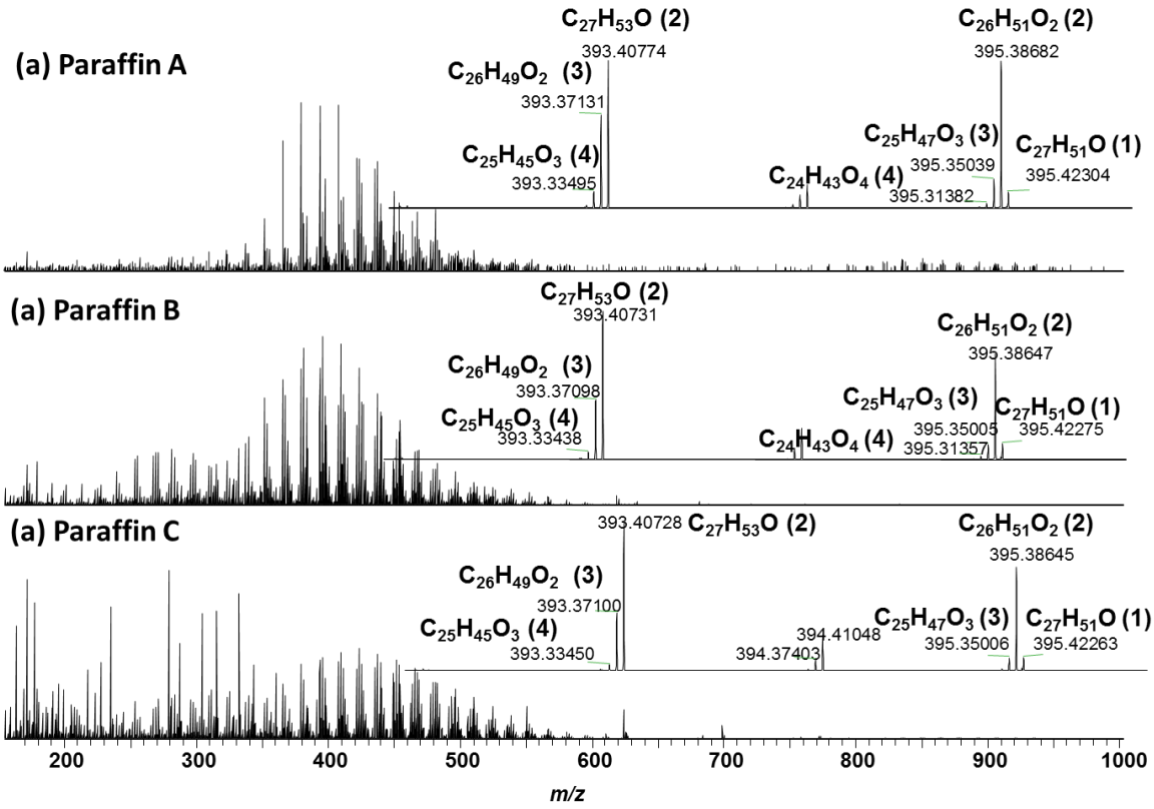

Figure 9. DART(+)Orbitrap mass spectra for paraffin samples. The right side inserts show paraffin detection in oxygenated form (O_x classes). The number between parentheses corresponds to DBE value.

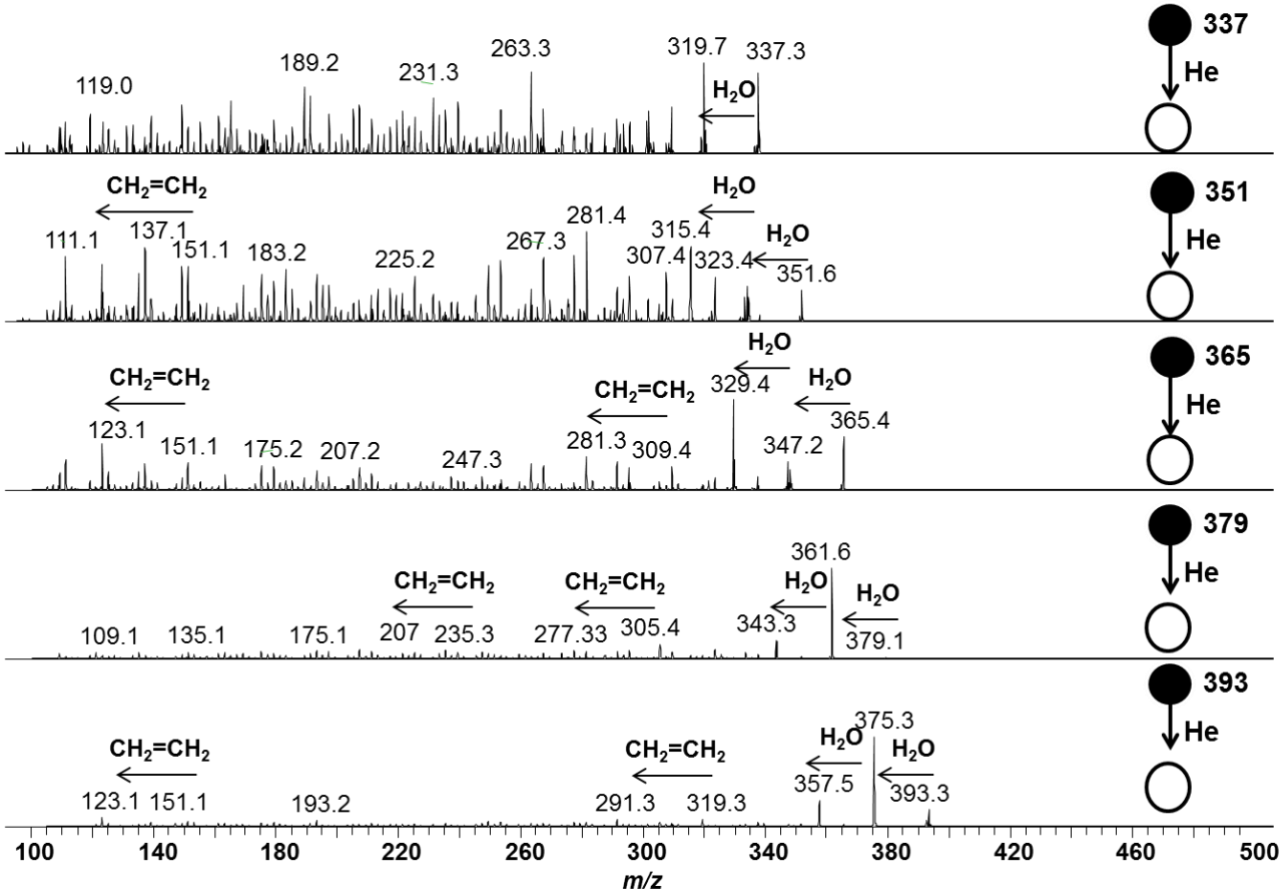

Figure 10. DART(+)MS/MS for ions with *m/z* 337, 351, 365, 379 and 393.

3.4 Porphrin compounds analyzes

The detection ability of DART(+)-MS technique regarding standard porphyrin and metal porphyrin compounds were evaluated, **Figure 11** and **12**, respectively. The **Figure 11a** shows the DART(+)-Orbitrap MS for the 5,10,15,20-tetraphenyl-21H,23H-porphine compound, detected as $[M + H]^+$ ion with *m/z* 615.2502, where M = $C_{44}H_{30}N_4$. Its chemical structure was confirmed from CID experiments, **Figure 11b**, in which the two neutral losses of 77 Da and one of 16 Da identifies the presence of two phenyl rings and one amine group (C_6H_5 and NH_2). The standard metal porphyrin compound was also detected by DART(+)-

Orbitrap MS, with lower ionization efficiency, as $[M + H]^+$ ion with *m/z* 680.1763, where M = $C_{44}H_{28}N_4OV$, **Figure 12a**. Its connectivity and its structure were confirmed from DART(+)-MS^2 and DART(+)-MS^3 experiments, in which two neutral losses of 77 Da happened simultaneously (*m/z* 680 → 603 and *m/z* 603 → 526 transitions **Figures 12b-c)**.

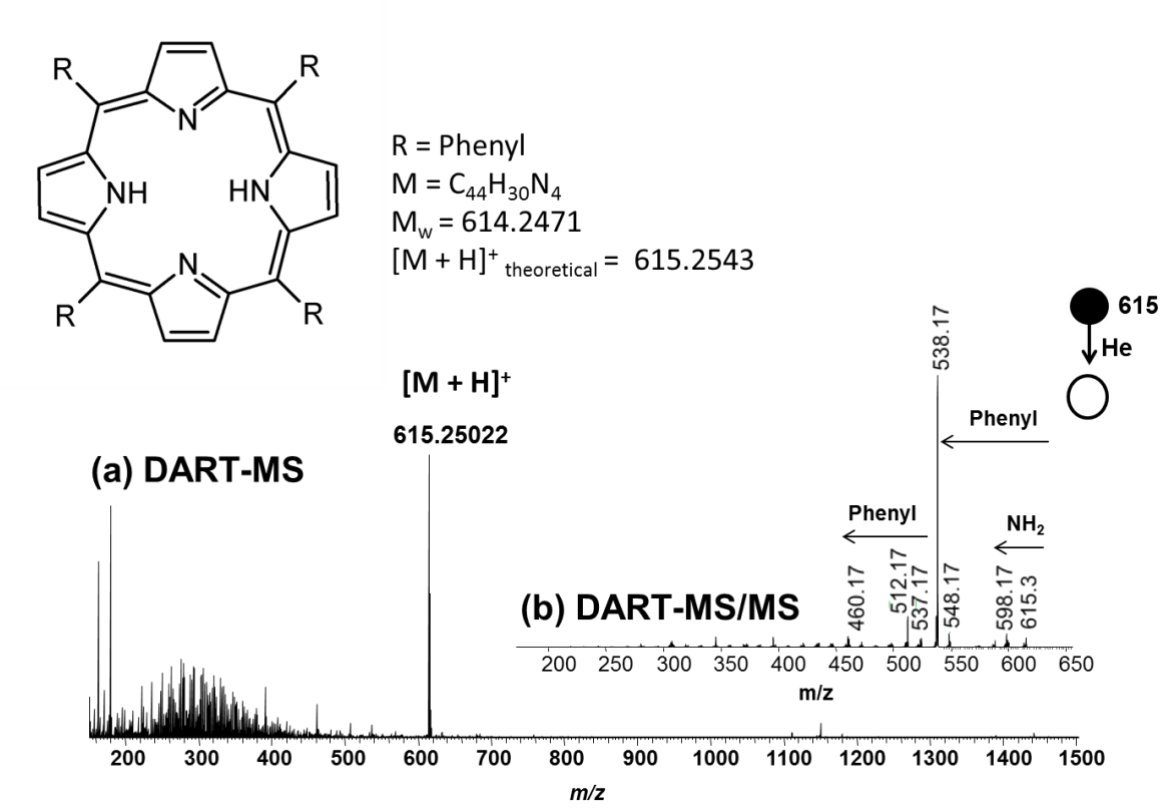

Figure 11. (a) DART(+) mass spectrum of porphyrin standard using He at 400 °C and **(b)** DART(+)MS/MS for the ion with *m/z* 615.

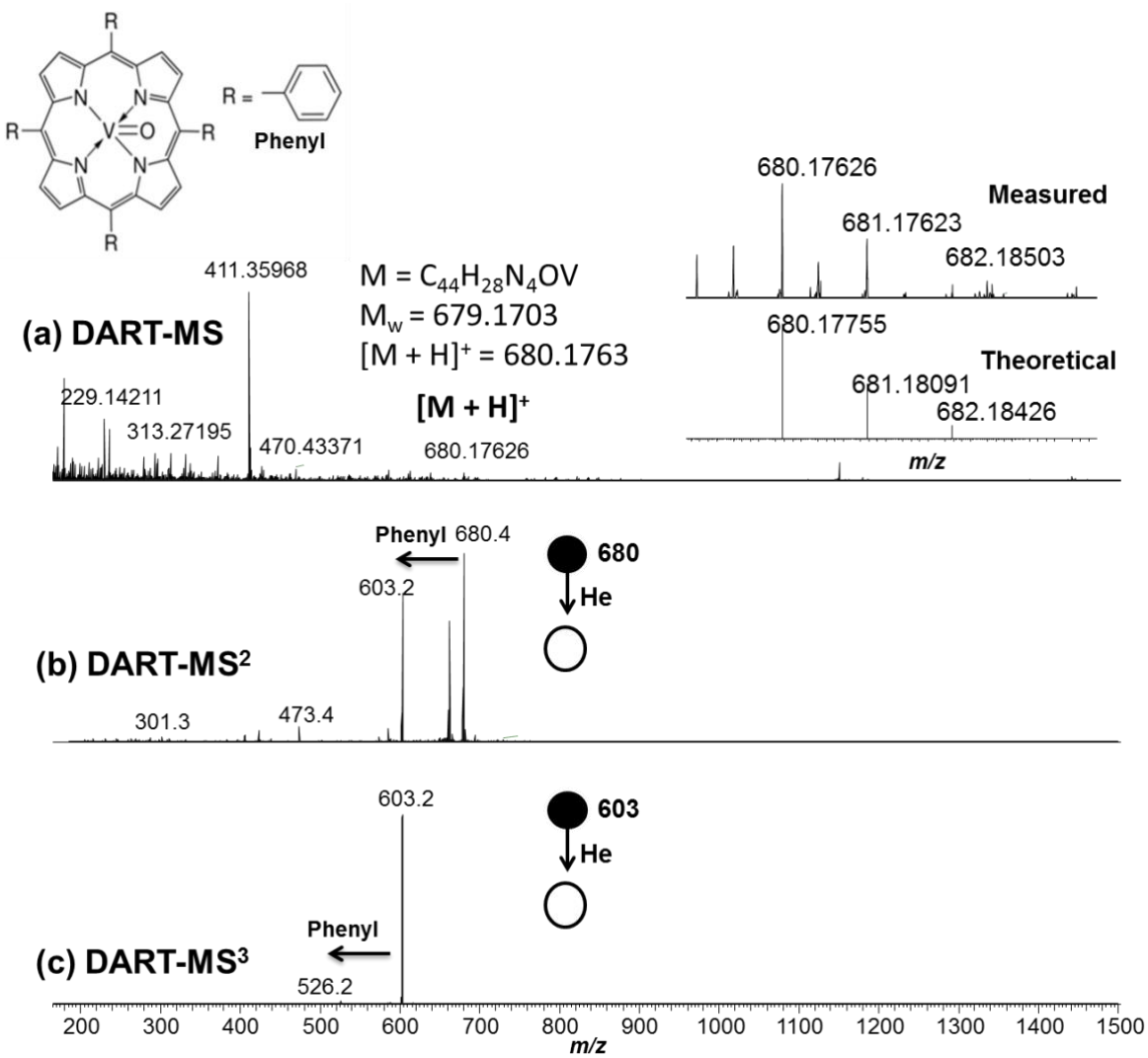

Figure 12. (a) DART(+) mass spectrum of vanadium porphyrin standard and **(b)** DART(+)MS^2 and **(c)** DART(**+**)MS^3 for ions with *m/z* 680 and 603, respectively.

4. Conclusion and Perspectives

The DART(+)-hybruid ion-trap-Orbitrap MS is a powerful, simple, and easy analytical tool that can be applied to petroleoum analysis to asses assessing chemical composition at molecular level. Cellulose-based substrates together with high temperature (400 ^{o}C), He as a gas heater and crude oil concentrations higher than 6 mg mL^{-1} increased the sensibility of DART source. Nitrogen-containing species were detected as protonated molecules in crude oil samples, following by NO[H] and O[H] class species.

DART(+) also rendered hydroxylated HCs species (O_x classes, where x ranged from 1 to 4) with DBEs of 1 to 4 for paraffin samples. Oxidation reactions occur at high temperature and atmospheric pressure between HCs species and generated short-lifetime oxygen-based species such as OH, OOH radicals and H_3O^+. DART(+)-MS and CID experiments (MS^2 and MS^3) were also able to identify porphyrin standard compounds as $[M + H]^+$ ions with *m/z* 615.2502 and 680.1763, where M = $C_{44}H_{30}N_4$ and $C_{44}H_{28}N_4OV$, respectively.

5. Acknowledgments

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