Characterization of deasphalted crude oils using GC-APLI-TIMS-TOF MS

Clement A. Olanrewaju,[1] *Cesar E, Ramirez,*[1-2] *Francisco Fernandez-Lima*[1-3*].

[1]Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA.

[2]Advanced Mass Spectrometry Facility, Florida International University, Miami FL 33199, USA

[3]Biomolecular Sciences Institute, Florida International University, Miami FL 33199, USA.

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ABSTRACT

In the present work, a novel workflow based on complementary gas-phase separations is applied to the characterization of deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils. The coupling of gas chromatography (GC), atmospheric pressure laser ionization (APLI), and trapped ion mobility spectrometry - mass spectrometry (TIMS-MS) resulted in the effective separation and candidate assignment of PAHs and similar compounds. The analytical power of the GC-APLI-TIMS-TOF MS is based on the separation of the isomeric content using

the GC and TIMS (R = 50-90 with S_r = 0.18 V/ms) gas-phase separations, followed by the high mass resolution and mass accuracy (<2ppm) of the TOF MS analyzer. Previously reported PAH-like known compounds (130 compounds) uniquely assigned based on their [retention time, RT; collisional crossection, CCS; mass to charge, *m/z*] showed signature patterns and distinctive diagnostic ratios representative of the thermal maturity, lithology, and microbial contribution to each oil formation. The unsupervised T-Rex 4D analysis of the GC-APLI-TIMS-TOF MS generated for the first time an exhaustive list of PAHs and similar unknown components (~8500), each component characterized by a [RT; CCS; *m/z* value; chemical formula] and peak areas for each replica analysis (i.e., 12 totals, 3x per crude oil). The inspection of the PAHs and similar unknown compounds provided a list of unique identifiers for each crude oil (2-4% of the assigned compounds) as well as molecular components common to all crude oils (~50% of the assigned compounds). The analytical power of the GC-APLI-TIMS-TOF MS is illustrated using unsupervised PCA analysis, where the four oils can be easily separated in two principal components that account for 70% of the total variance.

INTRODUCTION

Over the last few decades, many analytical developments have been guided to a better characterization of crude oils[1]. While crude oil features can be observed using infrared and near-infrared spectroscopy, bulk sample measurements are limited and do not provide molecular information[2]. The molecular component characterization is traditionally limited to mass spectrometry (MS) based techniques. Multiple MS-hyphenated techniques have been successfully applied to the characterization of crude oils (e.g., gas chromatography−mass spectrometry (GC-MS)[3], two-dimensional gas chromatography−mass spectrometry (2D GCMS)

[4-7], liquid chromatography–mass spectrometry (LC-MS)[8, 9], and more recently ion mobility spectrometry -mass spectrometry (drift tube IMS, DT-IMS[10, 11], traveling wave IMS, TWIMS[12-18], field asymmetric IMS, FAIMS[19, 20], and trapped ion mobility, TIMS[21, 22])). Chromatographic separations and curve deconvolution is problematic for crude oils due to the large number of elemental compositions, high isomeric content, and large dynamic range. The unique advantages of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for the simultaneous determination of thousands of chemical components in a single analysis are well documented[23]. Moreover, when complemented with gas-phase separation techniques (e.g., GC-FT-ICR MS[24], LC-FT-ICR MS[25, 26] and TIMS-FT-ICR MS[27-30]), the molecular isomers can be separated and characterized; a typical drawback is the slow acquisition rates needed for ultrahigh resolution mass acquisitions in the case of online GC and LC which have ultimately restricted their use to high magnetic field platforms[31, 32]. Despite these recent advances in GC, LC, IMS and MS[20, 33-39] for the characterization of PAHs, there is still a constant need for improved technologies to further simplify and lower the cost of the molecular characterization in complex mixtures while increasing the confidence of compound identification with minimum ambiguity.

Previous studies have shown that atmospheric pressure laser ionization (APLI) is more suitable for accessing the PAH content in crude oils.[40] With the coupling of GC-APLI[41], the characterization of PAH like components using commercial MS analyzers was realized.[42, 43] Recently, we described the advantages of complementary gas-phase separations for the identification of isomeric PAHs from complex mixtures using GC-APLI-TIMS-TOF MS[44]; noteworthy is the analytical capability for untargeted screening of isomeric and isobaric compounds not available in traditional GC-EI-MS^n workflows.

In the present work, a novel workflow based on complementary gas-phase separations is presented for the characterization of deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils. By coupling gas chromatography (GC), atmospheric pressure laser ionization (APLI), and trapped ion mobility spectrometry – TOF mass spectrometry (TIMS-TOF MS), effective separation the isomeric content at the molecular formula level is showcased. Using a list of previously reported PAH-like known components, this workflow permits the crude oil identification based on the [RT; CCS; *m/z*] as well as their use as differentiation markers based on their relative abundance across the crude oils. Alternatively, the capability for deasphalted crude oil differentiation is demonstrated based on unsupervised T-Rex 4D analysis of the GC-APLI-TIMS-TOF MS datasets. For the first time, an exhaustive list of GC accessible deasphalted crude oil components is reported based on [RT; CCS; *m/z* value; chemical formula; relative abundance].

EXPERIMENTAL SECTION

Chemicals and Materials. Certified standards of Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12 were purchased from AccuStandard (New Haven, CT). Four crude oil samples categorized into light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) were used as received. (Note that Macondo oil was received from Professor Piero Gardinali, Department of Biochemistry and Chemistry, Florida International University). All solvents were optima grade or better and purchased from Fisher Scientific (Waltham, MA).

Sample Preparation. All standards were diluted in hexane before use to a final concentration of 4 mg/L. Details on the preparation of deasphalted crude oil samples can be found elsewhere[44].

Briefly, 50 mg of the crude oil were carefully weighed and mixed with 100 μL of the deuterated PAHs (Table S1). The mixture was homogenized and suspended in 30 mL of hexane causing precipitation of asphaltenes, and the resulting suspension was left overnight for equilibration. After that period, asphaltenes were removed by filtration using a glass wool in a glass funnel. The filtrate was finally concentrated to about 2 mL under a gentle stream of nitrogen gas and injected without further treatment.

GC-APLI-TIMS-TOF MS Analysis. Details on the GC-APLI-TIMS-TOF MS setup and operation can be found elsewhere[44]. Briefly, gas chromatography separation was performed using a Bruker Scion 436 Gas Chromatograph (GC) equipped with a Varian CP-8400 autosampler (Holland). The GC was equipped with a TG-PAH column (60 m X 0.25 mm, 0.1 μm: Thermo Scientific, USA). Aliquots of 1 μL were injected in split-less mode and the injection port was held at 270 ˚C. The GC column flow was 1.2 mL/min with the following temperature program: 100˚C held for 0.5 min, increased at 6˚C/min to 330˚C and then held for 10 min for a total run time of 48.83 min. The GC was interfaced via a transfer line heated to 350^0C to an APLI ionization source coupled to a commercial TIMS-TOF MS instrument (Bruker Daltonics, Inc., Billerica, MA). Details of the APLI source can be found elsewhere[24, 44]. Briefly, the APLI was equipped with a 266 nm laser beam (CryLas GmbH, Berlin Germany; Type 1HP266-50), orthogonal to the glass capillary source inlet. Other APLI source parameters were endplate offset 500 V, capillary 750 V, dry gas temperature 320 ˚C and vaporizer temperature 320 ˚C.

Parameters for TIMS operation were as follows: 0.51 – 1.01 $V \cdot s/cm^2$ inverse mobility range (ΔV_{ramp} = 63 V); 20 ms ion accumulation time; 350 ms ramp time, and a mobility scan rate Sr = 0.18 V/ms. The TOF instrument was operated in full scan, positive mode, and ion transmission was optimized for the *m/z* 75 – 950 range. Different from previous TOF systems, the timsTOF provides over four orders of dynamic range. The acquisition method mass and mobility calibrations were performed using APCI/APPI Tuning Mix calibration standard (Agilent Technologies G2432A). The mobility (K_0) values of 1.3663 and 1.0154 $cm^2\ V^{-1}\ s^{-1}$ were used for the *m/z* 322 and *m/z* 622 calibrants, respectively. These are the K_0 values recommended by the manufacturer and in close agreement with others reported in the literature[45-47]. Mobility values were correlated with the ion–neutral collision cross section (Ω, $Å^2$) using the Mason–Schamp equation[48]:

$$\Omega = \frac{(18\pi)^{1/2}}{16}\frac{z}{(K_B T)^{1/2}}\left(\frac{1}{m_1}+\frac{1}{m_b}\right)^{1/2}\frac{1}{K}\frac{760}{P}\frac{T}{273.15}\frac{1}{N^{\star}} \qquad (1)$$

where z is the charge of the ion, k_B is the Boltzmann constant, m_I is the ion mass, m_b is the bath gas molecule mass, T is the temperature (305 K), and $N^{\star}$ is the gas number density. All samples were analyzed in triplicates.

Data Processing: The GC-APLI-TIMS-TOF MS data was processed using Metaboscape 2021.0 (version 6.0.2 Build 744, Bruker Daltonik GmbH). The peak detection parameters were as follows: 1000 counts intensity threshold, 100 points minimum 4D peak size, 8 points minimum 4D peak size (recursive) and 120-450 *m/z* range. Data was first internally *m/z* calibrated using the labeled PAHs (Table S1) and then loaded into the Composer software for *m/z* calibration using internal standards and homologous series; a $C_{1\text{-}100}H_{1\text{-}200}O_{0\text{-}5}N_{0\text{-}5}S_{0\text{-}4}$ general formula, odd and even electron configurations, and a 2.0 ppm mass tolerance were used for the elemental composition assignment. The T-ReX 4D workflow yielded buckets with retention time, collisional cross section, *m/z* of precursor ion and peak areas for all crude oils analyzed in triplicate. Peak areas were normalized using the five internal deuterated standards (Table S1) using Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12 for the *m/z* range 128-156, 157-176, 178-206, 207-234 and 252-278, respectively.

RESULTS AND DISCUSSION

The analysis of the deasphalted crude oils using GC-APLI-TIMS-TOF MS resulted in the observation of radical cations $[M^{\bullet+}]$, hydride abstracted ions $[M-1]^{+}$ and methyl abstratcted ions $[M-CH_3]^{+}$ ions over the *m/z* range 100-600 (Figure 1). In addition to direct APLI ionization, data suggest that charge transfer via dopant effect may be responsible for the ionization of low DBE compounds. The *m/z* range was limited by the volatility of the compounds during the GC separation. Inspection of Figure 1 shows complementary separation between the IMS and the GC domains, resulting in a net increase of the peak capacity of the analysis and a better separation of molecular features from these complex mixtures.

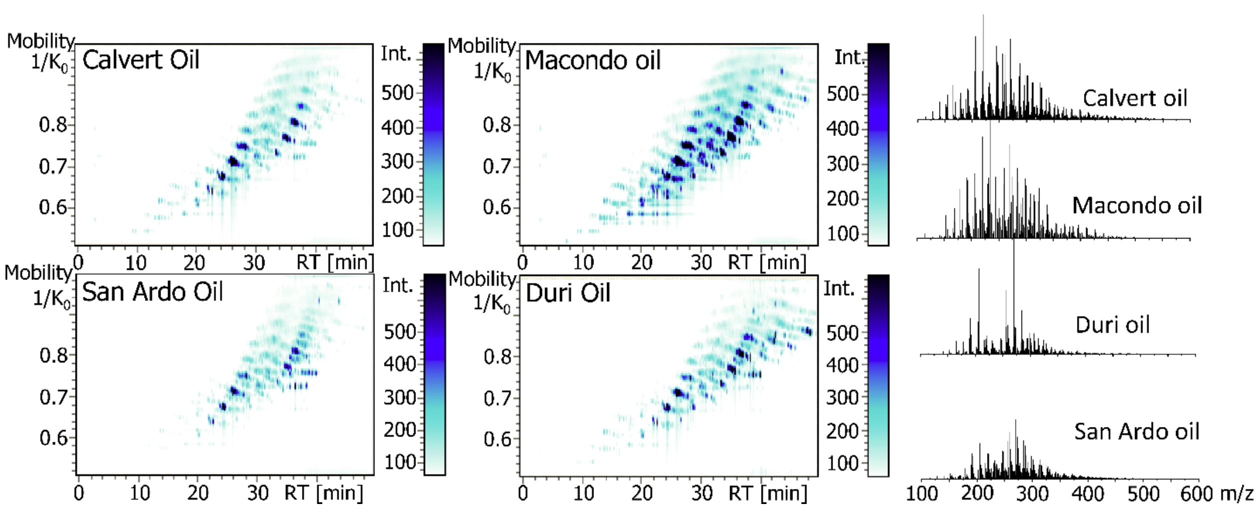

Figure 1. Typical 2D IMS-GC and MS projection plots for the analysis of deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils using GC-APLI-TIMS-TOF MS.

The isomeric complexity of the deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils is illustrated for the case of alkylated PAHs and PASHs isomers commonly used for diagnostic ratios (Figure 2). In addition to the separation of all the isomers, changes in relative abundance are observed based on the type of crude oil. Each molecular feature is characterized by their retention time (or index), CCS and *m/z* value (see details in Table S2). Chemical formula assignment was performed with sub-ppm mass errors and isomer determination was based on previously reported retention index and mobility measurements[44]. The added TIMS separation when compared with traditional GC-HRMS workflows resulted in high mobility resolving power R~ 50-90 at Sr = 0.18 V/ms (R = CCS/ΔCCS), with the added benefit of accurate CCS confirmation during the assignments. Previous reports of TIMS analysis of PAHs have shown mobility resolving powers of R = 80−120 at slower scan rates[21, 44]. The current scan rate resolution (or expected resolving power) was chosen to efficiently sample the GC domain (i.e., 350 ms intervals across a typical 0.1−0.2 min GC base peak, leading to at least 18 points per GC peak).

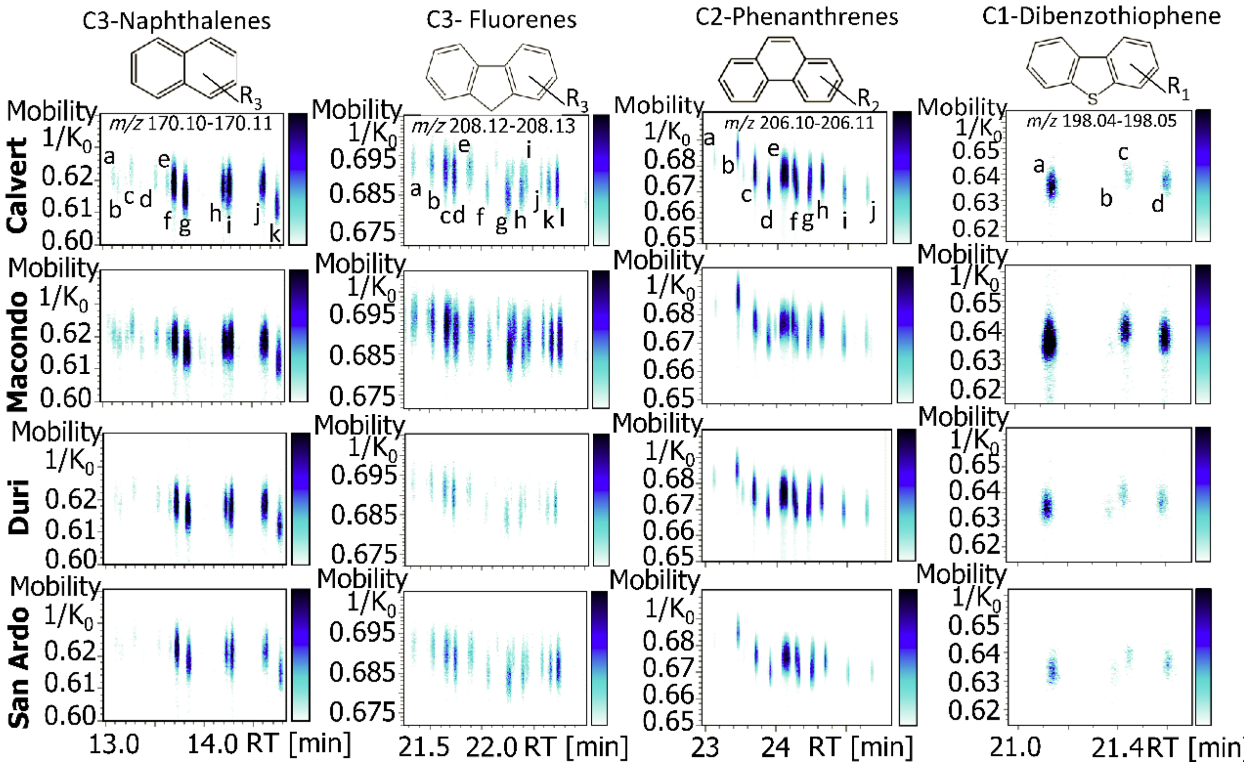

Figure 2. Typical 2D IMS-GC projection plots of alkylated PAHs and PASHs isomers commonly used for diagnostic ratios during the analysis of deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils using GC-APLI-TIMS-TOF MS.

Traditional GC-MS workflows base the oil comparison in group of isomers (e.g., C0-C4-Naphthalenes); however the resolution achieved in GC-APLI-TIMS-TOF MS workflow permits the evaluation at the molecular level of the deasphalted crude oils based on reported retention time (or index), CCS and chemical formula of standards and known components previously reported (~130 components, Figure 3)[44]. Most of 130 components were observed in all the oils and their relative abundances change from light to medium to heavy crude oils and within light oils (see Table S3); all components were normalized using deuterated analog standards to correct for variations between replica runs. The analysis of the triplicate runs revealed small deviations in the retention time (RSD < 1%), mobility (RSD< 0.6%) and *m/z* assignments (RSD < 1ppm). Of particular interest is the measurement of sixteen priority pollutants by the Environmental Protection Agency (EPA) due to their high toxicity, mutagenicity, and carcinogenicity risks (highlighted in red in Figure 3)

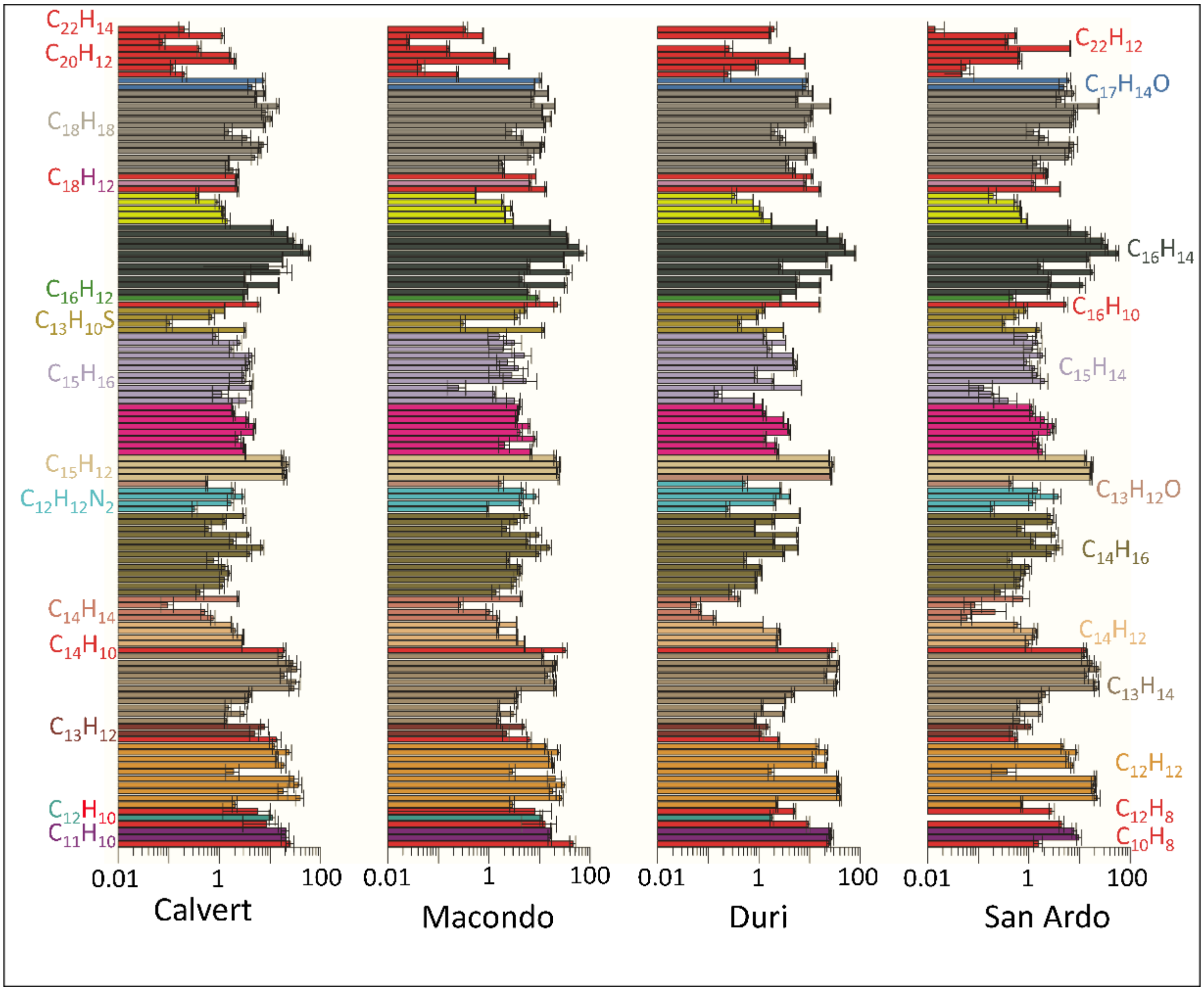

Figure 3. Variation of previously identified compounds in ref[44] in the deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils. Notice the sixteen EPA PAHs highlighted in red. Mixed color were used at chemical formula $C_{12}H_{10}$ and $C_{18}H_{12}$ to differentiate Biphenyl and Triphenylene from EPA PAHs with the same chemical formula. Error bars represent the standard deviation across triplicate measurements and data are normalized using internal deuterated standards.

The relative abundances of particular PAHs can be used for the evaluation of thermal maturity, oil rock lithology, and microbial contribution indicators across crude oils[49-51]. Traditionally, alkyl homologs of Phenanthrene (Phe), dibenzothiophene (DBT), phenyl dibenzothiophenes (PhDBT) and benzo[b]naphthothiophenes (BNT) are utilized[51-53]; a typical caveat during traditional GC-MS analysis is the number of potential interferences. To this end, complementary GC-TIMS-HRMS has the added advantage in achieving accurate estimations by filtering interferences coming from fragments and isobars (see SI excel, Metaboscape raw worksheet). Eleven PAHs diagnostic ratios are displayed in Figure 4 and summarized in Table S4. Results show crude oils facile differentiation using the spider plots. For example, the ratio of dibenzothiophene and phenanthrene (DBT/Phe) has been used as an indicator of crude oil lithology with values >1 defined as carbonates while values <1 as shale lithology[54]. The DBT/Phe values for the oil samples are within the range of 0.006-0.023 (Table S4), suggesting crude oils with shale lithology. The (1+4)-/(2+3)-MDBT values in the oil samples vary between 0.476-1.000 also suggesting shale lithology[52]. The abundance of benzo[b]naphthothiophenes is characterized by the predominance of benzo[b]naphtho[2,1]thiophene. This observation is consistent with previous reports on crude oil samples[55] and it has been attributed to significant microbial contribution on the source rock that expelled the oils[52]. All crude oil shows three isomers of phenyl-dibenzothiophenes (Ph-DBT) which have been unambiguously identified using co-injection of synthetize standards and retention indices[51]. Result show that all crude oils are characterized by predominance of 4-PhDBT, 3-PhDBT and 2-PhDBT isomer indicating high thermal maturity of the oils[51].

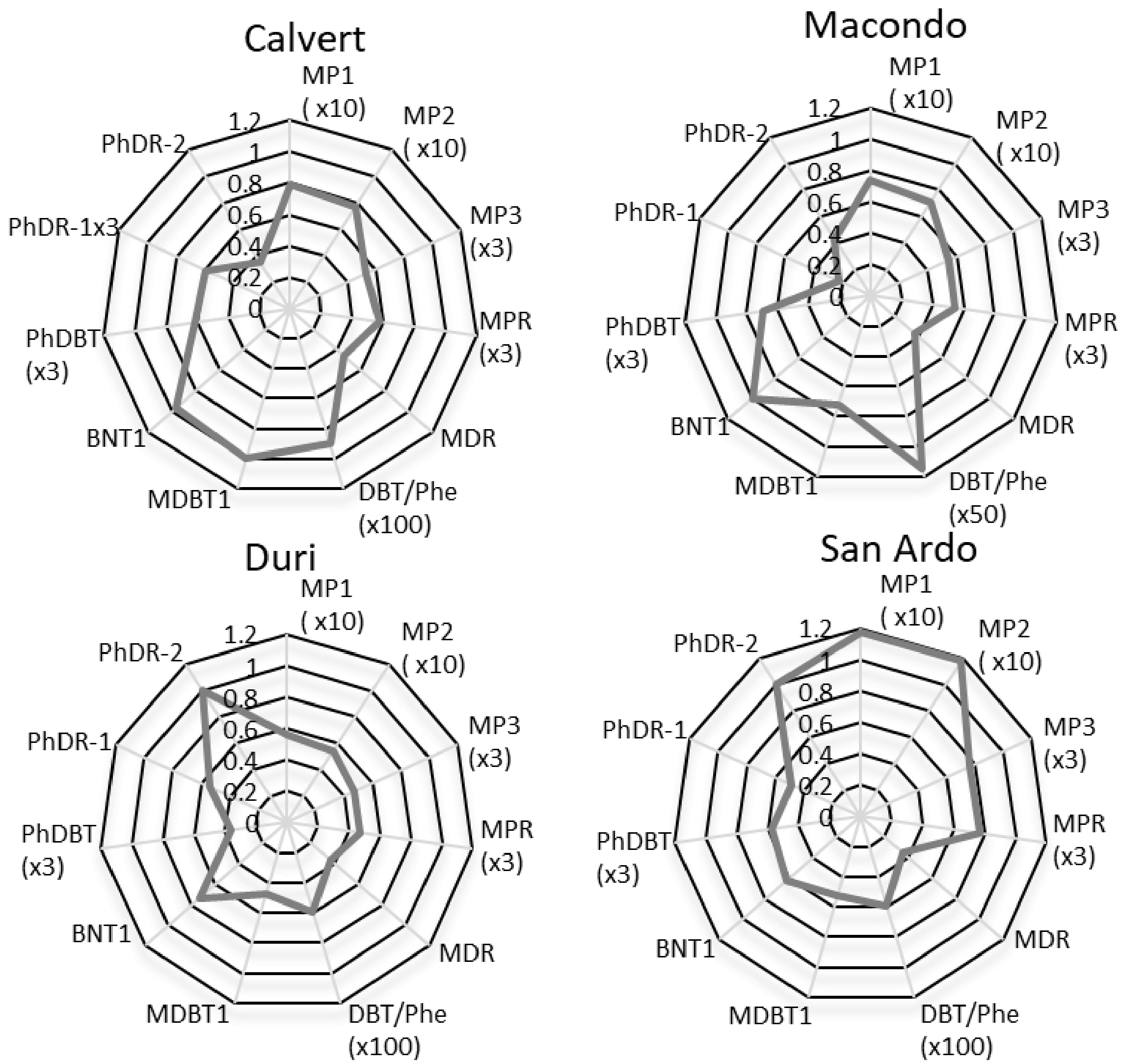

Figure 4. Variation of eleven diagnostic ratios representing thermal maturity, lithology, and microbial contribution to the oil formation for the deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils. See details in Table S4.

In addition to the evaluation of the deasphalted crude oils using known molecular components (~130 listed), further analysis can be performed using the known unknowns. While the GC-TIMS-TOF MS workflow provide accurate RT, CCS, and *m/z* measurements, which leads to the candidate assignment of the elemental composition and relative quantification, an identification with significant certainties will require the comparison with known standards. Moreover, in the case of PAHs, the use of MS/MS strategies for structural elucidation are limited due to the large similarity across fragmentation patterns, especially for highly isomeric samples.

The unsupervised T-Rex 4D analysis of the GC-APLI-TIMS-TOF MS data of the four deasphalted oils resulted in the observation of 8586 buckets, each characterized by a RT, CCS, *m/z* value, chemical formula (< 2ppm criteria) and peak areas for each replica analysis (i.e., 12 totals, 3x per oil). The principal component analysis (PCA) revealed that the four oils can be easily separated in two principal components that account for about 70% of total variance (Figure 5a, Figure S2). Differences between the light oils were easily separated in the PC1 component, while differences across the light, medium and heavy oils were easily separated in the PC2 component.

The chemical formula analysis permitted candidate assignment of the heteroatom classes. The internal standards and known compounds described in Figure 3 (and Table S3) were also observed in the bucket list and were used for the validation of the elemental formula assignment. Closer inspection of the heteroatom distribution shows that, while most of the classes are present in all the oils, their number is unique to each oil (Figure 5b and S1). In addition to the differentiation of the crude oils using PCA and heteroatom classes, the unknowns that are common and unique across the four samples can be better visualized using a Venn diagram (Figure 5c). For simplicity purposes and to account for detection variability of the low abundant species across replica measurement, we used a binary system for presence (1) or absence (0) based on the detection in at least 2 of the 3 replicas above a peak area threshold (1500, defined as 3x the lowest measured peak areas).

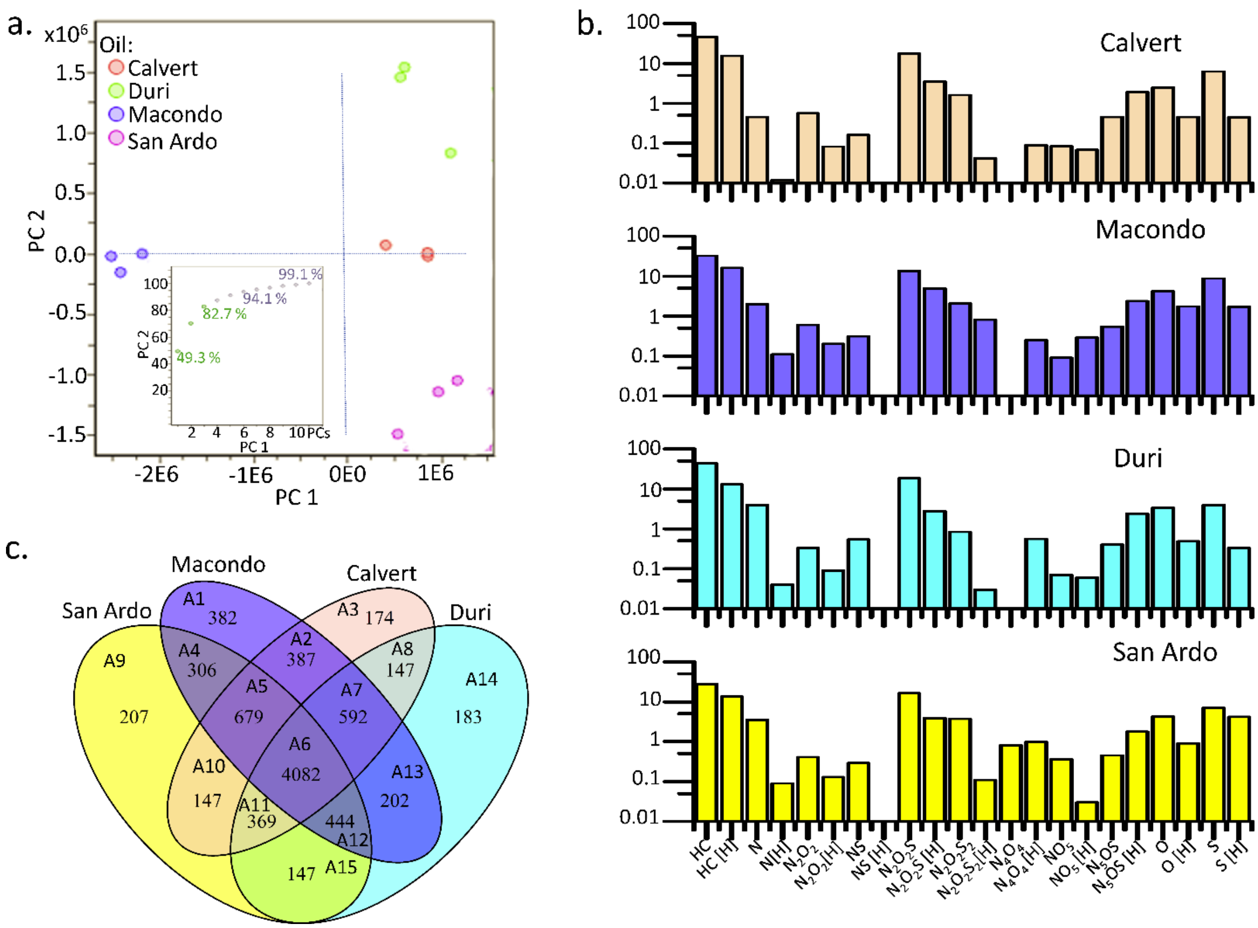

Figure 5. Summary of the unsupervised T-ReX 4D analysis of the GC-APLI-TIMS-TOF MS of the deasphalted light (Macondo and Calvert), medium (Duri) and heavy (San Ardo) crude oils. a) Principal Components Analysis, b) Heteroatoms class distribution and c) Venn Diagram showing common and unique components across the four crude oils.

Different from previous crude oil differentiation strategies, the unique and common bucket assignment is based on the [RT, CCS, *m/z*] vectors, which differentiates across isomeric content per molecular chemical formula, thus significantly increasing the specificity of the candidate assignment. The highest number of assignments is found to be common to all four oils (A6 with

4082 members), while there are unique compounds to each deasphalted crude oils: Calvert (A3, 174), Macondo (A1, 382), Duri (A14, 183) and San Ardo (A9, 207). Number of compounds for the Venn regions can be found in SI. This result showcases the high fingerprinting capability of the T-Rex 4D - GC-TIMS-TOF MS workflow. The list of unique compounds observed for each deasphalted crude oil can be easily used as markers to differentiate them apart from the differentiation based on the known 130 compounds previously described in Figure 3, and does not require quantitative measurement to uniquely identify/differentiate the crude oil. Further structural identification of these unique compounds requires the use of standards and/or complementary theoretical and experimental strategies like the ones described in ref [44]; a major caveat during the analysis of PAH-like compounds is the poor structural information that can be extracted from the MS/MS profiles. Nevertheless, the integration of MS/MS to the GC-TIMS-TOF MS workflow can provide significant structural information since the GC and IMS domains mostly account for potential isomeric interferences.

CONCLUSIONS

The application of GC-APLI-TIMS-TOF MS to the analysis of common deasphalted crude oils resulted in the effective separation and identification of PAH and similar compounds from complex mixtures. The analytical power of the GC-APLI-TIMS-TOF MS is based on the separation of the isomeric content using the GC and IMS separations, in addition to the high mass resolution and accuracy of the TOF MS analyzer. The comparison of the relative abundance across the four crude oils using previously reported PAH-like known compounds (130 compounds) uniquely identified based on their [RT; CCS; *m/z*] showed signature patterns. Moreover, these compounds provided distinctive diagnostic ratios (11x) representative of the thermal maturity, lithology, and microbial contribution to each oil formation.

The unsupervised T-Rex 4D analysis of the GC-APLI-TIMS-TOF MS permitted the classification of the four crude oils in 8586 buckets, each bucket characterized by a [RT; CCS; *m/z* value; chemical formula] and peak areas for each replica analysis (i.e., 12 totals, 3x per crude oil). This bucket list not only included the 130 known compounds and standards (used for verification of the algorithms), but also provided for the first time a comprehensive list of unknowns. While this list of unknowns is exhaustive, is limited to the GC accessible compounds from the deasphalted crude oils. The inspection of the unknows provided the identification of unique and common molecular components to each crude oils. The unique components to each crude oil can be use as identifiers solely based on their presence and represented 2-4% of the total number of assigned compounds; near half of the components were common to all four crude oils. Unsupervised PCA analysis of the GC-APLI-TIMS-TOF MS dataset revealed that the four oils can be easily separated in two principal components that account for 85% of total variance; the PC 1 and PC2 have a variance of 50% and 20%, respectively. We attribute this specificity to the high resolution obtained in the GC and IMS (R-50-90) separations, leading to the isomeric breakdown of each molecular formula.

ASSOCIATED CONTENT

Supporting Information List of known PAH compounds and internal standards used for calibration, retention time, retention index, measured *m/z* and collision cross section, Diagnostic ratios of target PAHs, Relative abundances of the known PAHs for the four crude oils, DBE plots of most abundant class and PCA score plot and 3 D projection, T-Rex 4D bucket table (excel file).

AUTHOR INFORMATION

Corresponding Author

*Telephone: 305-348-2037. Fax: 305-348-3772. E-mail: fernandf@fiu.edu

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

1. Marshall, A. G.; Rodgers, R. P., Petroleomics: The Next Grand Challenge for Chemical Analysis. *Acc. Chem. Res.* **2004,** 37, 53-59.
2. Marshall, A. G.; Rodgers, R. P., Petroleomics: Chemistry of the Underworld. *Proc. Natl. Acad. U.S.A.* **2008,** 105,, 18090-18095.
3. Jira, W., A GC/MS method for the determination of carcinogenic polycyclic aromatic hydrocarbons (PAH) in smoked meat products and liquid smokes. *European Food Research and Technology* **2004,** 218, (2), 208-212.
4. Pollo, B. J.; Alexandrino, G. L.; Augusto, F.; Hantao, L. W., The impact of comprehensive two-dimensional gas chromatography on oil & gas analysis: Recent advances and applications in petroleum industry. *TrAC Trends in Analytical Chemistry* **2018**, 105, 202-217
5. Marshall, A. G.; Rodgers, R. P., Petroleomics: Chemistry of the underworld. *Proceedings of the National Academy of Sciences* **2008,** 105, (47), 18090-18095.

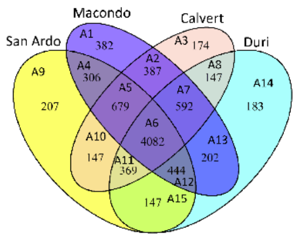
6. Tessarolo, N. S.; Silva, R. C.; Vanini, G.; Pinho, A.; Romão, W.; de Castro, E. V.; Azevedo, D. A., Assessing the chemical composition of bio-oils using FT-ICR mass spectrometry and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. *Microchemical Journal* **2014,** 117, 68-76.
7. Hilaire, F.; Basset, E.; Bayard, R.; Gallardo, M.; Thiebaut, D.; Vial, J., Comprehensive two-dimensional gas chromatography for biogas and biomethane analysis. *J Chromatogr A* **2017,** 1524, 222-232.
8. Kamínski, M.; Kartanowicz, R.; Gilgenast, E.; Namieśnik, J., High-performance liquid chromatography in group-type separation and technical or process analytics of petroleum products. *Critical reviews in analytical chemistry* **2005,** 35, (3), 193-216.
9. Kim, E.; Cho, E.; Moon, S.; Park, J.-I.; Kim, S., Characterization of petroleum heavy oil fractions prepared by preparatory liquid chromatography with thin-layer chromatography, high-resolution mass spectrometry, and gas chromatography with an atomic emission detector. *Energy & Fuels* **2016,** 30, (4), 2932-2940.
10. Fernandez-Lima, F. A.; Becker, C.; McKenna, A. M.; Rodgers, R. P.; Marshall, A. G.; Russell, D. H., Petroleum Crude Oil Characterization by IMS-MS and FTICR MS. *Analytical Chemistry* **2009,** 81, (24), 9941-9947.
11. Becker, C.; Qian, K.; Russell, D. H., Molecular Weight Distributions of Asphaltenes and Deasphaltened Oils Studied by Laser Desorption Ionization and Ion Mobility Mass Spectrometry. *Analytical Chemistry* **2008,** 80, (22), 8592-8597.
12. Ponthus, J.; Riches, E., Evaluating the multiple benefits offered by ion mobility-mass spectrometry in oil and petroleum analysis. *International Journal for Ion Mobility Spectrometry* **2013,** 16, (2), 95-103.
13. Szykuła, K. M.; Wicking, C.; Whitmarsh, S.; Creaser, C. S.; Reynolds, J. C., Characterization of Crude Oil and Its Saturate, Aromatic, and Resin Fractions by High-Field Asymmetric Waveform Ion Mobility Spectrometry–High-Resolution Mass Spectrometry. *Energy & fuels* **2018,** 32, (11), 11310-11316.
14. Fasciotti, M.; Lalli, P. M.; Klitzke, C. c. F.; Corilo, Y. E.; Pudenzi, M. A.; Pereira, R. C.; Bastos, W.; Daroda, R. J.; Eberlin, M. N., Petroleomics by traveling wave ion mobility–mass spectrometry using CO2 as a drift gas. *Energy & fuels* **2013,** 27, (12), 7277-7286.
15. Lalli, P. M.; Jarvis, J. M.; Marshall, A. G.; Rodgers, R. P., Functional Isomers in Petroleum Emulsion Interfacial Material Revealed by Ion Mobility Mass Spectrometry and Collision-Induced Dissociation. *Energy & Fuels* **2017,** 31, (1), 311-318.
16. Le Maître, J.; Hubert-Roux, M.; Paupy, B.; Marceau, S.; Rüger, C. P.; Afonso, C.; Giusti, P., Structural analysis of heavy oil fractions after hydrodenitrogenation by high-resolution tandem mass spectrometry and ion mobility spectrometry. *Faraday Discussions* **2019,** 218, (0), 417-430.
17. Farenc, M.; Paupy, B.; Marceau, S.; Riches, E.; Afonso, C.; Giusti, P., Effective Ion Mobility Peak Width as a New Isomeric Descriptor for the Untargeted Analysis of Complex Mixtures Using Ion Mobility-Mass Spectrometry. *Journal of the American Society for Mass Spectrometry* **2017,** 28, (11), 2476-2482.
18. Ahmed, A.; Cho, Y.; Giles, K.; Riches, E.; Lee, J. W.; Kim, H. I.; Choi, C. H.; Kim, S., Elucidating Molecular Structures of Nonalkylated and Short-Chain Alkyl (n < 5, (CH2)n) Aromatic Compounds in Crude Oils by a Combination of Ion Mobility and Ultrahigh-Resolution Mass Spectrometries and Theoretical Collisional Cross-Section Calculations. *Analytical Chemistry* **2014,** 86, (7), 3300-3307.

19. Vetere, A.; Schrader, W., 1-and 2-Photon ionization for online FAIMS-FTMS coupling allows new insights into the constitution of crude oils. *Analytical chemistry* **2015,** 87, (17), 8874-8879.
20. Lababidi, S.; Schrader, W., Online normal-phase high-performance liquid chromatography/Fourier transform ion cyclotron resonance mass spectrometry: Effects of different ionization methods on the characterization of highly complex crude oil mixtures. *Rapid Communications in Mass Spectrometry* **2014,** 28, (12), 1345-1352.
21. Castellanos, A.; Benigni, P.; Hernandez, D.; DeBord, J.; Ridgeway, M.; Park, M.; Fernandez-Lima, F., Fast screening of polycyclic aromatic hydrocarbons using trapped ion mobility spectrometry–mass spectrometry. *Analytical Methods* **2014,** 6, (23), 9328-9332.
22. Tose, L. V.; Benigni, P.; Leyva, D.; Sundberg, A.; Ramírez, C. E.; Ridgeway, M. E.; Park, M. A.; Romão, W.; Jaffé, R.; Fernandez-Lima, F., Coupling trapped ion mobility spectrometry to mass spectrometry: trapped ion mobility spectrometry–time-of-flight mass spectrometry versus trapped ion mobility spectrometry–Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Communications in Mass Spectrometry* **2018,** 32, (15), 1287-1295.
23. McKenna, A. M.; Williams, J. T.; Putman, J. C.; Aeppli, C.; Reddy, C. M.; Valentine, D. L.; Lemkau, K. L.; Kellermann, M. Y.; Savory, J. J.; Kaiser, N. K.; Marshall, A. G.; Rodgers, R. P., Unprecedented Ultrahigh Resolution FT-ICR Mass Spectrometry and Parts-Per-Billion Mass Accuracy Enable Direct Characterization of Nickel and Vanadyl Porphyrins in Petroleum from Natural Seeps. *Energy & Fuels* **2014,** 28, (4), 2454-2464.
24. Benigni, P.; DeBord, J. D.; Thompson, C. J.; Gardinali, P.; Fernandez-Lima, F., Increasing Polyaromatic Hydrocarbon (PAH) Molecular Coverage during Fossil Oil Analysis by Combining Gas Chromatography and Atmospheric-Pressure Laser Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). *Energy & Fuels* **2016,** 30, (1), 196-203.
25. Rockenbach, I. I.; Jungfer, E.; Ritter, C.; Santiago-Schübel, B.; Thiele, B.; Fett, R.; Galensa, R., Characterization of flavan-3-ols in seeds of grape pomace by CE, HPLC-DAD-MSn and LC-ESI-FTICR-MS. *Food research international* **2012,** 48, (2), 848-855.
26. Lababidi, S.; Panda, S. K.; Andersson, J. T.; Schrader, W., Direct coupling of normal-phase high-performance liquid chromatography to atmospheric pressure laser ionization Fourier transform ion cyclotron resonance mass spectrometry for the characterization of crude oil. *Analytical chemistry* **2013,** 85, (20), 9478-9485.
27. Benigni, P.; Fernandez-Lima, F., Oversampling Selective Accumulation Trapped Ion Mobility Spectrometry Coupled to FT-ICR MS: Fundamentals and Applications. *Analytical Chemistry* **2016,** 88, (14), 7404-7412.
28. Benigni, P.; Porter, J.; Ridgeway, M. E.; Park, M. A.; Fernandez-Lima, F., Increasing Analytical Separation and Duty Cycle with Nonlinear Analytical Mobility Scan Functions in TIMS-FT-ICR MS. *Analytical Chemistry* **2018**, 90(4), 2446-2450
29. Benigni, P.; Thompson, C. J.; Ridgeway, M. E.; Park, M. A.; Fernandez-Lima, F., Targeted High-Resolution Ion Mobility Separation Coupled to Ultrahigh-Resolution Mass Spectrometry of Endocrine Disruptors in Complex Mixtures. *Anal. Chem.* **2015,** 87, (8), 4321-4325.
30. Leyva, D.; Jaffe, R.; Fernandez-Lima, F., Structural Characterization of Dissolved Organic Matter at the Chemical Formula Level Using TIMS-FT-ICR MS/MS. *Analytical Chemistry* **2020,** 92, (17), 11960-11966.

31. Hendrickson, C. L.; Quinn, J. P.; Kaiser, N. K.; Smith, D. F.; Blakney, G. T.; Chen, T.; Marshall, A. G.; Weisbrod, C. R.; Beu, S. C., 21 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer: A National Resource for Ultrahigh Resolution Mass Analysis. *Journal of the American Society for Mass Spectrometry* **2015,** 26, (9), 1626-1632.
32. Schaub, T. M.; Hendrickson, C. L.; Horning, S.; Quinn, J. P.; Senko, M. W.; Marshall, A. G., High-Performance Mass Spectrometry: Fourier Transform Ion Cyclotron Resonance at 14.5 Tesla. *Analytical Chemistry* **2008,** 80, (11), 3985-3990.
33. Cavanna, D.; Zanardi, S.; Dall'Asta, C.; Suman, M., Ion mobility spectrometry coupled to gas chromatography: A rapid tool to assess eggs freshness. *Food Chemistry* **2019,** 271, 691-696.
34. Adams, K. J.; Smith, N. F.; Ramirez, C. E.; Fernandez-Lima, F., Discovery and targeted monitoring of polychlorinated biphenyl metabolites in blood plasma using LC-TIMS-TOF MS. *International journal of mass spectrometry* **2018,** 427, 133-140.
35. Adams, K. J.; Ramirez, C. E.; Smith, N. F.; Muñoz-Muñoz, A. C.; Andrade, L.; Fernandez-Lima, F., Analysis of isomeric opioids in urine using LC-TIMS-TOF MS. *Talanta* **2018,** 183, 177-183.
36. Purves, R. W., Enhancing Biological LC-MS Analyses Using Ion Mobility Spectrometry. *Advances in the Use of Liquid Chromatography Mass Spectrometry (LC-MS): Instrumentation Developments and Applications* **2018,** 79, 205.
37. Tose, L. V.; Benigni, P.; Leyva, D.; Sundberg, A.; Ramírez, C. E.; Ridgeway, M. E.; Park, M. A.; Romão, W.; Jaffé, R.; Fernandez-Lima, F., Coupling trapped ion mobility spectrometry to mass spectrometry: trapped ion mobility spectrometry–time-of-flight mass spectrometry versus trapped ion mobility spectrometry–Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Communications in Mass Spectrometry* **2018,** 32, (15), 1287-1295.
38. Zheng, X.; Aly, N. A.; Zhou, Y.; Dupuis, K. T.; Bilbao, A.; Paurus, V. L.; Orton, D. J.; Wilson, R.; Payne, S. H.; Smith, R. D., A structural examination and collision cross section database for over 500 metabolites and xenobiotics using drift tube ion mobility spectrometry. *Chemical science* **2017,** 8, (11), 7724-7736.
39. Kondyli, A.; Schrader, W., High-resolution GC/MS studies of a light crude oil fraction. *Journal of Mass Spectrometry* **2019,** 54, (1), 47-54.
40. Constapel, M.; Schellenträger, M.; Schmitz, O.; Gäb, S.; Brockmann, K.; Giese, R.; Benter, T., Atmospheric-pressure laser ionization: a novel ionization method for liquid chromatography/mass spectrometry. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry* **2005,** 19, (3), 326-336.
41. Schiewek, R.; Schellenträger, M.; Mönnikes, R.; Lorenz, M.; Giese, R.; Brockmann, K.; Gäb, S.; Benter, T.; Schmitz, O., Ultrasensitive determination of polycyclic aromatic compounds with atmospheric-pressure laser ionization as an interface for GC/MS. *Analytical chemistry* **2007,** 79, (11), 4135-4140.
42. Schmitt-Kopplin, P.; Englmann, M.; Rossello-Mora, R.; Schiewek, R.; Brockmann, K. J.; Benter, T.; Schmitz, O. J., Combining chip-ESI with APLI (cESILI) as a multimode source for analysis of complex mixtures with ultrahigh-resolution mass spectrometry. *Analytical and bioanalytical chemistry* **2008,** 391, (8), 2803-2809.
43. Schiewek, R.; Lorenz, M.; Giese, R.; Brockmann, K.; Benter, T.; Gäb, S.; Schmitz, O. J., Development of a multipurpose ion source for LC-MS and GC-API MS. *Analytical and bioanalytical chemistry* **2008,** 392, (1-2), 87-96.

44. Olanrewaju, C. A.; Ramirez, C. E.; Fernandez-Lima, F., Comprehensive Screening of Polycyclic Aromatic Hydrocarbons and Similar Compounds Using GC–APLI–TIMS–TOFMS/GC–EI–MS. *Analytical Chemistry* **2021,** 93, (15), 6080-6087.
45. Naylor, C. N.; Reinecke, T.; Ridgeway, M. E.; Park, M. A.; Clowers, B. H., Validation of calibration parameters for trapped ion mobility spectrometry. *Journal of The American Society for Mass Spectrometry* **2019,** 30, (10), 2152-2162.
46. Hernandez, D. R.; DeBord, J. D.; Ridgeway, M. E.; Kaplan, D. A.; Park, M. A.; Fernandez-Lima, F., Ion dynamics in a trapped ion mobility spectrometer. *Analyst* **2014,** 139, (8), 1913-1921.
47. Chai, M.; Young, M. N.; Liu, F. C.; Bleiholder, C., A transferable, sample-independent calibration procedure for trapped ion mobility spectrometry (TIMS). *Analytical chemistry* **2018,** 90, (15), 9040-9047.
48. Mason, E. A.; McDaniel, E. W., Transport properties of ions in gases. *NASA STI/Recon Technical Report a* **1988,** 89, 15174.
49. Lu, Z.; Chen, S.; He, Q.; Li, Y.; Zhang, J.; Wu, Q., Relationship between methylphenanthrene distribution and organic matter maturity: a case study of Yangchang Formation Chang 7 source rocks, Erdos Basin, China. *Petroleum Science and Technology* **2018,** 36, (20), 1718-1724.
50. Radke, M., Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology* **1988,** 5, (3), 224-236.
51. Zhu, Z.; Li, M.; Tang, Y.; Qi, L.; Leng, J.; Liu, X.; Xiao, H., Identification of phenyldibenzothiophenes in coals and the effects of thermal maturity on their distributions based on geochemical data and theoretical calculations. *Organic Geochemistry* **2019,** 138, 103910.
52. Ogbesejana, A. B.; Bello, O. M.; Akintade, O. O.; Okunola, O. J.; Osamudiamen, P. M.; Kabo, K. S.; Ali, T.; Uduma, U. A., Dibenzothiophenes, phenyldibenzothiophenes, and benzo [b] naphthothiophenes in crude oils and source rock extracts from the Niger Delta Basin, Nigeria, and their applications as source facies, depositional environments, and thermal maturity indicators. *Arabian Journal of Geosciences* **2021,** 14, (7), 1-22.
53. Ogbesejana, A. B.; Ningning, Z.; Sonibare, O. O., The distribution and significance of dimethyldibenzothiophenes, trimethyldibenzothiophenes and benzo[b]naphthothiophenes in source rock extracts from offshore Niger Delta basin, Nigeria. *Petroleum Science and Technology* **2019,** 37, (18), 1978-1986.
54. Hughes, W. B.; Holba, A. G.; Dzou, L. I., The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochimica et Cosmochimica Acta* **1995,** 59, (17), 3581-3598.
55. Li, M.; Wang, T. G.; Simoneit, B. R.; Shi, S.; Zhang, L.; Yang, F., Qualitative and quantitative analysis of dibenzothiophene, its methylated homologues, and benzonaphthothiophenes in crude oils, coal, and sediment extracts. *J Chromatogr A* **2012,** 1233, 126-36.

TOC graphic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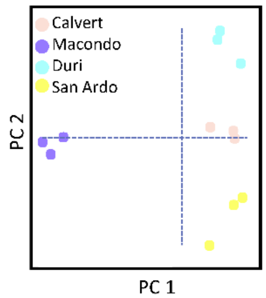
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