Analytics driving kinetics: advanced mass spectrometric characterization of petroleum products

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Abstract

The current state-of-the-art in analysis techniques for petroleum fractions has progressed substantially during the last decade. This has helped to further improve the lumping procedures and modeling approaches of these complex systems. Recent advances in gas chromatography (GC), GC-field ionization mass spectrometry (GC-FIMS), and comprehensive gas chromatography (GC \times GC) have made it possible to determine the compositions of fractions with up to 45 carbon atoms and in some cases up to C80. The combination of MS techniques with other selective detectors and reversed-phase column combinations has made it possible to quantify even traces of heteroatomic compounds in these complex hydrocarbon matrices. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), in some cases combined with $GC \times GC$ for the lighter part, has pushed the characterization of larger macromolecules in particular asphaltenes. Matrix-assisted laser desorption/ionization (MALDI) is also used widely for this purpose but has the disadvantage that quantification is not obvious. The development of more detailed characterization techniques has not remained unnoticed in the petrochemical society, and more recently in the petrochemical kinetic modeling society. More detailed characterization of petrochemical fractions has made the implementation of detailed kinetic models for simulation and optimization possible including more and more molecular detail. Additionally, advances in photo-ionization mass spectrometry (PI-MS) have allowed the detection of reactive intermediates and direct kinetic measurements in time-resolved experiments. It can only be expected that this trend will continue and that the application field will move from now primarily petrochemistry, (from catalytic cracking, over hydrotreating and hydrocracking, to pyrolysis, combustion, and steam cracking) to larger-scale chemical recycling and biomass conversion processes.

Keywords

mass spectrometry, comprehensive gas chromatography, GC-field ionization mass spectrometry, Fourier transform ion cyclotron resonance mass spectrometry, matrix-assisted laser desorption/ionization

1 Introduction

Nowadays, the petrochemical industry is continually striving to improve the performance of its installations. Despite the long tradition and wide knowledge base about these processes, there is still a place to improve their performance in order to achieve savings in energy, improve selectivity, and to better protect the environment. To this end, accurate mathematical simulation models are an indispensable tool and many chemical engineers use simulation programs routinely. It is well known that the analytical characterization of petroleum fractions plays a crucial role to predict physicochemical and thermodynamic properties, while the kinetic models describe chemical transformations of these streams via the occurring reactions.¹⁻⁴ However, petroleum and the products obtained thereof contain a variety of compounds, usually but not always hydrocarbons. As the number of carbon atoms increases, the complexity of petroleum fractions also rapidly increases.⁵⁻⁷ Consequently, detailed analysis of the individual constituents of higher boiling fractions becomes increasingly difficult. In these cases, chemical engineers rely on the average properties of the mixture (e.g. the average molecular weight, the specific density, the H/C-ratio, etc.), so-called commercial indices of the mixture^{8,9}. Measurements of bulk properties are generally easy to perform and, therefore, quick and economical. Several properties may correlate well with certain compositional characteristics and are widely used as a quick and inexpensive approach to determine those characteristics. The most important properties of a whole crude oil are its boiling-point distribution, density (or API gravity)⁶, and viscosity.¹⁰ These global characteristics can be either used directly to develop kinetic models or indirectly. In this last case, a reconstructed composition of the mixture is determined based on the global properties.

Understanding the chemical composition of heavier crude oils is of the utmost importance for the oil industry and has been a long-term goal of the analytical community.^{11, 12} However, the characterization of these products is not always simple. Many different analytical techniques have been used for the analysis of crude oil such as nuclear magnetic resonance (NMR),¹³ Fourier transform infrared (FTIR) spectroscopy,¹⁴ liquid/gas chromatography (LC/GC)¹⁵, and mass spectrometry (MS).^{16, 17} The advanced MS is one of the most informative methods for the analysis of multicomponent mixtures which makes it indispensable in the investigation of the composition of samples.¹⁸ It has been already reported that the success of MS depends on converting compounds into gas-phase ions.¹⁹ To be able to achieve this from compounds with high sensitivity, the expansion of MS has initiated. The key factor that makes the application of MS possible, is the methods of ionization such as electron ionization (EI), chemical ionization (CI), electrospray ionization (ESI),²⁰⁻²³ atmospheric pressure photoionization (APPI),²⁴⁻²⁹ atmospheric pressure chemical ionization (APCI),²⁹⁻³² atmospheric pressure laser ionization (APLI)³³⁻³⁵, and laser desorption/ionization including matrix-assisted laser desorption/ionization (LDI^{7, 36-41} and MALDI,⁴²⁻⁵⁸ respectively), and field desorption ionization (FDI).⁵⁹⁻⁶² For example, the use of field desorption ionization, plasma desorption, fast-atom bombardment (FAB), laser desorption, and thermo-spray ionization, non-volatile compounds could successfully be converted into gas-phase ions.^{19, 63-65} Especially, with the introduction of LDI and MALDI, the characterization of various petroleum products has been enabled that previously was difficult or impossible by using MS.^{46, 49, 66-68} MALDI is considered a soft ionization technique where the ions are generated in the gas phase for the MS analysis of non-volatile analytes. The term soft means that minimum internal energy is transmitted to the analytes during the ionization process.⁴⁶ Besides, LDI and MALDI, fast atom bombardment (FAB).^{69, 70} liquid secondary ion mass spectrometry (LSIMS).⁷¹ and ESI are considered soft techniques too. Moreover, since ESI and MALDI were introduced in the 1980s, significant progress has been made, for example characterizing minute quantities of non-volatile and high-mass compounds even in complex mixtures. It has been utilized within the industry since the earliest models of mass spectrometers were made. Furthermore, Trimpin et al.¹⁹ presented the proposed mechanism of ionization, implications for instrumentation, and unique applications utilizing matrix-assisted ionization (MAI), laser spray ionization (LSI), and solvent-assisted ionization (SAI) with small portable mass spectrometers, (ultra) high-resolution MS, automation, ion mobility spectrometry (IMS), MS/MS using advanced collision-induced dissociation (CID) and/or advanced fragmentation technology such as electron transfer dissociation (ETD). With these methods, it is possible to identify and characterize both large and small sample molecules, either with spatial or temporal resolution information.

Apart from all these advances within MS, the use of Fourier Transform Ion Cyclotron Resonance Mass spectrometry (FT-ICR-MS) allows to detect and assign unique elemental formulas to thousands of molecules in a crude oil sample and is considered the gold standard for MS analysis of petroleum.^{4, 72-78} Furthermore, conjugation of MS detector with gas chromatography (GC),⁷⁹ liquid chromatography (LC),⁸⁰ and capillary electrophoresis (CE),⁸¹ the structural information of complex samples can be disclosed.

The majority of the petroleum studies is performed using gas chromatography (GC) coupled to a quadrupole ion mass analyzer (qMS) using electron impact (EI) ionization which may enable the separation, detection, and identification of molecules up to C40.⁷ On the one hand, one-dimensional gas chromatography mass spectrometry (1D GC-MS)^{82, 83} and tandem MS (MS-MS)⁸⁴ are useful techniques due to the vapor pressure or final boiling point being compatible with the maximum temperatures of gas chromatograph (GC) columns.⁸⁵ On the other hand, the use of 1D-GC can incompletely deconvolute the compounds in the complex samples (aka co-elution phenomena), even though it is equipped with enhanced separation capabilities of the multiple reaction monitoring (MRM) or MS-MS techniques. Therefore, there is the necessity to develop new techniques to improve the separation of crude oil. At the current time, GC-MS has been widely used for qualification, while GC coupled with flame ionization detector (GC-FID) has been applied for the quantification of hydrocarbon components due to their stable and linear response.^{86, 87} The advent of comprehensive two-dimensional gas chromatography (GC \times GC) can improve significantly separation due to its high chromatographic resolution, high peak capacity, and selectivity.⁸⁸ By using GC \times GC, the sample components can be eluted into chemical classes, a so-called "group-tile" that may simplify the process of characterization and quantification. Numerous studies have shown the advantages of $GC \times$ GC, i.e. the characterization of naphtha,^{89, 90} gasoline,⁹¹⁻⁹⁴ kerosene and diesel cuts,⁹⁵⁻⁹⁸ but also for trace analysis⁹⁹⁻¹⁰¹, and the control of the chemical processes.^{102, 103}

Figure 1 represents a scheme of these advanced mass spectrometry techniques and ionization sources discussed in this review paper. The main goal of this review paper is to point out the advantages and disadvantages of the most important techniques used in the characterization of fuels and chemical products. The main novelty of this review is its specific focus on applications of MS to petroleum products and the additional discussion on how advances in MS diagnostics are valuable to kinetic model development for petroleum processes. Recent advances in the field of mass spectrometry from the aspect of petroleum fractions and their physical and thermodynamical properties are addressed in the second section. Substantial attention is paid to GC and LC systems coupled to MS analyzers, focusing on applications of GC-FIMS, GC \times GC-TOF-MS, and GC \times GC-qMS. Afterward, ICP-MS is introduced and the most recent findings are stressed in this section. The last part is dedicated to the FT-ICR-MS system coupled to different ionization sources such as APPI, ESI, APCI, APLI, LDI, MALDI, and FDI. And finally, a summary of this overview with a future outlook is presented in the last section.



Figure 1. Overview of advanced mass spectrometry techniques and ionization sources for petroleum product characterization discussed in this review paper. Note that also other combinations of ionization methods and analyzers are possible.

2 Petroleum fractions and products

2.1 Composition of crude oil and oil refining

Crude oil is rarely used in its raw form, therefore, it is processed into different products forming a complex mixture of hydrocarbons ranging from methane to asphalt, wherein proportions of paraffins, olefins, naphthenes, and aromatics can be varied.^{104, 105} Petroleum is a mixture of compounds formed from carbon and hydrogen atoms with impurities such as nitrogen, sulfur, oxygen, and certain metals. They often consist of alkanes, cycloalkanes, aromatics, and polyaromatic hydrocarbons.¹⁰⁶ Olefins, on the other hand, are rarely present in petroleum fractions, but they are important products in the refinery, for example from catalytic cracking and steam cracking. Additionally, olefins are abundant in pyrolysis oil of plastic waste, which is a new alternative feedstock that will be integrated in refineries.¹⁰⁷ Petroleum hydrocarbons are commonly found in reservoirs, petroleum products, and fuel products. A small portion leaks into the environment such that they are also found as contaminants or pollutants in soil, sediments, and water. Petroleum hydrocarbons are a blend of a large number of compounds that are derived from fossil fuels.¹⁰⁸ Further on, refining processes can be generally divided into three major types:

- 1. separation
- 2. conversion
- 3. finishing

From the product quality point of view, it is well known that the co-production of water and crude oil in a form of an emulsion is undesirable.¹⁰⁹ Separation of crude oil and water during the processing of petroleum is of utmost importance, and over the years, researchers were focusing on understanding this separation process. Destabilization of crude oil-in-water emulsions is crucial for the purification of produced water and clean-up of oil spills.¹⁰⁹⁻¹¹¹ Various techniques may be utilized for the separation of the compounds. Distillation is the most important separation process in which compounds are separated based on the

difference in their boiling points.^{105, 112} The goal of crude oil distillation is to fractionate crude oil into lightend hydrocarbons (C1-C4), naphtha, kerosene, diesel, and heavier fractions including atmospheric and vacuum gas oils and residues.¹¹² Besides distillation, other physical separation processes can be considered too, such as absorption, stripping, and extraction. As an example, in a refinery gas plant that produces light gases, the heavy hydrocarbons (C5 and heavier) in the gas mixture are separated through their absorption by a liquid oil solvent.¹¹³ During the conversion process, various chemical changes occur with hydrocarbons in reactors. Thus, the purpose of these reactions is to convert hydrocarbon compounds from one type to another.

The most important reaction in which heavy hydrocarbons are converted to lighter hydrocarbons is called "cracking".¹⁰⁵ Catalytic cracking, visbreaking, delayed coking, hydrocracking and steam cracking are commonly used for this purpose,¹¹⁴⁻¹¹⁸ while reactions such as isomerization or alkylation are used to produce high octane number gasoline. The last step in refining is the finishing step where the purification of various product streams takes the place. The removal of the impurities can be done by different processes such as desulfurization or acid treatment of petroleum fractions. Further on, once the desalting process is over, the crude oil enters the atmospheric distillation column, where compounds are separated according to their boiling points. In general, hydrocarbons in crude oil have boiling points between -160°C (boiling point of methane) and more than 600°C (characteristic boiling point of heavy compounds in the crude oil). However, it is well known that the carbon-carbon bond in hydrocarbons breaks down at temperatures about 350°C. This process is called cracking and it is undesirable during the distillation process since it changes the structure of hydrocarbons. For this reason, compounds with boiling points above 350°C are removed from the bottom of an atmospheric distillation column. They are sent to a vacuum distillation column where the pressure is about 50-100 mm Hg, thus, the hydrocarbons are boiled at much lower temperatures. Since distillation cannot completely separate the compounds, no pure hydrocarbon can be obtained as a product. In general, a group of hydrocarbons can be separated through distillation by the boiling point of the lightest and heaviest compounds in the mixtures. A mixture of methane and ethane that has a boiling range between -180°C and -80°C is considered the lightest product of an atmospheric column. This gaseous mixture is known as fuel gas, which is a petroleum fraction. In fact, during distillation, a crude is converted into a series of petroleum fractions where each one is a mixture of a limited number of hydrocarbons with a specific range of boiling points. Fractions with a wider range of boiling points contain greater numbers of hydrocarbons.

All petroleum fractions have a known boiling range, except the residuum for which the upper boiling point is usually not known. The boiling point of the heaviest component in crude oil is not known, but it is quite high. The problem of the nature and properties of the heaviest compounds in crude oils and petroleum residue is still under investigation by researchers.^{119, 120} Theoretically, it can be assumed that the boiling point of the heaviest component in crude oil is infinity. Atmospheric residue has compounds with carbon numbers greater than 25 while vacuuming residue has carbon numbers greater than 50. Some of the petroleum fractions produced from distillation columns with their boiling point ranges and applications are given in Table 1.

Table 1. General Summary of Product Types and Distillation Range¹²¹

Detrolours frontion	troleum fraction Approximate hydrocarbon range	hydrocarbon	Approximate boiling range	
Petroleum fraction		°C	°F	
Atmospheric distillation				
Light gases	C ₂ -	- C4	-90 to 1	-130 - 30

Light gasoline	$C_4 - C_7$	-1 - 83	30 - 180
Naphtha	$C_{7}-C_{11}$	83 - 205	180 - 400
Kerosene	$C_{11} - C_{16}$	205 - 275	400 - 525
Light gas oil (LGO)	$C_{16} - C_{21}$	275 – 345	525 - 650
Sum	$C_2 - C_{21}$	-90 - 345	-130 - 650
Vacuum distillation (VD)			
Heavy gas oil (HGO)	$C_{21} - C_{31}$	345 - 455	650 - 850
Vacuum gas oil (VGO)	$C_{31} - C_{48}$	455 – 655	850 - 1050
Residuum	$> C_{48}$	655+	1050+
Sum	$C_{21} - C_{48+}$	345 - 655+	650 - 1050
Total crude	$C_2 - C_{48+}$	-90 -655+	-130-650+

It can be seen from the table that the boiling point and equivalent carbon number ranges are approximate, therefore, they may vary according to the desired specific product. For example, the fraction containing light gases is mainly a mixture of ethane, propane, and butane; however, some heavier compounds (C_{5+}) may be detected in this fraction too. The fraction is fractionated to obtain ethane (a fuel gas), propane, and butane (petroleum gases). In addition, the isobutane is separated from the gas mixture and used as a feed for alkylation. These fractions may undergo further processes to produce desired products.

2.2 Physical and Thermodynamic Properties

The characterization of crude oils and petroleum fractions depends on the properties of pure hydrocarbons. The most used properties of fluids are distillation data, boiling point, specific gravity composition (PNA content), molecular weight, refractive index, elemental analysis (CHNSO composition), kinematic viscosity at 37.8 and 98.9°C.

2.2.1 Boiling point and distillation curves

It is known that pure compounds have a single value for the boiling point, while for the mixtures, vaporization may occur, hence, the boiling points may vary.¹¹³ For a defined mixture, the boiling point may be represented by several boiling points for each component present in the mixture with respect to their composition. In a petroleum mixture, the boiling point of the lightest component is called the initial boiling point (IBP), while the heaviest component is called the final boiling point (FBP). Petroleum fractions having a wider range of boiling points usually contain more compounds than those with a more narrow boiling point range. The reason for that lies in the continuity of hydrocarbon compounds in the fraction.¹¹³ It is expected that a boiling range for a pure component is zero, hence that the distillation curve is horizontal. On

the other hand, for gas oil, the IBP may be found at 248 °C and FBP at 328 °C, meaning that the boiling range is 80 °C, while crude oils may have boiling ranges of more than 550 °C.

2.2.2 Specific Gravity

Specific gravity (SG) for liquid oils can be defined by Eq. 2.2.2.1¹²²:

$$SG_{oil} = \frac{\rho_{oil}}{\rho_{water}} \tag{2.2.2.1}$$

where ρ_{oil} is the oil density and ρ_{water} is the water density. To measure the specific gravity, a temperature of 15.5°C is used, however, absolute density is usually reported at 20 °C.

Besides the specific gravity, there is another parameter for oil density called API gravity (Eq. 2.2.2.2):

$$API = \frac{141.5}{sG} - 131.5 \tag{2.2.2.2}$$

It is well known, that heavy oils have low API and light oils have high API gravities. Usually, the density of petroleum fractions and crude oils is carried out using a pycnometer or a Mettler/Parr densitometer.

2.2.3 Molecular Weight

Molecular weight is another property that may provide us with information about petroleum products. The average molecular weight can be determined using different experimental methods, such as a vapor pressure method, a size exclusion chromatography (SEC) method, and a cryoscopy method.¹¹⁹ The vapor pressure method is based on the measurement of the difference between the vapor pressure of the sample and that of a known reference solvent with a vapor pressure greater than that of the sample. For heavy petroleum fractions and asphaltenic compounds, the SEC method is commonly used to measure the distribution of the molecular weight of the fraction. This method is also called gel permeation chromatography (GPC) and is described in the ASTM D 5296 test method. The molecular weight range that can be covered using this ASTM method is limited by the elution volume of polystyrene standards, i.e. molecular weights can in general be detected between 2000 to 2×10^6 g/mol. The third, and most widely used method of determining the molecular weight is the cryoscopy method, which is based on freezing point depression.

2.2.4 Viscosity

The viscosity of petroleum fractions is another property of high importance. Viscosity may vary from several thousand to several million poises. It increases with a decrease in the API gravity and for residues and heavy oils with the API gravity of less than 10 (specific gravity of above 1). Viscosity is an important parameter because it may be used to estimate other physical properties, the composition, and the quality of petroleum products. The viscosity is a temperature-dependent property; therefore, its values need to be reported with specified temperatures. In reality, kinematic viscosity is measured at temperatures of 37.8°C and 98.9 °C, while for very heavy fractions it is reported at temperatures above 38°C i.e., 50°C or 60°C.¹¹³

2.2.5 Refractive Index

The refractive index is a property that may be used as an input parameter for other correlations, and it is defined as a ratio of the speed of light in a vacuum and the speed of light in the medium. The refractive indices of petroleum products are usually not known; thus, they should be predicted. For this purpose, it can be used the following equation (Eq. 2.2.5.1)^{113, 122}:

$$n = \left(\frac{1+2I}{1-I}\right)^{1/2} \tag{2.2.5.1}$$

In which *n* is the refractive index at 20°C, and *I* is the Huang characterization parameter at 20°C that can be calculated from the mean average boiling point and the specific gravity of the petroleum fraction. It is known that refractive indexes of hydrocarbons may vary from 1.35 to 1.6, while for aromatics, the values can be greater than those for naphthenes. Paraffins and paraffinic oils have lower refractive indices.¹¹³

2.3 Methods for compositional analysis of petroleum products

Since the petroleum fractions are mixtures composed of different types of hydrocarbon compounds, it is of crucial importance to determine the overall effects of the chemical composition of transportation fuel on its physical properties. Therefore, a reliable characterization of detailed hydrocarbon and heteroatom composition is essential.¹²³ In fact, the compositional information of petroleum fractions can be obtained through different methods.

- separation by solvents
- chromatography methods (e.g. GC, HTGC, GC × GC, HPLC, and TLC)
- spectroscopy methods (e.g. UV-VIS, IR, Raman, and NMR)
- spectrometry methods (e.g. MS)

Separation by solvents is based on the solubility of compounds in a mixture. According to the chosen ASTM standard, different solvents may be used. For example, when ASTM D 2007 test method is performed, *n*-pentane is used as the solvent, while for ASTM D 4124, the solvent is *n*-heptane. SARA (Saturates-Aromatics-Resins-Asphaltenes) analysis, shown in Figure 2, can be used for heavy petroleum fractions, residues, and fossil fuels (coal liquids), as they have high contents of aromatics, resins, asphaltenes, and residue¹²⁴. This analysis is relatively quick and has several applications in the oil industry.¹²⁵ Further on, the elemental analysis may give us information on carbon, hydrogen, nitrogen, sulfur, and oxygen contents (CHNS&O). Various information can be obtained from elemental analysis such as the C/H ratio and/or sulfur content of a petroleum mixture, which will indicate oil quality. For example, sulfur content for very heavy fractions may reach up to 6-8%, while the nitrogen content up to 2.0-2.5 wt%.



Figure 2. SARA-separation scheme. Adapted from ¹²⁴

Spectroscopy is a valuable tool in detecting basic and bulk properties of petroleum samples and it is also usable in the primary analysis of unknown type oil samples. For example, Infrared Spectroscopy (IR) can be used to identify functional groups and hydrogen bonding in a mixture and also structural parameters such

as paraffinic, aromatic, and naphthenic character of hydrocarbons. While Nuclear Magnetic Resonance spectroscopy (NMR) can detect different average chemical structures and compositions in petroleum samples.

The detailed information of composition in petroleum fractions such as PONA (paraffins, olefins, naphthenes, and aromatics), PNA (paraffins, naphthenes, and aromatics), and PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics) is often required. It is already known that petroleum fractions are free of olefins, therefore, the compositional analysis would be expressed as PINA, or in case that paraffins and isoparaffins are combined in one fraction, simply as PNA composition. This type of analysis, in general, is used for light and narrow boiling range petroleum products such as distillates from atmospheric crude distillation units. In turn, the detailed compositions on the molecular level of oil fractions can be obtained by applying chromatography methods in combination with mass spectrometry.

In the framework of this review, only advanced analytical techniques consisting of advanced chromatography methods coupled with mass spectrometry are discussed.

3 Advances in analytical tools for complex petroleum mixtures

Despite research related to alternative resources, petroleum is still of substantial importance for the production of energy, as well as the precursor for materials, like plastics and medicines.¹²⁶ During the last decade, the progress in analytical chemistry has been enormous for petroleum fractions and continuous research efforts have led to more advanced chromatographic techniques resulting in a more detailed mixture characterization. Researchers continue striving to improve the separation and detection techniques, therefore, in the field of the analysis of heavy petroleum fractions significant progress has been made.¹²⁷⁻¹³⁵

An in-depth compositional characterization of petroleum crude oil can be obtained by applying new techniques and the advancement of existing analytical tools. Chromatographic techniques (GC and LC) coupled to MS have played a dominating role in revealing thousands of different species and even some of the isomers present in petroleum and petrochemical samples.

Over the years, huge progress has been made on one-dimensional (1D) GC which can separate between 100 and 150 peaks in one run. However, this technique is insufficient for the separation of the individual constituents in complex samples (*i.e.* crude oils and petrochemical products). Hence, the introduction of the two-dimensional (2D) GC has proven its superiority over 1D-GC. Although the comprehensive two-dimensional GC × GC can be used to provide a detailed specification of saturates and aromatic hydrocarbons, this technique is only suitable to characterize fractions having medium-boiling components. Alternatively, $LC^{15, 136-139}$ has been applied to separate the components in the very high-boiling and non-boiling petroleum fractions beyond the reach of GC × GC by class or group level based on their polarity, hydrophobicity, and bonding affinities. LC is most used for the analysis of crude oil with 80 % heavy oil fraction that needs temperatures higher than 350 °C to vaporize.¹⁴⁰

Nevertheless, these chromatography techniques cannot provide individual molecular-level information due to their limitations in terms of solubility and low peak resolution. Frequently, gas or liquid chromatographic separation is applied to reduce the sample complexity first, followed by MS to identify the chemical compositions in samples. Given the fact that MS can distinguish different ions based on their different mass-to-charge ratio (m/z) by secondary measurement methods such as flight time, flight path, or resonance frequency. Molecules are first ionized in an ion source and then ions are separated by a mass analyzer. Lastly, ions are detected with an ion detector together with a computer data system.

MS is composed of a considerable number of different assemblies of ionization methods, mass analyzers, and detectors. In which ionization methods play an important role in the successful application of MS. No one ionization method is optimal for the total spectrum of oil samples and therefore, depending on the nature

of analytes, a suitable ionization mode can be applied. For example, an APPI¹⁴¹⁻¹⁴⁵ should be applied to access the aromatic compounds and an ESI can be used for polar components, etc.

The ionization techniques can be divided into three groups: (1) gas-phase techniques, including EI and CI due to thermal evaporation of the sample performed before the ionization; (2) liquid-phase techniques, consisting of ESI, APPI, and APCI in which spraying of the solution with the sample under analysis occurs instead of evaporation; (3) desorption techniques, including LDI and MALDI, in which the object under analysis is sublimated by laser radiation pulses from a condensed (generally solid) phase.¹⁴⁶ Another way to divide ionization methods is based on ion source operation pressure: 1) Conventional ionization techniques operate in high vacuum (EI, CI, MALDI, FI, and FDI) from which EI, CI, FI, and FDI use high temperatures; 2) Atmospheric pressure ionization methods include ESI, APCI, APPI, APLI, and AP-MALDI.

The newest, powerful, and most fast progressing MS ionization field is Ambient Ionization (AI), which can transfer analytes directly from their natural environments to a high vacuum system of mass spectrometers. AI has been mainly used in the petroleum field to analyze the saturated hydrocarbon mixtures, petroleum model-molecule compounds (ellipticine, perylene, diphenylbenzoquinoline, benzo(ghi)perylene, coronene, rubrene, 9-phenylanthracene, benzo[c]benzofuran, benzo- [c]benzothiophene, and the hormone estradiol; 5,10,15,20- tetraphenyl-21H,23H-porphine, 5,10,15,20-tetraphenyl21H, 23H-porphine vanadium (IV) oxide, and fullerene), naphthenate deposits, some petroleum constituents (hydronaphthalenes, thiophenes, alkyl-substituted benzenes, pyridines, fluorenes, and polycyclic aromatic hydrocarbons), and characterization of crude oil samples, and their respective distillation cuts. Progression and possible non-polar sample capability of AI makes it a really interesting ionization method in petroleomics.¹⁴⁷

While ionization methods are techniques to attain gas-phase ions, mass analyzers are responsible for distinguishing different ions based on their mass-to-charge (m/z) values after ionization. Many types of mass analyzers have been introduced, of which four mass analyzers are suitable with complex and heavy petroleum samples, including Time of Flight Mass Analyzers (TOF), Magnetic Sector Mass Analyzers, Electrostatic Sector Mass Analyzers, Fourier Transform Ion Cyclotron Resonance (FT-ICR) analyzers, and Orbitrap analyzers. Quadrupole and ion traps having low resolution can also be used in petroleum analysis such as crude, lubricant, and base oil samples. Some factors should be considered when different analyzers are used, including accuracy, resolution, mass range, scan speed, measurement speed, maintenance requirements, and price. Mass spectrometry has achieved significant improvements to expand the range of analytical samples, however, no mass analyzer is superior in all aspects as well as compatible with all ionization methods.

Analysis of petroleum samples is not straightforward in terms of selecting a suitable ionization method and mass analyzer. Depending on sample type (e.g. molecular weight range, complexity, and polarity), a suitable ionization method will be applied. **Table 2** presents an overview of different ionization methods published for analyzing the petroleum samples.

Ionization method	Application	Notes
EI (Electron Ionization)	Conventional method	High fragmentation, difficult to identify the heavy molecules
Soft- EI	Petroleum heavy fractions; ¹⁴⁸⁻¹⁵⁰ Petrole fuels ^{151, 152}	Even Fragmentation is not prominent, but the resulting spectra is still complex. Significant ion dissociation with labile hydrocarbons.

Table 2. Overview of ionization methods and their application in petroleum samples

Cold-EI	Linear alkanes up to C70; ¹⁵³ Jet fuel. ¹⁵¹	Intensity of molecular ions are enhanced compared to normal EI.
Soft-Cold-EI	Linear alkanes (C12-C40); ¹⁵⁴ Squalane, C ₂₄ H ₅₀ ¹⁵⁵	Soft-Cold EI retains molecular ion reproducibly. Fragmentation is smaller compared to soft or cold EI method.
FI/FDI (Field Ionization/Field Desorption Ionization)	Saturated hydrocarbon and the low-mass hydrocarbon polymers; ¹⁵⁶ Sewing machine oil; ¹⁵⁷ Sulfur/coker vacuum gas oil ¹⁵⁸	
FI	Petroleum based waxes; ¹⁵⁹ Diesel fuel; ^{123, 160-163} Broad range of nonpolar hydrocarbons; ^{164, 165} Base oils; ¹⁶⁶ Olefins; ¹⁶⁷ Heavy hydrocarbons; ^{168, 169} Petroleum heavy fractions ¹⁷⁰⁻¹⁷³	Much petroleum studies already from 1960-1970, a laborious method.
FDI	Petroleum heavy fractions ¹⁷⁴⁻¹⁷⁶	
AI (Ambient Ionization)	Condensed aromatics; ¹⁴⁷ Paraffinic samples; ^{147, 177} Lubricant oils ¹⁷⁸⁻¹⁸¹	Can be applied for nonpolar and polar compounds, without sample preparation step.
APPI (Atmospheric Pressure Photo Ionization)	Base oils; ¹⁸² Petroleum oil; ¹⁸³ SARA fractions of crude oil; ^{184, 185} Canadian Athabasca bitumen middle distillate; ¹⁸⁶ Asphaltenes; ^{27, 187-197} N-, S-, and O-containing compounds in petroleum (heavy) fractions; ^{25-28, 55, 129, 175, 198-224} Polychlorinated naphthalenes (PCNs); ²²⁵ Polycyclic aromatic hydrocarbons (PAHs) ^{207, 226-229}	Isobaric ions require high resolution. More suitable for nonpolar samples than APCI and ESI. Can quantitatively measure polar fractions and nonpolar fractions simultaneously. Too high ionization potential can be a problem with certain samples and may require dopant and low ionization effiency. ²³⁰ (References from 2015-2021).
APCI (Atmospheric Pressure Chemical Ionization)	Lubricant base oils; ¹⁶⁶ Asphaltene fractions; ^{193,} ^{194, 231-234} Bitumen; ²³⁵ S-containing compounds; ^{28,} ^{182, 232, 236-239} polychlorinated naphthalenes (PCNs); ²²⁵ polycyclic aromatic hydrocarbons (PAHs); ^{28, 78, 226, 233, 240} Cycloalkanes; ^{78, 241, 242} Steroids compounds; ²⁴³ N-, O-containing compounds ^{28, 206, 232, 244, 245}	More suitable for non-polar samples than ESI but less than APPI. Thermal degradation and fragmentation are problems. Limited suitability with labile and heavy samples due to the vaporization process. (References from 2015-2021).
ASAP (Atmospheric Solid Analysis Probe) APGC (Atmospheric Pressure Gas Chromatography) DART (Direct Analysis in Real Time)	Paraffins, isoparaffins, and alkylbenzenes; ^{147, 246} S-containing compounds ¹²⁹	
LDI	Pitch and petroleum vacuum residue; ⁷ Asphaltenes; ^{192, 247-250} sulfur-rich heavy oil	Aggregation and fragmentation occur if mass above 500 Da. ²³⁰

(Laser Desorption Ionization)	fractions; ²⁵¹ N-, S-, and O-containing compounds in petroleum heavy fractions ²⁵²	
L ² DI	Asphaltenes; ²⁵³ Asphaltene molecule distributions ^{254, 255}	Aggregation
MALDI (Matrix Assisted Laser Desorption Ionization)	Oil resins; ²⁵⁶ Molecular structures of asphaltenes; ⁷ Vanadyl porphyrins; ^{257, 258} Polycyclic aromatic hydrocarbons (PAHs); ^{58, 259- ²⁶³ Molecular weight distribution of kerogen²⁶⁴ Heavy Oils and Vacuum Residua;^{7, 51, 265-269} Asphaltenes;^{7, 270-272} Petroleum Porphyrin;^{7, 55, 273} Biofuel Research;⁷ Molecular weight of pitches;^{263, 274-283} Naphthenic acids;^{284, 285}}	Well suited to heaviest samples. Aggregation, low shot-by-shot reproducibility, sample preparation requirements. ²³⁰ (References from 2015-2021).
LIAD (Laser Induced Acoustic Ionization)	LIAD/CIMn- (H2O)+ CI with base oils; ²⁸⁶ LIAD with saturated heavy petroleum products and intermediates; ²⁸⁷ Petroleum distillates; ²⁸⁸ Petroleum aromatics; ²⁸⁹ AP/LIAD-CI saturated hydrocarbon mixtures; ²⁹⁰ LIAD/EI with asphaltenes and asphaltene model compounds; ²⁹¹ LIAD-APCI non-polar hydrocarbons ²⁹²	LIAD/EI could detect from complex petroleum sample without significant fragmentation, limited study.
APLI	Polycyclic aromatic hydrocarbons (PAHs); ^{34, 228, 293-295} Aromatic, sulfur-, and oxygen-compounds; ³³	Suitable for polyaromatic compounds
ESI (Electrospray Ionization)	Vanadium compounds; ²⁹⁶ Non-polar aromatic compounds; ²⁹⁷ thiols; ²⁹⁸⁻³⁰⁰ Sulfides; ^{301, 302} N-, S-, and O-containing species; ^{129, 198, 205, 207, 212, 214, 221, 224, 236, 244, 303-347 Porphyrins;³⁴⁸⁻³⁵² Molecular structure of Asphaltenes;^{185, 216, 353, 354} naphtenic acids;^{284, 285, 355-360} petroleum sulfonates;³⁶¹⁻³⁶⁴ acidic compounds;^{213, 215, 216, 323, ^{362, 365-372} Polycyclic aromatic hydrocarbons (PAHs);^{226, 373} Naphthenoaromatics;³⁷⁴}}	Suitable, common method for polar samples Limited suitability for nonpolar samples with HCOONH4 as ionization promoter (References from 2015-2021).
Nano-ESI	Bitumens, heavy vacuum gas oils, and light and heavy distillates; ³⁷⁵	Nonpolar samples, mainly for automated measurement and very limited study.
EASI (Easy Ambient sonic- Spray Ionization)	Gasoline; ³⁷⁶ Biodiesel ^{376, 377}	Favorable for ionization of the more polar compounds, need only small amount of sample
DESI (Desorption Electrospray Ionization)	Saturated hydrocarbons; ³⁷⁸ Lubricant oil matrix; ³⁷⁹ petroleum crude oil; ¹⁴⁷ Nano-DESI petroleum crude oil ³⁸⁰	Rapid and sensitive analysis of a broad range of compounds, without sample preparation step. Some disadvantages of this technique are: efficiency of ionization and droplet formation might be affected by matrix; measurement automation and reproducibility problems; and difficulties in quantification and complex data processing ⁴⁰²

Each ionization technique possesses advantages as well as disadvantages, thus sometimes multiple techniques can be applied to complement each other. The limitation of EI/CI/APCI ionization methods is that they require thermal evaporation and this possibly results in thermal degradation limiting heavy molecular weight samples. ESI mainly is used for polar components in petroleum samples, but also few studies have been reported using this technique for nonpolar samples.^{77, 146} Furthermore, ESI and MALDI are used preferably for ionization of acidic and basic compounds, and nonpolar molecular ions are hardly detected.²⁸⁷ MALDI and other LDI methods often suffer from sample aggregation during measuring heavy petroleum samples.³⁸¹ APPI couples preferably with high-resolution mass analyzers such as FT-ICR or Orbitrap mass analyzer due to the production of isobaric ions when applying this technique. Besides, the FI/FDI methods suffer from laborious measurement practice and reproducibility could be an issue. Field ionization and desorption methods are most suited to quantitative measurements of base oil fractions and are mostly coupled to FT-ICR.

Not only ionization methods, but mass analyzer also plays an important role in selecting a suitable method for analysis of a specific sample. **Table 3** will present a comparison of typical performance parameters of mass analyzers.

Mass analyzer	FT-ICR	Orbitrap	Quadrupole	Sector	TOF
Mass limit	30 000	50 000	4000	20 000	>1 000 000 10 000
Resolution	>1 000 000	450 000	<4000	100 000	5 000 80 000
Accuracy	<1 ppm	<3 ppm	100 ppm	<5 ppm	<5 ppm <50 ppm
Ion sampling	Pulsed	Pulsed	Continuous	Continuous	Pulsed
Advantages	Costly, high resolution, suitable for tandem mass spectrometry	Quite costly, high resolution, suitable for tandem mass spectrometry	Small size, reasonable price, tolerant of high pressure, suitable for electrospray	Quite costly, capable of high resolution, capable of exact mass, medium mass range, reliable	Highest mass range, very fast scan speed, reasonable cost, suitable for pulsed ionization method (i.e. MALDI)
Disadvantages	High vacuum required, low temperature	High vacuum required, low aptitude with	Mass range limited to about 3 000 m/z, poor	Not tolerant of high pressures, Expensive,	Low resolution linear but

Table 3: Comparison of typical performance parameters of mass analyzers^{230, 382, 383}

	required, massive size	low and very low energy ions	adaptability with pulsed ionization methods (i.e. MALDI)	massive size, relatively low scanning	suitable for reflector TOF
Suitability	Heavy and nonpolar base oil type samples	Heavy and nonpolar base oil type samples	Commonly coupled to GC for light petroleum samples.	Moderate heavy samples	Commonly coupled to GC for light petroleum samples, more accurate resolution than quadrupole.

The application of mass spectrometry in the petroleum field is enormous, the following parts will only provide recent advances in gas chromatography and liquid chromatography coupled to MS, inductively coupled plasma mass spectrometry, and Fourier transform ion cyclotron resonance mass spectrometry with different ionization sources.

3.1 Gas Chromatography coupled to Mass Spectrometry (GC - MS)

In the respect of separation capability, GC can be generally categorized into one-dimensional (1D-GC) and comprehensive two-dimensional gas chromatography (GC \times GC). In the past decade, GC \times GC appeared as an important analytical tool and an excellent choice for studying the composition of complex samples. This powerful separation technique was invented in the early 1990s by Phillips.³⁸⁴ A schematic of the GC \times GC setup is shown in Figure 3. It can be seen that the first column is housed in one oven while the second column is in a separate one. The reason for it is to enable more temperature control.





In order to maintain the separation obtained in the first-dimension column, the narrow fractions trapped by the modulator and released in the 2^{nd} column should be no wider than one-quarter of the peak widths in the 1^{st} dimension.^{386, 387} The term "comprehensive" refers to this aspect of comprehensive GC × GC. As a consequence of this characteristic, and since the modulation time must equal the 2^{nd} dimension run time, the separation on the second column should be very fast, in the order of 2 to 8 seconds. This will render very narrow 2^{nd} dimension peaks and demand of correspondingly fast analyzers such as a Time-of-Flight Mass Spectrometer (TOF-MS).

Recent publications are mainly focused on the coupling of GC × GC to primary detection, *i.e.* TOF-MS³⁸⁸⁻³⁹¹ and qMS, which has rapidly become the preferred option. Today, a majority of all published studies are devoted to applications such as environmental, ³⁹²⁻³⁹⁴ biological³⁹⁵⁻³⁹⁷, and petrochemical analysis.^{88, 103, 385, 386, 389, 398-402}

Until today, GC × GC - MS is applied to petrochemical samples such as gasoline, $^{91, 92, 403-408}$ jet fuels, $^{405, 409}$ light gas oils, $^{410, 411}$ diesel fuels, $^{91, 99, 100, 404, 406}$ crude oils, $^{95, 406, 412}$ non-aromatic solvents, 95 kerosene, $^{95, 410, 413}$ wash oils, 414 biomarkers, $^{415-417}$ and environmental pollutants in soil and sediments, $^{404, 416, 418-422}$ in water 423 .

Wang et al.¹⁶¹ have performed a two-dimensional separation (GC × MS) study of diesel composition and compared it with the GC × GC technique. A GC × MS chromatogram is shown in Figure 4. The advantage of GC × MS is the class separation of the compounds. It can be noticed that the groups within a compound class are well-separated based on their parent masses. The specific element-containing compound distribution can be generated through the extraction of specific mass groups due to the exact mass operation. For qualitative analysis, GC × MS is a technique where one experiment may generate a wide range of information. Furthermore, it may also perform quantitative analysis when appropriate response factors for various compound groups are available. The power of two/multiple dimensional separations started exposing its advantages for complex mixture analysis. Still, the biggest challenge is a combination of two or more different analytical techniques to study a specific complex separation problem. With the utilization of GC × MS advances in analytical techniques are pushed one step forward.



Figure 4. $GC \times MS$ chromatogram of a refinery stream boiling at diesel temperature range.¹⁶¹

Further on, the ASTM Committee D2 has developed a heart-cutting gas chromatography (GC-GC) method for the analysis of methanol in crude.⁴²⁷ GC-GC has experienced a revival due to the advanced technology of modern columns and instruments.⁴²⁸ Dumont et al.⁴²⁹ have published a paper on heart-cutting GC-GC combined with isotope ratio mass spectrometry (IRMS). There is a limited number of publications on this topic, as there are no commercially available instruments. Therefore, it seems that combining these techniques is quite challenging since GC needs to be coupled to reactors. GC-GC may be combined with IRMS via combustion or HTC reactors but it should be taken into account the specific flow settings, back-flush options for reactor regeneration, etc.

Ruiz-Guerrero et al.⁴³⁰ have compared GC × GC coupled to a Sulfur Chemiluminescence Detector (SCD) with standard methods, which are employed in the petroleum industry, such as X-ray fluorescence (XRF), conventional GC-SCD, and High-Resolution Mass Spectrometry (HRMS) for the speciation of S-containing compounds in middle distillates. The results achieved in their study were found to be similar to the total sulfur content obtained by the standard XRF method. On the other hand, the comprehensive technique has an advantage of an excellent separation of the classes, which makes GC × GC a preferred tool for the quantification of individual components.

HRMS^{170, 231, 431-434} is considered an important analytical technique due to its ability to determine structure and elemental composition of crude oil constituents. When assisted by MS/MS techniques, structural information can be obtained from mass sequences and trends associated with heteroatom content. Moreover, use of FT-ICR, orbitrap, and TOF-MS in a combination with ionization techniques, such as ESI, APPI, APCI, or laser LDI, has largely contributed to the recent advances in petroleum science. Beside these advances, recently a novel circular design based on traveling-wave ion mobility spectrometry (IMS) has been presented. Researchers⁴³⁵ mentioned that this so-called cyclic IMS (cIMS) may overcome practical limitations in scaling drift tube devices. Ruger et al.⁴³⁴ have explored the capabilities of cIMS-HRMS for analysis of petrochemical samples with high isobaric and isomeric complexity. They mentioned that the cIMS-HRMS was capable to address different core structural motives of PAHs and heterocycles.

3.1.1 GC- Field Ionization Mass Spectrometry (GC-FIMS)

Field ionization is considered a soft ionization technique in which a relatively small quantity of internal energy is supplied to the molecule. Compared to electron impact ionization, field ionization may afford substantially reduced fragmentation and much higher molecular ion intensities. Therefore, it can assign the peaks to different types of compounds straight forward and allow the quantitation based on the intensity of molecular ions. For example, Shiraishi and co-workers have investigated the molecular mass distributions of sulfur-containing hydrocarbon types in a vacuum gas oil (VGO) before and after desulfurization by means of FI-MS. The result showed that substituted tetrahydro-dibenzothiophenes appeared to be the most refractory compounds with respect to desulfurization.¹⁷¹

Field ionization mass spectrometry is a valuable technique in combination with gas chromatography for analyzing complex mixtures, particularly fossil fuels. The combination of chromatographic separation and mass spectrometric resolution in GC-FIMS analysis have enabled accurate mass measurements nominally isobaric ions having different elemental compositions.^{436, 437} Briker et al.¹²³ have developed a modified GC-FIMS method for detailed hydrocarbon type determination of diesel fuel. Diesel fuels were analyzed by GC-FIMS, and the calculated hydrocarbon type composition profile was compared with that determined by other standard techniques. Selected ion chromatograms demonstrated the separation of isoparaffins and normal paraffins in typical diesel fuels.¹²³ The results for total saturates, aromatics, monoaromatics, and polyaromatics obtained by GC-FIMS have shown a good correlation with the results achieved from LC separation and SFC. Furthermore, analysis of a gasoline sample showed excellent agreement between GC-FIMS and detailed hydrocarbon analysis, or PIONA for total cycloparaffin content, and reasonable agreement for iso- and normal paraffin contents. Experiments with internal standard verified the accuracy of the GC-FIMS method for selected hydrocarbon isomers.¹²³

It should be noticed that GC-FIMS can give more information than GC-MS because it provides information about n-paraffin and isoparaffin contents, as well as each compound type which is reported by carbon number. Qian et al. have reported on the online coupling of supercritical chromatography (SFC) with FI-TOFMS, in parallel with UV absorption detection and flame ionization detection (FID), for quantitative molecular analysis of petroleum middle distillates.⁴³⁸ Recently, the method has been extended by the incorporation of a silver-loaded silica column for the analysis of olefins in catalytically cracked products.¹⁶⁷ Further, this group has also applied the concept of Kendrick mass defect (KMD) in the analysis of catalytically cracked hydrocarbon products. They demonstrate that the KMD parameter may be treated as an independent analytical dimension that is orthogonal to nominal mass.⁴³⁹ In another study, this group also has described the use of nominal mass classes, accurate mass analysis, and Kendrick mass defect in conjunction with $GC \times GC$ separation to determine full chemical compositions in terms of hydrocarbons and sulfur-containing molecules across the whole carbon number range of vacuum gas oil distillates at the molecular level. In particular, all masses were first separated into nominal mass classes. Subsequently, KMD plots (KMD versus molecular weight) within each nominal mass class were generated for easy recognition of the homologs series. Then, KMD windows of identified homologs were then imposed to the 2DGC data for complete resolution and full accounts of petroleum molecules (petroleum types and carbon numbers).¹⁷⁰ Moreover, Wang and co-workers have reported a comparison of GC-FI-TOFMS with GC \times GC for the analysis of diesel fuel samples. A conclusion has been given that the two techniques are complementary to each other.¹⁶¹

To investigate the compositions of diesel fuels, Ogawa et al. have made an effort in optimum instrumental parameters for the FIMS analysis.¹⁶⁰ Using GC-FIMS, Ha et al.⁴⁴⁰ developed different methods for delumping detailed analytical information for the determination of the detailed molecular composition of middle-distillates. The authors have integrated PIONA and GC-FIMS results and determined an accurate and complete hydrocarbon-type distribution profile.

It can be concluded that field ionization is a preferable method for hydrocarbon analysis, proving by the number of recent reports on the mass spectrometric characterization of petroleum.

3.1.2 Comprehensive 2D Gas Chromatography coupled to Time-of-Flight Mass Analyzer ($GC \times GC$ -TOF-MS)

The use of chromatographic techniques prior to mass spectrometric detection is widely applied for the characterization of complex petroleum oils as shown earlier.⁴⁴¹ Among different chromatographic techniques, comprehensive gas chromatography $GC \times GC$ provides enhanced peak capacity and separating powers. Furthermore, time of flight mass spectrometry is often coupled to $GC \times GC$, due to its high resolution and high peak capacity, giving a powerful tool in the analysis of complex petroleum samples.

Many different ionization methods can be used for a time-of-flight-mass analyzer, in which Electron Ionization (EI) at 70 eV - a standard technique is often employed. By using the EI method, molecules can be identified based on analyzing their fragmentation mass spectra and matching them with a published EI MS library (NIST library).⁴⁴² Many publications have been reported using GC × GC-EI-TOF-MS for analyzing the aromatic components in the petroleum samples.⁴⁴³⁻⁴⁴⁵ In one of the scientific papers published by Hamilton et al.¹⁰² demonstrated the usefulness of GC × GC-EI-TOF-MS for the analysis of the feed and the product from the hydrocracker coal liquefaction process. This comprehensive approach successfully solved issues encountered when using traditional GC-MS. For example, n-alkanes and other saturates could be identified in more detail. Furthermore, the most desirable product fraction, which corresponds to naphtha or diesel fuel substitute could be analyzed. In a study published by von Mühlen et al.,⁴⁴⁶ the content of nitrogen-containing compounds has been identified in heavy gas oil fractions by GC × GC-EI-TOF-MS based on a separation strategy that incorporated a non-polar 1D column phase and 2D polar phase. The researchers applied a solid-liquid fractionation scheme for the separation of neutral and basic N-compounds prior to chromatographic analysis. In this way, they could identify 228 N-containing compounds, including

alkyl indoles, alkyl carbazoles, alkyl benzocarbazoles, alkyl quinolines, alkyl-indene pyridines, alkyl benzoquinolines, and alkyl dibenzoquinolines (Figure 5). The authors mentioned that 108 out of these 228 components were not present in the commercial MS library but according to retention times in the first and second dimension, analytical standard co-injection, and the structured pattern of the separation space with specific m/z values, they could identify all the compounds. Compared to the previous studies, it is obvious that MS can provide additional benefits for molecular identification. For example, $GC \times GC$ -EI-TOF-MS can provide additional analytical information over and above classically used retention times in 1D and 2D.



Figure 5. $GC \times GC$ -TOFMS 2D-color diagram (EIC mode) showing group-type separations of the neutral fraction of an HGO sample (left) and of the basic fraction (right), highlighting the region of elutions of nitrogen-containing compounds. (A) Alkyl-indoles from C0 to C3. (B) CC at the lower region of the TID corresponds to alkyl carbazoles from C0 to C12. (C) BC C corresponds to alkyl benzocarbazoles from C0 to C6. ⁴⁴⁶

Recently, Mostafapour et al. have proposed a combination of $GC \times GC$ -EI-TOF-MS with multivariate chemometric methods (e.g., N-way partial least squares) for identification of the most influential chemical components on the toxicity values of different aromatic oil fractions (fresh and weathered), with a potential to reduce the number of fractionation steps, which needed to obtain necessary chromatographic and mass spectral information.⁴⁴⁷ This approach was also used to investigate the presence of aryl hydrocarbon receptor agonist and androgen receptor antagonist in the fresh and artificially weathered samples of North Sea crude oil and residual heavy fuel oil.⁴⁴⁸

A comprehensive evaluation of ionic liquid (IL) columns for separation and identification of sulfur- and nitrogen-containing compounds in naphtha and diesel samples has been performed by using $GC \times GC$ -EI-TOF-MS. The use of an ionic liquid capillary column (sets DB-5MS/IL-59 and IL-59/DB-5MS) resulted in the detection of a higher number of sulfur compounds compared to the utilization of usual stationary phases such as DB-17. The IL-59/DB-5MS column combination provided better results for the analysis of nitrogen compounds, including a higher number of tentative identification of detected compounds and higher 2D chromatographic space occupation.⁴⁴⁹

In another study, Wang and his workers have reported the combination of GC \times GC-EI-TOF MS and electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enabled to identify and quantify the unique compounds in the DB301 condensate, involving a high abundance of diamondoid and ethanodiamondoid (1–2 cages) hydrocarbons. In addition, the dicyclic monoterpene pinane (*trans* and *cis* isomers) and aromatic amine fused with the pinane skeleton were also determined.⁴⁵⁰ Furthermore, ethanodiamondoids, pinanes, and aromatic amine were discovered for the first time in naturally occurring petroleum liquids.^{450, 451}

The use of GC \times GC coupled to a Flame Ionization Detector (FID) and a Time-Of-Flight Mass Spectrometer (TOF-MS) enabled to characterize for the first time two PFO's derived from naphtha (N-PFO) and vacuum gas oil (V-PFO). The result reveals that both samples are highly aromatic, with the H/C ratios lower than 1 and with a significant content of compounds with solubility characteristics typical for asphaltenes and coke. In addition, the dominant chemical family in both samples are diaromatics with a concentration of 28.6 and 27.8 for N-PFO and V-PFO, respectively.⁴⁵²

Although electron ionization at 70 eV is often hyphened with mass spectrometers, most molecules have significantly lower ionization energies, the mass spectra contain an abundance of small fragment ions, and the molecular ions are barely visible or absent. Therefore, many organic compounds, such as the isomeric alkane structures found in the unresolved complex mixture, are indistinguishable because they have similar mass fragmentation i.*e.* m/z 43, 57, 71, 85, 99.⁴⁵³ Alternatively, soft ionization can be applied using lower energy to ionize the compound, resulting in less fragmentation. As a result, the obtaining spectra contain a molecular ion in greater abundance and fewer, but more distinctive fragmentation ions that make the identification of specific isomers within oil samples was accomplished.¹⁷⁰ Alam and his co-workers have reported that the use of variable ionization time-of-flight mass spectrometry, ranging from 10 eV(lower ionization energy) to conventional 70eV EI allowed determining the structures of aliphatic and aromatic compounds in the unresolved complex mixture (UCM) of hydrocarbons isolated from a biodegraded crude oil.⁴⁵³

Several soft ionization techniques used in GC × GC-TOF-MS such as field ionization (FI)^{164, 170, 437, 439} and photon ionization (PI)⁴⁵⁴⁻⁴⁵⁸ for analysis of the petroleum has been successfully explored. GC × GC-TOF-MS coupled with multiple ionization methods, such as electron ionization, photon ionization, and chemical ionization has been evaluated for petroleum base oil analysis. The detailed structural elucidation of hydrocarbon classes including saturated branched alkanes, naphthenic, polycyclic, and aromatic compounds were implemented for the understanding of the complex molecular composition of base oils through evaluating the ionization mechanisms and extent of fragmentation for a wide range of molecules.¹⁵⁰

Recently, Borisov et al. have just published a short review using mass spectrometry for the analysis of crude oils and some oil refining products. In this review, the ionization techniques, as well as their application, were thoroughly discussed.⁷⁷

Table 4 presents the application of $GC \times GC$ -TOF-MS in the analysis of petroleum published in the period from 2015-2021.

Authors, publishing year	Application	Combined with other
		techniques

Cheng B et al 459 2015	Distributions of low molecular weight	
	alkylbenzenes (C-0-C-4) in 37 oils from three	
	hasing in China	
Li S E at al 460 2015	Saturated hydrocarbons (a.g. branched alkanes	
Li, 5. F., et al. , 2015	and naphthenes of low to medium molecular	
	weight) in crude oils	
	weight) in clude ons.	
Li S. E. at al 461 2015	Molecular compositions (paraffin hydrocarbons	
LI, S. F., et al. 7, 2015	wolcally and aromatics in particular 1.2	
	cycloarkanes and aromatics, in particular $1-5$	
	cyclic parantins with a short-chain arkyr gloup,	
	homologous socies) of unresolved complex	
	minimologous series) of unresolved complex	
Mastafanan S. et al 447 2015	Identification of the most influential abamical	
Mostarapour, S., et al, 2015	Identification of the most influential chemical	Multivariate chemometric
	components (alkyl substituted three- and four-	methods (N-way partial least
	ring aromatic hydrocarbons) on the toxicity	squares or N-PLS)
W 1462 001 F	Values of different fuel off fractions	
Wang, H. T., et al. 402, 2015	Identification and validation of	
	decahydronaphthalene isomers in crude oil and a	
	source rock extract sample.	
Zhang, W. F., et al. ⁴⁰³ , 2015	Distinguish the oil sources based on biomarkers	
	(tri-aromatic steroid (TAS) series)	
Weng, N., et al., 464 2015	Aromatic biomarkers and aromatic	GC-MS
	hydrocarbons in heavy oil	
Zhu, G. Y., et al., ⁴⁶⁵ 2015	n-Alkanes from $nC(3)$ to $nC(34)$ and in	
	diamondoid hydrocarbons in condensate	
Zhu, G. Y., et al., ⁴⁶⁶ 2015	Adamantane compounds, diamantane	
	compounds, and sulphur-containing compounds	
	(including the benzothiophene series, and the	
	(including the benzothiophene series, and the dibenzothiophene series) in condensate	
Araujo, B. Q., et al. ⁴⁶⁷ , 2016	(including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon	
Araujo, B. Q., et al. ⁴⁶⁷ , 2016	(including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils	
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016	(including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in	
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample 	
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen 	GP-MSE
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and 	GP-MSE (Gas Purge Microsyringe
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil 	GP-MSE (Gas Purge Microsyringe Extraction)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel 	GP-MSE (Gas Purge Microsyringe Extraction)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel 	GP-MSE (Gas Purge Microsyringe Extraction)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Oiao, L., et al., ⁴⁷² 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al. ⁴⁶⁸ 2016	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al. ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics diaromatics and 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591) GC × GC - FPD (Elama Photometric Dataction)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils Hydrocarbons and sulfur compounds in thermal oxidation of jet fuels 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591) GC × GC – FPD (Flame Photometric Detection)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017 Laakia, J., et al., ⁴⁷⁶ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils Hydrocarbons and sulfur compounds in thermal oxidation of jet fuels 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591) GC × GC - FPD (Flame Photometric Detection)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017 Laakia, J., et al., ⁴⁷⁶ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils Hydrocarbons and sulfur compounds in thermal oxidation of jet fuels tricyclic terpanes, steranes, tetracyclic terpanes, pentacyclic terpanes, and pentacyclic terpanes in the Bravilian ocude oils 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591) GC × GC – FPD (Flame Photometric Detection)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017 Laakia, J., et al., ⁴⁷⁶ 2017	 (including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils Hydrocarbons and sulfur compounds in thermal oxidation of jet fuels tricyclic terpanes, steranes, tetracyclic terpanes, pentacyclic terpanes, and pentacyclic terpanes in the Brazilian crude oils 	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591) GC × GC – FPD (Flame Photometric Detection)
Araujo, B. Q., et al. ⁴⁶⁷ , 2016 Cappelli Fontanive, F., et al., ⁴⁴⁹ 2016 Gao, X. B., et al., ⁴⁶⁸ 2016 Parsons, B. A., et al., ⁴⁶⁹ 2016 Ristic, N. D., et al., ⁴⁷⁰ 2016 Potgieter, H., et al., ⁴⁷¹ 2016 Qiao, L., et al., ⁴⁷² 2016 Zhang, W. F., et al., ⁴⁶⁸ 2016 Chattopadhyay, K., et al., ⁴⁷³ 2017 Jennerwein, M. K., et al., ⁴⁷⁴ 2017 Kulsing, C., et al., ⁴⁷⁵ 2017 Laakia, J., et al., ⁴⁷⁶ 2017 Hu, S. Z., et al., ⁴⁷⁷ 2018	(including the benzothiophene series, and the dibenzothiophene series) in condensate Steranes in branched-cyclic hydrocarbon fractions of crude oils Sulfur-, Nitrogen-containing compounds in Diesel and naphtha sample Diamondoid series, pyrrolic nitrogen compounds and biomarkers such as terpane and sterane series in crude oil Aromatic species, alkenes and alkynes in diesel fuel Nitrogen-Containing Compounds in shale oil Cyclic/olefinic structures in complex petrochemical streams Chlorinated paraffins in sediments Diamondoids in crude oil samples Hydrocarbon class composition (paraffins, naphthenes, monoaromatics, diaromatics, and polyaromatic hydrocarbons) and trace level of benzene, toluene, ethylbenzene, and xylene in Raffinate Column Bottom Separation of carbon numbers between C-10 and C-60 in crude oils Hydrocarbons and sulfur compounds in thermal oxidation of jet fuels tricyclic terpanes, steranes, tetracyclic terpanes, pentacyclic terpanes, and pentacyclic terpanes in the Brazilian crude oils	GP-MSE (Gas Purge Microsyringe Extraction) GC × GC - NCD GP-MSE HPLC (ASTM D6591) GC × GC – FPD (Flame Photometric Detection)

Liang, Z. R., et al., ⁴⁷⁸ 2018	Semi-volatile organic compounds (alkane	
	species) within engine emissions derived	
	lubricants	
Lin, C. H., et al., 479 2018	Polyaromatic hydrocarbons in pretreatment of	NMR
· · · ·	slurry oil	
Vale, D. L., et al., ⁴⁸⁰ 2018	Property prediction of crude oil	N-PLS
Vanini, G., et al., 481 2018	alkanes, aromatics, and oxygen-, nitrogen- and	ESI(-)-FT-ICR MS
	oils	
Walters, C. C., et al., 482 2018	Biomarker analysis of saturated hydrocarbon	$GC \times GC$ coupled to FID and
	fractions.	TOF-MS (EI/FI)
Zhu, G., et al., 451 2018	Ethanodiamondoids in petroleum (ZS1C	
Jannarwain M at al 483 2010	Quantification of aromatics and paraffins in	
Jenner wenn, WI., et al., 2019	middle distillates	
Scarlett, A. G., et al., 484 2019	Molecular fossil biomarkers (diamondoid	
	hydrocarbons, demethylated hopanes and	
	secohopanes, mono- and tri-aromatic steroid) in	
Sec. 1. 485 2010	degraded oils	
Scarlett, A. G., et al., ³⁰² 2019	the maltene fractions	
Zhang, Z. Y., et al., 486, 487 2019	Diamondoids in condensate oil samples	
Ljesevic, M., et al., ⁴⁸⁸ 2019	Polycyclic aromatic hydrocarbons (PAHs) from	
	petroleum and fossil fuels	
Kafer, U., et al., ⁴⁸⁹ 2019	Detailed Chemical Characterization of Bunker	DIP-, and TGA-HRTOFMS
Giri A et al ¹⁵⁰ 2019	Compositional elucidation of heavy netroleum	GC × GC-EI/PI/CI/EI-TOEMS
	base oil	
Boswell, H. A., et al., ⁴⁴² 2020	Characterization of base oils through thermal	
	and flow modulators	
	Nanhthenic acids in oils	
Bowman, D. T., et al., 490 2020		
Bowman, D. T., et al., ⁴⁹⁰ 2020 Gieleciak, R., et al., ⁴⁹¹ 2020	Sulfur-containing hydrocarbons in the bitumen-	$GC \times GC$ -TOFMS/SCD/FID, SARA fraction
Bowman, D. T., et al., ⁴⁹⁰ 2020 Gieleciak, R., et al., ⁴⁹¹ 2020 Karakhanov, E., et al., ⁴⁹² 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of	GC × GC-TOFMS/SCD/FID, SARA fraction
Bowman, D. T., et al., ⁴⁹⁰ 2020 Gieleciak, R., et al., ⁴⁹¹ 2020 Karakhanov, E., et al., ⁴⁹² 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions	GC × GC-TOFMS/SCD/FID, SARA fraction
Bowman, D. T., et al., ⁴⁹⁰ 2020 Gieleciak, R., et al., ⁴⁹¹ 2020 Karakhanov, E., et al., ⁴⁹² 2020 Mohler, R. E., et al., ³³⁷ 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS
Bowman, D. T., et al., ⁴⁹⁰ 2020 Gieleciak, R., et al., ⁴⁹¹ 2020 Karakhanov, E., et al., ⁴⁹² 2020 Mohler, R. E., et al., ³³⁷ 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS
Bowman, D. T., et al., ⁴⁹⁰ 2020 Gieleciak, R., et al., ⁴⁹¹ 2020 Karakhanov, E., et al., ⁴⁹² 2020 Mohler, R. E., et al., ³³⁷ 2020 Spaak, G., et al., ⁴⁹³ 2020 Tong, R. L., et al., ⁴⁹⁴ 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Ware M., et al. 459 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel	$\begin{array}{c} GC \times GC\text{-TOFMS/SCD/FID,}\\ SARA \ fraction \end{array}$ Orbitrap ESI-MS $\begin{array}{c} GC\text{-MS,} \ ^1\text{H-NMR, and FTIR} \\ GC \times GC \times GC \ -\text{TOFMS} \end{array}$
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020	Naphtheme actus in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Lai, T. T., et al., 341 2020	Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum ras oil	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC - TOFMS FTIR FT-ICR MS
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 492 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 494 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Lai, T. T., et al., 496 2020 Zhang Z, Y, et al. 497 2020	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR FT-ICR MS GC-MS
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 492 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Lai, T. T., et al., 497 2020 Zhang, Z. Y., et al., 497 2020	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR FT-ICR MS GC-MS
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 494 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 450 2020 Lai, T. T., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR FT-ICR MS GC-MS
Bowman, D. T., et al., 491 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 492 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Lai, T. T., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil Diamondoids and ethanodiamondoids in crude	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR FT-ICR MS GC-MS
Bowman, D. T., et al., 491 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Lai, T. T., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020 Zhu, G. Y., et al., 498 2020 Erança D. et al. 500 2021	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil Diamondoids and ethanodiamondoids in crude oil	$GC \times GC \text{-TOFMS/SCD/FID},$ $SARA \text{ fraction}$ $Orbitrap ESI-MS$ $GC-MS, ^{1}H-NMR, \text{ and FTIR}$ $GC \times GC \times GC \text{ -TOFMS}$ $FTIR$ $FT-ICR MS$ $GC-MS$ $HT_{C}C \times GC \text{ - FID}$
Bowman, D. T., et al., 491 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 493 2020 Trinklein, T. J., et al., 494 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Lai, T. T., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020 Zhu, G. Y., et al., 499 2020 Franca, D., et al., 500 2021	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil Diamondoids and ethanodiamondoids in crude oil Chemical characterization of Brazilian pre-salt oils.	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC -TOFMS FTIR FT-ICR MS GC-MS HT-GC × GC - FID
Bowman, D. T., et al., 490 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 450 2020 Xu, J. J., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020 Zhu, G. Y., et al., 498 2020 Zhu, G. Y., et al., 500 2021 Jencik, J., et al., 501 2021	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil Diamondoids and ethanodiamondoids in crude oil Chemical characterization of Brazilian pre-salt oils. Evaluation of the fuel properties of Fischer-	$\begin{array}{c} GC \times GC \text{-TOFMS/SCD/FID,} \\ SARA fraction \\ \end{array} \\ \hline \\ Orbitrap ESI-MS \\ \hline \\ GC-MS, ^1H-NMR, and FTIR \\ \hline \\ GC \times GC \times GC - TOFMS \\ \hline \\ FTIR \\ \hline \\ FT-ICR MS \\ \hline \\ GC-MS \\ \hline \\ HT-GC \times GC - FID \\ \hline \\ \\ ^1H-NMR, FTIR \\ \end{array}$
Bowman, D. T., et al., 491 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 492 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 496 2020 Xu, J. J., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020 Zhu, G. Y., et al., 500 2021 Jencik, J., et al., 500 2021	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil Diamondoids and ethanodiamondoids in crude oil Chemical characterization of Brazilian pre-salt oils. Evaluation of the fuel properties of Fischer- Tropsch diesel blends with conventional diesel	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC - TOFMS FTIR FT-ICR MS GC-MS HT-GC × GC - FID ¹ H-NMR, FTIR
Bowman, D. T., et al., 491 2020 Gieleciak, R., et al., 491 2020 Karakhanov, E., et al., 492 2020 Mohler, R. E., et al., 337 2020 Spaak, G., et al., 493 2020 Tong, R. L., et al., 494 2020 Trinklein, T. J., et al., 495 2020 Wang, M., et al., 496 2020 Xu, J. J., et al., 496 2020 Zhang, Z. Y., et al., 497 2020 Zhu, G. Y., et al., 498 2020 Zhu, G. Y., et al., 500 2021 Jencik, J., et al., 501 2021 Jiao, S. H., et al., 502 2021	Naphthetic actas in ons Sulfur-containing hydrocarbons in the bitumen- derived gas oi activity of sulfide catalysts in hydrotreating of oil fractions Oxygen-containing organic compounds in groundwater at a crude oil spill site Diamondoids and semi-volatile aromatics in oil/condensate samples Alkanes, aromatics, N-, O-containing compounds, and polyheteroatomic compounds in distilates jet fuel Comprehensive Molecular Compositions of DB301 Crude Oil Polycyclic aromatic compounds in Carboniferous-Permian coaly source rocks Nitrogen-containing compounds in the vacuum gas oil Diamondoids and ethanodiamondoids in the GT1 oil Gas Invasion on the Composition of Crude Oil Diamondoids and ethanodiamondoids in crude oil Chemical characterization of Brazilian pre-salt oils. Evaluation of the fuel properties of Fischer- Tropsch diesel blends with conventional diesel Sequential pretreatments of an FCC slurry oil	GC × GC-TOFMS/SCD/FID, SARA fraction Orbitrap ESI-MS GC-MS, ¹ H-NMR, and FTIR GC × GC × GC - TOFMS FTIR FT-ICR MS GC-MS HT-GC × GC - FID ¹ H-NMR, FTIR

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Kumar, S., et al., 505 2021	Elucidation of aromatic hydrocarbon biomarkers	GC-MS
	(riterpenoids and aromatic steroids)	
Li, J. F., et al., ⁵⁰⁴ 2021	Diamondoids, ethanodiamondoids, and	
	thiadiamondoids in condensate samples	
Liang, M., et al., ⁵⁰⁵ 2021	Polycyclic aromatic hydrocarbons (PAHs)	
Pontes, N. S., et al., ³⁰⁴ 2021	Identification of nitrogen, oxygen, sulfur, and	ESI(+/-)-Orbitrap HRMS
	mixed heteroatomic classes	
Zhu, G. Y., et al., ⁵⁰⁶ 2021	Characteristics of petroleum system in the Tarim	
	basin	

3.1.3 $GC \times GC$ coupled to Quadrupole Mass Analyzer ($GC \times GC$ - qMS)

It is already known that volatile organic compounds (VOCs) play an important role in air pollution, such as the formation of boundary layer ozone and secondary organic aerosols (SOA), while some VOCs may significantly affect human health. However, the accurate measurement of VOCs still is a challenge for the scientific community. In general, techniques GC and/or GC-MS are currently utilized for the monitoring of VOCs that encompasses more than 100 toxic or ozone-depleting target compounds. Since GC × GC has been applied for analysis of atmospheric VOCs,⁵⁰⁷⁻⁵⁰⁹ a significant improvement in terms of separation and complete compound information has been achieved. In general, the thermal modulation GC × GC requires high consumption of cryogens, such as liquid nitrogen or liquid carbon dioxide. However, even with cryogens, the system is not able to reliably trap compounds more volatile than C4.⁵⁰⁸ Utilizing a solid-state modulator that includes the Peltier cooling device equipped with a special modulation column in GC × GC - qMS could successfully modulate light hydrocarbons down to C2 without the use of any cryogens.⁵⁴⁵

Guan and his co-workers⁵¹⁰ have developed a hybrid primary dimension column in which the first part of the column is temperature-dependent for a better separation of the C2-C4 components. They analyzed standard PAMS and TO-15 gas mixtures. Researchers demonstrated that all target compounds from C2 to C12 in PAMS and TO-15 lists can be analyzed in the single-channel GC × GC-qMS system. Figure 6 shows the GC × GC chromatograms of the standard PAMS and TO-15 gas mixtures. A signal-to-noise ratio (S/N) of >30 is used for peak detection. It can be noticed that ethylene and ethane have a low response, while acetylene was not found. The sensitivity loss of these compounds was attributed to incomplete trapping in the pre-concentrator as there was no apparent break-through observed. For the TO-15 gas mixture, researchers confirmed that all the targeted compounds in the standards were successfully separated with decent resolution. The common species present in both standards are highlighted in the red circles.



Figure 6. $GC \times GC$ -qMS chromatogram of PAMS (up) and TO-15 (down) gas mixtures. Insert is a zoom-in display of a coelution pair of cyclohexane and 2,3-dimethyl pentane (PAMS sample). Peaks marked with red circle indicate common compounds present in both PAMS and TO-15. Reproduced with permission from⁵¹⁰, Copyright 2019 Elsevier.

3.2 Liquid Chromatography coupled to Mass Spectrometry (LC-MS)

Over the last decades, liquid chromatography coupled to mass spectrometry (LC-MS)^{138, 139, 511-514} has evolved from a scientific curiosity into a routinely applied technique finding increasingly more use in routine field laboratories. Compared to traditional chromatography techniques, LC-MS may offer additional selectivity and confirmation of identity by determining the mass/charge ratio of the ions or recording MS data which can result in three-dimensional data sets. Although LC-MS is famous for its complexity, it is often applied to the most complex samples. As mentioned, the LC-MS technique has the ability to give three-dimensional data. First of all, the compounds are separated in time. Afterward, the generated ions in the ionization source are separated according to their m/z ratios in the mass analyzer of MS. In the end, the MS detector measures the abundance of each ion. The MS detector can enable more reliable identification of the compounds eluting from LC compared to visible spectrophotometry (UV-Vis) or fluorescence detectors. Thus, LC-MS may significantly reduce the risk of false-positive identification.

Furthermore, it should be pointed out that one of the most useful types of liquid analytical techniques is high-performance liquid chromatography (HPLC).⁵¹⁵⁻⁵¹⁸ The advantage of the HPLC lies in its ability to be applied to samples with high boiling points and a quite short time (just a few minutes) which is required to analyze a sample. The most common detectors used in liquid chromatography are refractive index detector (RID) and wavelength UV detector, where UV spectroscopy is particularly useful for the identification of all types of aromatics in asphaltene fractions.¹¹³ HPLC is extensively used for the characterization of crude oils, petroleum distillates, and coal-derived liquids. The hydrocarbon separation and identification is one of the main applications of HPLC, while particularly it is used for the identification of asphaltene and resin type constituents in nonvolatile feedstocks.

Islas-Flores et al.⁵¹⁹ made a comparison between HPLC and open-column chromatography (OPC) in one of their scientific articles. They have reported that the separation of oil samples using HPLC is rather simple and effective, as well as that yields are comparable to results achieved by traditional OPC.

There are different modes of HPLC that may be afforded by using normal- or reversed-phase columns. The possibility of column switching may allow carrying out the desired separation with adequate resolution, rapidity, and accuracy.⁵²⁰ For example, it is known that the type and amount of polycyclic aromatic hydrocarbons (PAHs) may vary widely among different crude oils. Therefore, the analysis of any sample to isolate fractions containing PAHs involves using normal-phase HPLC separation. Afterward, the fractions are subjected to reversed-phase HPLC for the separation of individual PAH isomers.

Saravanabhavan et al.¹²⁵ studied an offline multi-dimensional HPLC technique for the group separation and analysis of PAHs in a heavy gas oil fraction (boiling range 287-481°C). They precipitated waxes present in the heavy gas oil fraction using cold acetone at -20 °C. Recovery studies showed that the extract contained 93% (+/- 1%; n = 3) of the PAHs that were originally present while the waxy residue contained only 6% (+/- 0.5%; n = 3) meaning that PAHs were not lost during the precipitation of wax. PAHs present in the extract were fractionated, based on the number of rings, into five fractions using a semi-preparative silica column. These fractions were analyzed using reverse-phase HPLC coupled to a diode array detector. UV spectra of the chromatographic peaks were used to differentiate among PAH groups. They proved the usefulness of this method by analyzing PAHs present in the heavy gas oil fraction crude. This study has shown very promising results pointing out the suitability of the current method for PAH profiling in oil fractions.

Magi et al.⁵²¹ combined LC-diode array detection (DAD) and MS for the determination of porphyrins and metalloporphyrins in marine matrices. The authors coupled HPLC to UV-Vis DAD, and then MS was coupled at the exit of the DAD system to verify if it was possible to obtain reliable electron impact (EI) spectra and achieve a more specific technique. An excellent separation and low retention times, as well as good detection limits and linearity, were achieved during the analysis of porphyrins by using HPLC-DAD-MS. The results achieved from experiments done with Zn, Cu, and Fe octa-ethyl-porphyrins indicated that this method may be applied to other classes of porphyrins or other homologous compounds.

Encinas et al.⁵²² applied high-pressure LC-DAD-MS to study the determination of fullerene C_{60} in the atmospheric particulate fraction. The detection and quantification of fullerenes are of crucial importance for the determination of their environmental fluxes and evaluation of the environmental risk. However, fullerenes are not easy compounds to study.⁵²³ LC-MS is found as the most common technique to study fullerenes. Fullerenes can absorb light within the range of 300-350 nm, therefore UV-Vis is considered a powerful detector for their analysis in combination with LC, due to its wide range of linearity and high sensitivity. The researchers⁵²² investigated the presence of fullerene C_{60} in air samples which were collected from different outdoor and indoor locations in the city of Vitoria-Gasteiz (Spain), as well as at the exhaust outlets of various combustion engines with and without catalytic converters. In the outdoor samples in the region of high-density traffic, they detected the concentrations of fullerene C_{60} of 2.27 pg/m³, which was expected due to combustion processes at high temperatures of fullerene. However, it was interesting that detected fullerene C_{60} was mainly found in situations of high photochemical activity when the concentrations of primary pollutants from the combustion processes were low. The authors mentioned that

the maximum concentration of fullerene C_{60} was detected in indoor samples and was 10.5 pg/m³. Results obtained for the samples from the exhaust outlets of various engines without catalytic converters showed concentrations of fullerene C_{60} above 170 pg/m³, while in the case of vehicles with catalytic converters, the detected concentration of fullerene C_{60} was lower than the limit of quantification. No significant variations were noticed in the emission to air related to the type of fuel used. These results have been contributed to the currently available information regarding the fullerene C_{60} and its environmental behavior. This way of fullerene characterization and their evaluation in the air will allow new investigations on its potentially harmful ecological impact.

3.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

It is well known that coal impurities cannot be controlled because they occur naturally during coal genesis under a long period of microbiological and geological processes. Besides, trace elements may form part of coal impurities, and cause environmental problems.⁵²⁴ Additionally, various fractions are used to produce petroleum fuels, such as gasoline and diesel. Apart from hydrocarbons, nitrogen, oxygen, and trace metals, crude oil also contains some sulfuric compounds. During the conversion via combustion of petroleum fuels into energy, the sulfuric compounds are oxidized, and thus, producing sulfur oxides. All these impurities are released into the atmosphere, which results in pollution of the air and acid rain.⁵²⁵ Inductively coupled plasma mass spectrometry (ICP-MS) is considered an excellent technique for trace element detection in different sample matrices. ICP-MS was developed by Houk⁵²⁶ over 30 years ago, however, there are still many older techniques that are in use by some laboratories. Many factors are usually considered when evaluating the suitability of a technique for installation in the laboratory, especially from a perspective of small laboratories, where the price of equipment plays a crucial role, as ICP-MS instrument is quite expensive. Nonetheless the price, ICP-MS is an instrument with a lot of advantages. It is a multi-element capability, which allows multiple elements to be measured simultaneously in a single analysis. ICP-MS provides a very short analysis time and simple sample preparation, therefore, it offers a high sample throughput in the laboratory.⁵²⁷ Numerous features are provided by ICP-MS such as high sensitivity, wide linear dynamic range, wide elemental coverage and multi-element capability which make it very attractive for the laboratory. However, one of the biggest disadvantages of ICP-MS is the use of the high volatility of petroleum fuels. They can make the plasma unstable, and its carbon-rich matrix may cause problems for ICP-MS, such as clogging of the nebulizer and carbon deposition on the sampler and skimmer cones after sample application.⁵²⁵

Mketo et al.⁵²⁴ have developed a novel microwave-assisted hydrogen peroxide digestion procedure followed by ICP-MS analysis for trace elements determination in coal samples. Their method has been shown as cost-effective and environmentally friendly due to the utilization of the diluted hydrogen peroxide as a digestion reagent instead of concentrated inorganic acids that may release carcinogenic nitrous oxides.

Lu et al.⁵²⁵ have used the sector field (SF) ICP-MS for routine quality control of the total sulfur content of petroleum fuels at ultralow levels. They diluted fourteen fuel samples (gasoline- and diesel-type) with isopropanol (IPA) or IPA containing 10% toluene. It was reported that the variability of the sample components did not affect quantification by the SF-ICP-MS. Hence, their method is proven suitable for routine analysis of total sulfur content in petroleum fuels.

Further on, Moulian and his co-workers⁵²⁸ have developed a method for the separation of free porphyrins from asphaltenes based on their polarity using high-performance thin-layer chromatography (HP-TLC). They detected porphyrins by laser ablation (LA) ICP-MS and UV densitometry. It was found that eluted fraction contained free porphyrins, while the major fraction at the application point corresponded to trapped or highly polar porphyrins. Moreover, the molecular and elemental detection analysis of vanadium and vanadyl porphyrins was successfully performed. The combination of these two analyses proved the presence of a large number of porphyrins which remained inaccessible to molecular analyses. The reason for that was due to matrix effects, ionization preferences, and that the porphyrins are linked to archipelago asphaltenes.

Their results suggested that such a method for separation might be a good solution for pilot efficient processes using a hydrodemetalation step.



*Figure 7. Comparison of vanadium, nickel, and sulfur GPC-ICP HR MS profiles, before (no heat; red profile) and after heating (blue profile), for Boscan samples.*⁵²⁹

In another work done by Moulian et al.,²⁵⁷ researchers have coupled HP-TLC and extrography with elemental LA-ICP-MS and MALDI FT-ICR MS to characterize metals contained in the asphaltene reference sample. They wanted to determine which fractions contained vanadium and porphyrin types present in these fractions. The MALDI FT-ICR MS analyses showed migration of the porphyrins till they reach the solvent front. Their results indicated that a high quantity of free porphyrins or porphyrins with weak interactions with the island nanoaggregates in the acetone fraction was present.

Different studies^{211, 530-533} have been performed on using GPC technique together with ICP-MS detector for the characterization of the asphaltenes, separating them according to their size (hydrodynamic volume) or molecular weight, and subsequent detection of component species bearing heteroatoms. Gonzalez et al.⁵²⁹ recently published a study about the asphaltene characterization by GPC-ICP HR-MS. In this work, they reported cluster presence for whole asphaltenes, and their A1 and A2 subfractions. Tetrahydrofuran (THF) has been used as a solvent for measuring the dependence of these profiles on temperature and the exchange of clusters with other components. The comparison of GPC-ICP HR-MS profiles of measured isotopic detection of 32S, 51V, and 58Ni for asphaltenes, as well as for A1 and A2 subfractions, for Boscan crude oil, is represented in Figure 7. It can be seen that chromatogram profiles are separated by a valley which indicates that bands seen in the cluster zone should correspond to material with MW several folds higher than the one corresponding to the HMW sector. Researchers explained that this is consistent with the cluster as being an agglomerate of nanoparticles. Graphs represented in Figure 7a,d,g show the low retention times (22min) for the asphaltene clusters at low concentrations. Furthermore, profiles measured for A1 subfraction

at 25 °C (Figure 7b,e,h) showed very thin bands at low retention times which is expected for the material excluded from the columns. After heating, for the nickel profile it was detected a reduction in the excluded material and the LMW region, with an increment in the HMW and MMW signals. Contrary to A1, for the A2 subfraction a significant increase in the signal of the SHMW region, at the expense of a reduction in the other three regions were noted. From the results can be seen that under thermal stress the asphaltene fractionation causes changes in the arrangement of nanoaggregate in solution.

3.4 Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS)

Due to the complexity of the sample, a combination of chromatographic separation methods and mass spectrometry is preferred. However, the requirement of coupling a GC with an MS detector is that the analytes should be volatile. As a result, GC-MS is less suitable for increasingly heavier oil samples with heteroatoms such as the resin and asphaltene fractions. The new techniques equipped with improved ionization method and/or the analyzer allow performing a comprehensive analysis of the chemically very diverse components of a petroleum sample. These analytes range from non-polar (saturates) to polar constituents (asphaltenes), while masses go up to over 1,000 Da.⁵³⁴ This broad spectrum makes a novel ionization technique, enabling the analysis of all different components with equal efficiency, highly desirable. In addition, the ultra-complex nature of crude oils with over 100,000 chemically different constituents within the mass range 200-1,000 Da demands an ultra-high-resolution mass analyzer (HRMS) for precise analysis.⁵³⁵ Therefore, at the current moment, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS)^{170, 431, 433} is considered the most powerful technique for this application in terms of mass resolution and accuracy (Figure 8).⁵³⁶ It may resolve the ionized analytes according to their individual cyclotron frequencies, which are inversely related to the mass-to-charge ratios (m/z) of the analyte ions.³⁷ FT-ICR-MS can be utilized for very high-boiling and non-boiling petroleum fractions beyond the reach of GC/GC × GC through direct insertion or infusion. FT-ICR measures the motion of ion orbiting trapped in a magnetic field of an analyzer cell. To excite ions to higher cyclotron orbits is done by Radio Frequency (RF) field. Further on, the current that is gathered at the ends of a capacitor during relaxation is analyzed by Fast Fourier Transform (FFT) to reveal the ions cyclotron frequency that depends on m/z.



Figure 8. Schematic of the FT-ICR mass spectrometry principle.

FT-ICR MS can achieve resolutions approximately between 10 and 100 times higher than those of other analyzers.³⁸³ For example, Djokic et al. have reported the use of HT-GC × GC-FID/TOF-MS and APPI FT-ICR MS for the detailed characterization of hydrotreated distilled crude oil feedstock and a pyrolysis fuel oil produced during steam cracking of this feed. The result revealed that much higher carbon numbers were detected by using FT-ICR MS compared to HT-GC × GC-FID/TOF-MS. This can be directly attributed to the FT-ICR MS's ability to separate elemental compositions by number of carbon atoms which remain unresolved in complex, high boiling petroleum fractions using even state-of-the-art high temperature hyphenated chromatographic techniques HT-GC × GC-FID/TOF-MS.⁵³⁷

Recently, an FT-Orbitrap analyzer has been introduced, and its specified resolution can reach up to 100,000 at m/z 400. Additionally, FT-ICR instruments have maintained their supremacy by providing a combination of the highest resolution (350,000) and highest accuracy (50 ppb)⁵³⁸ available, thus leaving other analyzers far behind.



Figure 9. Excitation events in the ICR analyzer cell.

The principle involved in the function of an FT-ICR-MS system is extensively documented in the work of Marshall.^{539, 540} The cyclotron frequency of the individual ions is carried out in two steps. The first step implies the excitement of the trapped ions, which is followed by the detection of the motion of the excited ions. Initially, those trapped ions are composed of many m/z values, thus, they have a small amount of kinetic energy and cyclotron radii. Next, the excitation of the ions to a larger cyclotron radius may bring ions close enough to the detection plate. By the application of the RF signal, the excitation is carried out to excitation plates of the analyzer cell (Figure 9). Furthermore, when the RF signal frequency is on-resonance with the cyclotron frequency of a particular m/z, the ions will be excited to a larger ICR radius. Ions that have different cyclotron frequency from that of the RF signal will remain unaffected, and at the center of the cell. Once the RF signal frequency is turned off, the excitation is complete, and the ions may remain at a larger radius. A single petroleum FT-ICR mass spectrum can contain up to 50000 peaks, whereas detection is typically limited to 1000000 ions at a time. Thus, the number of ions corresponding to each resolved mass-to-charge ratio is relatively small, therefore, it is often desirable to sum at least 100 time-domain transients to increase the signal-to-noise ratio and dynamic range. A chip-based micro-ESI system has been successfully automated in combination with FT-ICR-MS analysis of petroleum samples.³⁷⁵ It is obvious that ICR accurate mass measurements may provide elemental compositions for thousands of petroleum components from a single mass spectrum. Further, the elemental compositions can be analyzed to reveal heteroatom content, double bond equivalents, and carbon distribution, and H/C ratios.²⁶ When coupled to MS/MS, it is possible to determine the number of carbon atoms in core structures and the number of carbon atoms in alkyl side chains.541-543

FT-ICR-MS has been seen as one of the most practical approaches to analyze sulfur compounds in nonvolatile residues like vacuum residues.²⁴ Due to its high resolving power, FT-ICR-MS is able to detect minute variations in mass in the order of an electron, as well as effectively resolve ions by assigning unique elemental compositions to each. Some ionization techniques are used in FT-ICR-MS such as electron ionization (EI), atmospheric pressure photoionization (APPI), electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), matrix-assisted laser desorption ionization (MALDI), and others have been developed. Depending on the compounds of interest, the different modes of ionization can be employed. For instance, for the analysis of sulfur aromatic and polar petroleum components, particularly, two ionization modes have been successfully employed - ESI and APPI.^{544, 545} In the following sections, the detailed ionization techniques used in FT-ICR-MS will be discussed.

3.4.1 Electron Ionization (EI)

Electron Ionization (EI) coupled to FT-ICR MS relies on thermal desorption of the sample in an inert heated inlet system prior to ionization. The operating temperature limit of the oven and thermal stability of the inert inlet coatings prevent operation above 400 °C. As a result, EI FT-ICR MS is not well suited for analysis of extremely heavy materials such as resides, but well suited for the analysis of light to moderately heavy distillates that may be lost to volatilization in FD analysis performed in a vacuum.⁵⁴⁶

However, the application of internal low-voltage EI FT-ICR MS (10-18 eV) allowed Hsu et al. and Guan et al. to obtain the accurate mass measurement of a heavy petroleum distillate (atmospheric pressure boiling range of 343-566 °C).^{537, 547} Similarly, Marshall et al. have reported the characterization of nonpolar volatile constituents in the low-, middle-, and high-boiling fractions from a VGO sample by the use of low-voltage (10 eV) external EI high-resolution and high-mass accuracy 7 T FT-ICR MS. The result revealed that for the first time hydrocarbons and sulfur-containing hydrocarbons have been completely mass-resolved across the full VGO range. Aromatic hydrocarbons are the major detected components in all three samples. In addition, many sulfur-, nitrogen-, and oxygen-containing compounds were directly observed.^{149, 548} Furthermore, Miyabayashi et al. modified a conventional EI FT-ICR MS to an in-beam EI FT-ICR MS that allowed to successfully detect molecular ions of non-volatile components in vacuum residues.⁵⁴⁹ Besides, the combination of different ionization techniques, such as in-beam electron ionization (EI), electrospray ionization (ESI), field desorption (FD), and liquid secondary ionization (LSI) was evaluated by this group to characterize extremely complex heavy oil sample.⁵⁵⁰

3.4.2 Atmospheric Pressure Photoionization (APPI)

Atmospheric Pressure Photoionization in both the positive and the negative ion mode is an efficient ionization technique for samples containing non-polar or low polar compounds such as polyaromatic hydrocarbons (PAHs) and sulfur aromatic species.⁵⁵¹

Muller et al.⁵⁵² have reported that using APPI FT-ICR-MS it is possible to quantify the compositions of vacuum gas oil by using innate sulfur compounds as internal standards. Specifically, the molecular weight and number of sulfur atoms per species were identified in the high-resolution measurement, in which their mass spectrometric abundance and the total sulfur content were combined to calculate the mass fraction of each aromatic sulfur species present. Furthermore, they quantified aromatic hydrocarbon compounds and nitrogen species which was based on an equimolar response compared to the aromatic sulfur species. The same approach was applied in the estimation of the composition of marine fuel oil feedstocks by APPI FT-ICR-MS.⁵⁵²

The use of the APPI FT-ICR-MS method has been also conducted to provide elemental compositions in the hydro-deoxygenated bio-oil blended with light gas oil, which contains components that are not GC-amenable.⁵⁵³

Marshall et al.⁵⁵⁴ performed off-line (+) APPI FT-ICR-MS characterization of GPC asphaltene fractions. The observed result revealed that earlier-eluting compounds were more aliphatic, and later-eluting fractions contain abundant highly-aromatic/alkyl-depleted species. A similar trend has been also observed for the parent whole crude oil, thereby suggesting that interactions between aliphatic moieties could be central in petroleum and asphaltene aggregation. In another study, Marshall and his co-workers⁵⁵⁵ have applied APPI (+) FT-ICR-MS but this time to reveal the coexistence of island and archipelago structural motifs through the application of the extrography separation to an unaltered Illinois coal No. 6 asphaltene. The results

showed that the Wyoming crude oil asphaltenes contain mainly island species, whereas coal asphaltenes contain archipelago and island compounds with high oxygen content. Moreover, the use of a new "multinotch" stored-waveform inverse Fourier transform isolation enables the unambiguous determination of island versus archipelago species in samples that contain compounds with high and low aromaticity.¹⁹⁰ Additionally, the combination of 9.4T FT-ICR-MS and infrared multiphoton dissociation allowed to determine the molecular composition of the asphaltene subfractions that were produced from Wyoming deposit n-heptane asphaltenes. The result disclosed that the compositional range of polyoxygenated compounds shifts toward lower aromaticity and present pivotal in asphaltene solubility, whereas oxygendepleted species are more aromatic.

Abdul Jameel et al.²⁷ reported about de-asphalting of heavy fuel oil (HFO) by using n-heptane as a solvent, and the molecular characterization of the acquired de-asphalted oil (DAO) using APPI (+) FT-ICR mass spectrometry, and ¹H and ¹³C NMR spectroscopy. They showed that de-asphalting had a significant improvement in reducing the kinematic viscosity of HFO by more than five times. Moreover, the heavy metals nickel and vanadium were significantly reduced, by more than 50%, while sulfur content was slightly reduced in the DAO. The ions for HFO and DAO were recorded with a mass to charge ratio (m/z) ranging from 150 to 1200. The authors noticed that the HC class species were slightly more in DAO (29.2%) compared to HFO (28.6%), while the S₁ class species were more in HFO. The higher amount of S₁ class of species in HFO (42.5%) and DAO (41.8%) may indicate the presence of a core thiophenic skeletal structure. They also reported an approximately 10% higher C/H ratio for APPI FT-ICR/MS than those reported by other techniques. It might be explained by an inherently non-quantitative nature of MS. Another reason might be the APPI ionization source used in their study. It is effective in ionizing non-polar hydrocarbon molecules such as benzo- and dibenzo-thiophenes, PAHs, and cycloalkanes, comprising the bulk of the fuel. However, it is less effective in ionizing highly polar molecules such as heteroatoms (N, O, S).

Giraldo-Davila et al.²⁶ have employed a combination of tools such as extrography, Soxhlet extraction and column chromatography fractionation for increasing compositional space accessibility in FT-ICR-MS analysis of a Colombian heavy crude oil. They used extrography followed by Soxhlet extraction with acetonitrile, methanol, n-heptane, and toluene to produce four subfractions with unique composition, as the extrography is found to be useful for selective isolation of metal-complexes, maltenes and asphaltenes. The metal-porphyrins enriched fractions were subjected to column chromatography to achieve increment of the compositional space accessibility in MS analysis for this particular group. The obtained FT-ICR-MS results show that fractionation enables the observation of 13 new compound classes which are usually undetectable when the whole crude oil sample is analyzed. Apart from this, the molecular analysis of the extracted fractions indicated that compositions with high heteroatom content exhibit preferential adsorption on alumina. Researchers mentioned several reasons to explain their results. First of all, to have a complete view into the composition of crude oil; secondly, to understand adsorption processes of particular compound families on mineral surfaces; and third, to access specific fractions, such as vanadyl porphyrins, with potential use in geochemistry. In the end, it can be concluded that fractionation methods coupled to FT-ICR-MS are outstanding strategies for the analysis of crude oil molecular composition, meaning that without selective fractionation of crude oil samples is not possible to conceive Petroleomics.



Figure 10. a) GC × GC color plot of the HTAL-FEED; b) HT-GC × GC-FID color plot of HTAL-PFO. Adapted from ⁵⁵⁶

Djokic et al.⁵⁵⁶ have combined the capabilities of GC \times GC-FID/TOF-MS and atmospheric pressure photoionization (APPI) FT-ICR-MS for the characterization of a hydrotreated distilled crude oil feedstock and a PFO produced during steam cracking of this feed. A good separation of the complex feedstocks was observed. In Figure 10a, the most dominant compounds classes showing the color plot obtained by analyzing the HTAL-FEED using high temperature (HT)-GC \times GC-FID can be seen. Next, in the chromatogram presented in Figure 10b, a wrap-around can be observed. The authors explained that the compounds which show wrap-around do not coelute with the analytes from the next modulation cycle, therefore, the obtained chromatographic separation and ordered structures were preserved. Since the compounds which contain five and more aromatics rings cannot be identified independently, the detected compounds were lumped and presented as penta+aromatics.

Furthermore, the researchers presented a comparison of the HT-GC \times GC-FID and FT-ICR-MS results shown in form of two DBE vs. carbon number plots (Figure 11). They noticed that both carbon number and DBE results for the HTAL-FEED sample differ between the methods and pointed out that the reason might lie in a mismatch on the DBE scale which can be explained by a structure-dependent sensitivity of the photoionization used for the FT-ICR-MS method. Probably, the molecules with higher DBE values are favorably ionized whereas aliphatic molecules are discriminated, and therefore, not detected.

From this study, it is obvious that much higher carbon numbers can be detected by using FT-ICR-MS, due to its ability to separate elemental compositions by a number of carbon atoms when compared to HT-GC \times GC.⁵⁵⁷⁻⁵⁶¹



Figure 11. Carbon number vs. DBE plots showing HTGC \times GC-FID data (red dots) in comparison to APPI FT-ICR MS data (empty circles) for HTAL-FEED with a) original FT-ICR MS and GC \times GC data scaled to the same order of magnitude (100%) and b) abundance with corrected APPI FT-ICR MS data. Reprinted from ⁵⁵⁶, with permission from Elsevier.

3.4.3 Electron Spray Ionization (ESI)

Electron Spray Ionization (ESI)^{24, 29, 551, 562-568} is another promising method to ionize non-volatile and complex molecular samples bearing polar functional groups, especially nitrogen- and oxygen-containing groups. A number of samples, such as gas-oil, vacuum residues, coal liquefaction products, bio-oil, crude oils, and tire pyrolysis oils have been analyzed using ESI ionization coupled to FT-ICR-MS.

Abdul Jameel et al.²⁴ have performed an investigation in which they characterized the sulfur species present in a sample of vacuum residue using FT-ICR-MS coupled with a positive ion ESI source. They developed a surrogate molecule of the fuel using data from the two ionization techniques and assigned unique chemical formulas based on the masses. Results showed that 99.6% of the detected species were polar molecules, out of which 37% were N-class, followed by NS- and OS-classes. Further on, they designed a single surrogate molecule based on the average molecular parameters (AMP) representing the average structure of the vacuum residue obtained from ESI FT-ICR-MS. It was mentioned that the proposed single molecule vacuum residue surrogate could be used for predicting various physical and thermochemical properties.

Cui et al.⁵⁶⁶ have used the negative-ion (-) ESI FT-ICR-MS to investigate the effect of pyrolysis temperature on neutral nitrogen and acidic species in Huadian shale oil. They analyzed the pyrolysis characteristics of neutral nitrogen and acidic species such as carbazole, phenol, and carboxylic acid compounds. The results showed valuable information about the molecular composition of heteroatom species in shale oil and the probable heteroatom core structures were suggested based on the DBE values.

In another work published by Cui and co-authors,⁵⁶⁷ they analyzed Huadian shale oil collected at five different processing temperatures using positive-ion (+) ESI FT-ICR-MS and GC-NCD. Their results indicated that the pyrolysis temperature exerts different effects on different types of heteroatom compounds. Therefore, it was concluded that the pyrolysis temperature can affect the number, relative abundance, DBE value distribution, and carbon number distribution of heteroatom compounds in shale oil.

Trubetskaya et al.⁵⁶⁹ have reported the use of FT-ICR MS technique coupled to an ESI source ionization in the characterization of tar and bio-oil samples from high-temperature biomass treatment. The direct infusion liquid tar sample in DMSO to FT-ICR-MS enables the identification of polar and non-volatile compounds,

such as sugars, proteins, and extractive derivatives. Moreover, the developed method using FT-ICR dynamic range of m/z can identify a broad spectrum of compounds that were difficult to detect with the other analytical techniques. Furthermore, the detailed molecular characterization of the sulfur compounds in vacuum residues was obtained by the combination of positive ion APPI for sulfur speciation and ESI the polar groups coupled to FT-ICR-MS.²⁴ The assigned masses reveal the presence of sulfur families, including sulfides, thiophenes, benzothiophenes, dibenzothiophenes, benzonaphthothiophene, and their derivatives in the vacuum residue sample. Moreover, the average structure of the sample was also designed based on the obtained average molecular parameters.²⁴

Recently, Xiang et al.⁵⁷⁰ have successfully applied FT-ICR MS coupled with ESI in the negative-ion mode to investigate the chemical composition of the heavy tars produced from the pyrolysis of biomass at various temperatures and heating rates. The result shows that the low temperature promotes the formation of heavy tars via the polymerization of bio-oil components and at slow heating rates the condensed aromatics are formed via the polymerization of small aromatics with one or two rings. On the other hand, high temperature promotes the breakage of the oxygen-containing functional groups, and highly condensed aromatics with more than 4 rings are formed at 800 °C via the strong secondary reactions especially at fast heating rates. This group has also explored the use of (-) ESI FT-ICR MS in combination with an ultraviolet fluorescence (UV-F) spectrometer to characterize the heavy components in bio-oils from the pyrolysis of cellulose, hemicellulose, and lignin, the molecular formulas of the heavy compounds and the large aromatic structures.⁵⁷¹ Furthermore, this technique has also been applied to investigate the effects of alkali/alkaline earth metal species on the formation of heavy components in bio-oil prepared from pyrolysis of original sample/acid-washed/impregnated sawdust (typical agroforestry waste) at various temperatures and heating rates.⁵⁷² In another study, the molecular structures comprising the bio-oil oligomer fraction and the pathways by which these structures form during biomass pyrolysis reactions were revealed by using the (-) ESI FT-ICR MS technique.⁵⁷³

3.4.4 Atmospheric Pressure Chemical Ionization (APCI)

The pyrolysis oil contents may be extensively ionized by using a sensitive and selective ion source, such as an APCI source, which is coupled to an ultrahigh-resolving (UHR) mass analyzer, i.e. FT-ICR-MS. APCI is considered a special form of chemical ionization (CI), where a corona needle regulated high voltage direct current (HV-DC) gradient is employed to generate a corona plasma which causes the formation of reactive species. These species ionize the analyte molecules in a subsequent secondary ionization process. Contrary to the other API techniques, APCI shows the best results for aliphatic hydrocarbons, thus is mainly used to analyze compounds with higher polarity, such as phosphoric acid esters and carbamates.^{30, 551} Combining GC with FT-ICR-MS by using a soft APCI ion source should enable separation and detection of molecules with the same monoisotopic mass with an ultrahigh mass resolution.

Zuber et al.³² presented a method for the analysis of the pyrolysis liquid from German brown coal by GC-FT-ICR-MS using an APCI source. They used a mixture of standard compounds (RMSC) to optimize the parameters of the APCI ion source and GC. They demonstrated a high analytical potential of GC-APCI-FT-ICR-MS by verifying different homologous series in the liquid sample analysis. Different compound classes were observed, increasing by the number of CH_2 groups, such as alkyl carboxylic acids, alkylene carboxylic acids, dicarboxylic acids, alkyl phenols, alkyl dihydroxy benzenes, and alkoxy alkyl phenols. Further on, to obtain more information about the structure, they studied double bond equivalent (DBE) versus carbon number (nC). They identified saturated and unsaturated monocarboxylic acids, as well as dicarboxylic acids, thiophenes, benzo-thiophenes, cycloalkanes, cycloalkenes, and PAH analogous structures, which were partially derived by oxygen- and sulfur-containing groups. Moreover, a satisfactory separation of molecules of higher polarity was observed due to the polar GC column. In particular, separation of the saturated and unsaturated monocarboxylic acids, and alkyl phenols was achieved.

Huba and co-workers²⁸ have published a comprehensive overview of the advantages and disadvantages of the three ionization techniques ESI, APPI and APCI coupled to HRMS. The overall conclusion for all three

sources was the lack of ionization of non-functionalized alkanes. Furthermore, their results indicated that APPI source may provide the best results when is the case of a comprehensive oil characterization. They explained that APPI can ionize the broadest range of compounds, provide the best overall ionization efficiencies, and ionization suppression compared to APCI. On the other hand, for ESI some severe limitations were detected. As a result, the number of different compound classes that are ionized with ESI was found to be significantly lower with respect to both APPI and APCI. Apart from this, the authors indicated several factors that may affect ionization efficiency such as the presence of easily protonated or deprotonated functional groups (primary factor), the presence/absence/type of heteroatoms, the methylation level, the size, the isomeric structure, and the presence/absence of a complex matrix.

Kondyli et al.⁵⁵¹ have investigated the efficiency of the combination of three different ionization methods ESI, APPI, and APCI for the analysis of a complex crude oil mixture. It was shown that ESI is the method of choice for the ionization of basic nitrogen compounds while APPI for the ionization of hydrocarbons and containing-oxygen compounds. The combination of different ionization methods provided complementary information about complex mixture constituents as the different polarity play a crucial role. Using ESI/APPI, the authors noticed a higher number of hydrocarbons and O_x species than with ESI alone. However, the APPI/APCI did not show significant changes since most of the detected compounds were commonly found among these methods. It was interesting to notice, that the last combination of the methods ESI/APCI did not allow the detection of many individual compounds. They could assign about 3262 compositions in common with both ESI and APCI, as well as with the combination of ESI/APCI. However, the highest number of individual compounds was detected only under APCI. The reason could be the fact that ESI is known for ion suppression, showing higher matrix effects compared with APCI.



Figure 12. Method integration of TG-APCI-FT-ICR-MS and GC \times GC-HRTOFMS exemplarily depicted for the 7 days aged model bitumen. Desorbable and pyrolyzable species are separated at the dashed line. Pie charts on the left side correspond to the class distribution found for desorption, while pie charts on the right side give the class distribution for the pyrolysis phase.⁵⁷⁴

TG-APCI-FT-ICR-MS is able to attribute sum formulae to semi-volatile to pyrolyzable compounds. Because of APCI, semi-polar to polar minorities are highlighted. The 2D survey view of the temperature-resolved mass spectra for the MS-mode and the MS/MS-mode color-coded with intensity shows the characteristic increase of the m/z with the increase of temperature in the desorption phase, while an enlarged m/z range is simultaneously covered in the pyrolysis phase. GC × GC-HRTOFMS enables the structural elucidation of volatile compounds. With EI, nonpolar compounds are covered as well. 2D-GC allows for group-type analysis of volatile compounds up to roughly m/z 600.⁵⁷⁴

Neumann and co-authors⁵⁷⁴ have investigated oxidative short-term aging of bitumen at the molecular level trying to achieve a detailed understanding of the complex chemical processes. They claimed that identification of the highly aged compounds will help in the design of durable and long-living pavements. APCI thermogravimetry (TG) FT-ICR-MS was combined with EI-GC×GC-HR-TOF-MS in this study (Figure 12), and consistent results on different chemical changes occurring during prolonged short term aging in a specially generated model bitumen were achieved. It was noticed that use TG-FT-ICR-MS can enable the attribution of sum formulae up to the highly complex heavy end of the model bitumen.

3.4.5 Atmospheric Pressure Laser Ionization (APLI)

Atmospheric pressure laser ionization is an ionization technique that utilizes pulsed laser light to produce molecular ions. In contrast to APCI, APLI is the technique that is applied for analysis of preferably non-polar compounds, such as PAHs,^{33, 575} and is about thousands of times more sensitive. Therefore, the advantage of multidimensional chromatography lies in the sensitivity and selectivity of APLI for the examination of complex petrogenic environmental samples.⁵⁷⁶

Panda et al.³³ have demonstrated APLI as a useful method for analysis of crude oil in one of their studies. The results showed that ions were potentially formed from small droplets. It was also noticed that the analyte solution did not fully vaporize, which has been pointed out as an advantage when the temperature-sensitive compounds are analyzed. Besides this finding, the extent of oxygenated ionic species recorded with APPI versus APLI was mentioned as important. Their results indicated that APLI mass spectra can more closely reflect the neutral precursor distribution and that this method is a complementary ionization technique to ESI.

Further on, Benigni and co-authors³⁴ have reported about analysis of fossil oils using GC-APLI-FT-ICR-MS. They analyzed organics in shale oil, petroleum crude oil, and heavy sweet crude oil. Compared to other ionization sources, their results showed that multiple PAH classes may be easily identified with a reduced number of contaminants and interferences. They pointed out that the addition of GC prior to APLI-FT-ICR-MS can increase the ionization efficiency and signal-to-noise ratio of lower abundance fractions. A higher molecular coverage, higher sensitivity, and the possibility to separate and identify molecular isomers from within a crude oil sample have been achieved. Moreover, it was shown that this combination GC-APLI-FT-ICR-MS contributed to an increase in the number of compounds detected in relation to APLI-FT-ICR-MS. Furthermore, it is known that APLI can provide enhanced sensitivity due to very high linear and two-photon cross-sections of the target analytes which may lead to saturation of the excitation and ionization transitions; and due to none of the LC solvents absorb the 248-nm laser radiation penetrating the ion source.

In a study published by Thiäner et al.³⁵ the combination of LC-APLI-MS has been demonstrated in the analysis of the mixture of 34 PAHs, including (1) phenanthrene, (2) anthracene, (3) 9-methylphenanthrene, (4) 9-methylanthracene, (5) fluoranthene, (6) pyrene, (7) 9,10-dimethylanthracene, (8) 1-methylpyrene, (9) 7H-benzo[c]fluorene, (10) benzo[ghi]fluoranthene, (11) benzo[c]phenanthrene, (12) chrysene, (13) benzo[*a*]anthracene, (14)5-methylchrysene, (15)6-methylbenzo[*a*]anthracene, (16)7.12dimethylbenzo[a]anthracene, (17) perylene, (18) benzo[b]fluoranthene, (19) benzo[j]fluoranthene, (20) benzo[*e*]fluoranthene, (21) benzo[*k*]fluoranthene, (22) benzo[*a*]pyrene, (23) 6-methylbenzo[*a*]pyrene, (24) 3-methylcholanthrene, (25) dibenzo[a,h]anthracene, (26) indeno[1,2,3-cd]pyrene, (27) benzo[ah]perylene, (28) anthanthrene, coronene (29), (30) dibenzo[a,l]pyrene, (31) dibenzo[a,e]fluoranthene, (32) dibenzo[a,e]pyrene, (33) dibenzo[a,i]pyrene, and (34) dibenzo[a,h]pyrene. They detected HMW-PAHs
which were separated with high chromatographic resolution. In environmental samples, the concentration of PAHs decreases with the increment of aromatic rings, and therefore, it may cause difficulties during the detection of PAHs with large numbers of rings. However, LC-APLI-MS is found to be a suitable method for detecting those small amounts of C24-C30 PAHs via their mass-to-charge ratios. In this study, researchers could detect 211 tentative 6- to 8-ring PAH compounds in a bituminous coal sample. It was noticed that compounds with 8 rings elute later than the compounds with 6 or 7 rings. Moreover, it was pointed out that the occurrence of similar PAH patterns in the high Mw range, in different environmental samples may indicate that selected compounds occur consistently. A similar case has been seen for several lower Mw PAHs.

In another study done by Thiäner et al.⁵⁷⁶ the identification of 7- and 8-ring PAHs in coals and petrol coke by HPLC-diode array detection (DAD) APLI-MS was presented. This method was for the first time used and evaluated for the identification of >C24-PAH. The authors⁵⁷⁶ mentioned that the use of APLI in this study had an advantage of high selectivity for aromatic compounds when compared to previous studies^{577, 578} where the combination of DAD and APPI was applied.

Rüger et al.⁵⁷⁹ recently published an interesting study about the laser ionization mass spectrometry using the VUV laser light under atmospheric pressure. This type of study was for the first time reported. They used a fluorine excimer laser operating at 157 nm (7.9 eV). The authors believed that this technique could trigger single-photon ionization pathways in contrast to the common APLI. It is known that in APLI, sulfur-containing polycyclic aromatic hydrocarbons (PASHs) show low ionization cross sections due to the short lifetime of the excited state in the resonance-enhanced multiphoton ionization (REMPI) process. However, by applying the atmospheric pressure single-photon ionization (APSPLI), the authors mentioned that is possible to obtain high ionization cross sections even for PASHs due to the single-photon process. Researchers have analyzed petroleum-derived and PAH mixtures by APSLI, which are considered highly complex materials.



Figure 13. GC-APSPLI at 157 nm of a light crude oil: (a) Survey diagram (time versus m/z) with total ion count (TIC) and base peak chromatogram (BPC) as inset, and (b) average mass spectrum color-coded according to the attributed compound class. Kendrick mass defect (KMD) diagrams of the light crude oil analyzed by thermal analysis coupled to FT-ICR-MS: (c) Deploying APSPLI (157 nm) and (d) APMPLI (266 nm). NM, nominal mass; CH, hydrocarbon class CxHy; CHS1, hydrocarbons with one sulfur as heteroatom CxHyS1; CHN1, hydrocarbons with one nitrogen as heteroatom CxHyN1; CHO1, hydrocarbons with one oxygen as heteroatom CxHyO1.⁵⁷⁹

Figure 13 shows GC-APSLI data of light crude oil obtained at 157nm. The survey diagram can be seen in Figure 13a, showing the insets of the total ion chromatogram (TIC) and base peak chromatogram (BPC), which reveals the characteristic, complex pattern of the petroleum-derived material. Furthermore, it can be noticed that the most dominant class of the compounds was CH-class but CHS₁-, CHO₁-, CHN₁-, and CHS₁O₁-class constituents were also detected with considerable abundance. It was found that APSPLI is able to ionize compounds from a broad compositional space, and that way overcomes the limitations of classical APLI. Based on the PAH mixture evaluation, it was shown the selective and sensitive ionization of constituents with an ionization potential below the photon energy of 7.9 eV. The researchers have proven the ionization process driven by single-photon ionization, which resulted in a low abundance of protonated species and molecular radical cations. The residual oxygen and water in the ion source atmosphere were detected, and they caused unwanted oxidized ionization artifacts. However, as the authors mentioned, they could be reduced by increasing the flow rate of the nitrogen gas purified by water and oxygen filter cartridges, and by ionizing the analytes at the position near the ionization chamber inlet. It is obvious that APSPLI can be successfully applied for the characterization of petroleum-derived materials.

3.4.6 Laser Desorption/Ionization (LDI)

Over the years, upgrading of mass spectrometry techniques has shown a considerable improvement in the determination of the composition, molecular weight distribution (MWD), and structure of carbonaceous species.^{19, 36, 44, 47, 54, 56, 102, 167, 170, 535, 580-585} Specifically, laser desorption/ionization mass spectrometry (LDI-MS) has been achieved a mass resolution capable of discerning chemical composition and structure in complex carbonaceous mixtures, particularly when used in combination with chromatographic separation. Therefore, this section is focused on the application of LDI-MS techniques for the characterization of specific carbonaceous molecules, such as polycondensed hydrocarbons and asphaltenes (heavy oil fractions).

The most enigmatic component of crude oils is asphaltenes due to the difficulty of establishing their chemical structure. Asphaltenes belong to a solubility class, usually like n-heptane or n-pentane insoluble fraction of oil or coal bitumen. Within the asphaltene research community, the size and molecular weight of the asphaltene molecules have been a long controversy. This has been obscured by the disagreement regarding the reliability of the MWD of asphaltenes determined with different experimental methods. However, results obtained from numerous LDI-MS measurements in different laboratories yield asphaltene MWDs with a major contribution within 300-1000 amu, and weights of about 500 amu.^{36, 580, 586-588} These studies have shown that they are in agreement with other mass spectrometry methods, such as plasma desorption MS,^{589, 590} field desorption MS,⁵⁸⁵ APCI-MS,⁵⁸⁶ ESI, FT-ICR-MS,⁵⁸¹ as well as with fluorescence depolarization and correlation spectroscopy solution studies.⁵⁹¹

Various research groups have successfully conducted studies based on the combination of direct ionization techniques and FT-ICR-MS, which enabled a simpler analysis of complex solid samples.^{592, 593}

It is known that direct ionization sources may exhibit drawbacks in comparison to classical ionization methods such as ESI, due to pronounced signal suppression and low detection selectivity.³⁷ Therefore, coupling LDI source with FT-ICR-MS seems to have a high potential for direct analysis of the volatile and reactive part of a complex solid sample. LDI-FT-ICR-MS^{73, 594-596} can offer a higher mass resolution, mass resolving power, and mass accuracy, enabling the analysis of complex petroleum mixtures on a molecular level.⁵⁹⁷ Due to different ionization efficiencies of the constituents of crude oil,⁵⁹⁸ high-resolution MS data have shown that it is possible to discriminate among different compounds.^{599, 600} The ability of LDI(+)-FT-ICR-MS technique to generate a huge number of variables per sample makes chemometrics more efficient tool for obtaining relevant information.



Figure 14. LDI(+)FT-ICR mass spectra of crude oil samples (a) S21, (b) S15, and (c) S41. Note that the Mw decreases as a function of the reduction of total nitrogen (wt%). Reproduced with permission from ⁴¹, Copyright 2015 Elsevier.

Terra et al.⁴¹ have used LDI-FT-ICR-MS to characterize 70 samples of Brazilian crude oil by identifying the main basic nitrogen and aromatic species. In Figure 14, the LDI(+)FT-ICR-MS of three representative Brazilian crude oils are presented. The content of basic nitrogen and aromatics for sample S21 was 0.1460% and 28.6%, while for sample S15 was 0.1020% and 21.9%, and sample S41 was 0.0680% and 28.0%, respectively. They noticed that the Mw and the concentration of pyridine derivatives change as a function of the total basic nitrogen values. This study showed that LDI-FT-ICR-MS may offer certain improvements over the standard approaches for the determination of petroleum quality parameters.

In a recent work of Zuber et al.³⁷ the application of a direct preparation and analysis method for LDI(-)-FT-ICR-MS analysis of organic solid samples was demonstrated. The researchers analyzed six carbonaceous samples with different degrees of coalification - one peat (PECZ), three brown coals (BCSO, BCSL, BCHA), one hard coal (HCPO), and an anthracite (ANIB). Various coal-related analytical standards were analyzed at different laser powers in order to investigate the influence of the laser applied on the detectable ions. Their results were used to achieve a more detailed insight into the structural properties of those complex solid samples. They presented the molecular formulas obtained for the peat and coal samples (see Figure 15). It was detected a higher total sulfur amount for the samples BCSO and BCSL than for the other samples, which has led to an enhanced assignment of sulfur-, oxygen-containing molecular formulas. Further on, it can be seen the lower number of assigned molecular formulas and lower relative abundances in oxygen-containing classes with $O \ge 7$ indicate a potentially higher degree of coalification of sample BCSO, in comparison to brown coals BCSL and BCHA. The authors claimed that these minor differences in the degree of coalification between samples can be distinguishable by the methods developed. This analytic procedure may give an opportunity to introduce reactive organic molecules of complex solid samples in their native state for mass spectrometric analysis. From the practical point of view, the apparent MWD obtained in LDI-MS measurements of complex polydispersed mixtures of self-aggregating compounds, such as the asphaltenes, is dependent on the experimental conditions.



Figure 15. Bar plots of the molecular formula lists for the LDI(-)-FT-ICR-MS analysis of the peat and coal samples using (A) the number of assigned molecular formulas and (B) the relative abundancies of selected molecular formula classes C_cH_h , N_1O_4 , S_1O_4 , and O_1-O_{10} .³⁷

Over the years, the LDI technique has developed rapidly and at this moment, is capable to provide valuable information related to the chemical composition and structure of complex carbonaceous mixtures. However, results relating to the MWD of typical asphaltenes obtained by LDI-MS were found to be inconsistent. It was reported that laser power and the surface concentration of asphaltenes are crucial parameters for controlling measured asphaltene molecular weights.³⁸¹ It is well known that asphaltenes have a strong propensity to aggregate and flocculation is one of their defining characteristics.⁶⁰¹ If in LDI experiments, the gas-phase aggregation of asphaltenes is dependent on the fused ring number of asphaltene PAHs, then, the coal asphaltenes might be distinguished from crude oil asphaltenes. Coal asphaltenes should have smaller fused ring systems than petroleum asphaltenes. In several studies, the evidence for this has been reported by comparing the UV-vis absorption and fluorescence,⁶⁰²⁻⁶⁰⁴ and the diffusion rates⁶⁰⁵ of the two different asphaltene types.

In 2005, Xu et al.⁶⁰⁶ used for the first time LDI-TOF-MS for a characterization of the petroporphyrins. The experiment has been shown as a reliable and effective for the analysis of petroporphyrins. The results

achieved via LDI-TOF-MS can be compared with those derived from the more conventional UV-vis spectrometry. They analyzed Tahe heavy crude oil (marine origin in China), and the results showed a much higher concentration of vanadium than nickel in the sample. The nickel porphyrins are extracted from the oil and purified afterwards. This type of analysis of petroporphyrins may provide useful information for the design of oil refineries and related processes.



Figure 16. LDI spectra of dried–droplet samples of the Arabian Light crude oil (ALCO) asphaltene with average sample densities of 200 μ g cm⁻² (panels a, b) and 1 μ g cm⁻² (panels c,d). Delayed or cw ion extraction and 40 μ J or 80 μ J laser pulse energies (266 nm) were employed as indicated. The spectra recorded with 40 μ J laser energy have been scaled by the factors indicated in each panel for direct comparison with the spectra measured with 80 μ J. The enhancement of the ion yield for molecular weights above 1000 amu is indicative of in–plume aggregation of the asphaltenes. ALCO asphaltene. Reproduced with permission from ⁶⁰⁷, Copyright 2007 John Wiley and Sons.

Haya et al.⁶⁰⁷ recorded the LDI spectra of the Arabian Light crude oil (ALCO) asphaltene. Figure 16 represents spectra obtained for dried-droplet samples with two different average surface densities of the ALCO asphaltene (1 and 200 μ g cm⁻²) after evaporation of the solvent. They could notice that LDI measurements with the lower laser energy applied resulted in peak distributions of 300-600 amu, while with an increase of the laser power, an enhancement of the signal associated with the heavier compounds has occurred. The authors mentioned that such enhancement becomes even more pronounced for the denser samples and under cw ion extraction conditions, which resulted in a neat displacement of the maximum of the spectrum to masses about 1500 amu and to a significant ion yield at molecular weights well above 3000 amu.

Hortal et al.³⁸¹ reported in one of their papers investigation based on the comparison of coal and petroleum asphaltenes. LDI experiments on coal versus petroleum asphaltenes help discern whether the island or archipelago model applies. They showed that asphaltenes have average molecular weights smaller than 1000 amu. For the coal asphaltenes average weights were found to be smaller than 500 amu, meaning that they are significantly lighter than petroleum asphaltenes, which the average weight range is typically found between 600 and 800 amu. Petroleum asphaltenes have a high mass tail, which may fall off rapidly above

1500 amu. These large PAHs coupled with relatively small molecular weights are consistent with the single fused ring molecular architecture of asphaltenes, i.e. island model.

Besides the applied ionization source, complex organic samples still require ultrahigh resolving analysis technique for in-depth characterization.³⁷ We have seen that the application of LDI/MALDI coupled to TOF has been used for the characterization of petroporphyrins,⁶⁰⁶ crude oils,⁶⁰⁸ and their fractions,^{583, 587} as well as for the determination of the MWDs of asphaltenes.^{36, 39, 381, 609}

3.4.7 Matrix-Assisted Laser Desorption Ionization (MALDI)

The analytical community has focused to understand the molecular constituents. Often the complex mixtures need hydrocracking or hydrotreating to be able to generate more valuable final products.⁷ In the introduction of this review, it was shortly mentioned the importance of ionization techniques in providing important insights to the chemical makeup of the residues but they seem to be insufficient when ionizing fractions having a higher content of heteroatoms and alkylation.^{7, 28} With the appearance of matrix-assisted laser desorption ionization (MALDI) and LDI, new technologies have moved a step forward. MALDI is a technique in which the organic matrix is used, and that way may facilitate the ionization of target analytes. There are several reviews explaining the MALDI process.^{46, 49, 66, 67} MALDI as an analytical method is found to be of wide interest because it represents an effective approach to obtain information on the molecular weight of macromolecules. It may lead to information on macromolecules mixtures although the ion suppression effects can be present to some extent. This is possible due to the privileged formation of singly charged molecular species ([M + H]⁺, [M-H]⁻, alkali cationized molecules).⁶⁶ Various mechanisms are proposed to explain MALDI ionization:⁵²

- (i) primary ion formation from the matrix (Ma);
- (ii) secondary ion formation of the analyte (A) originating from the gas phase interaction of reactive matrix ions and neutral molecules of the analyte.

Figure 17 represents the MALDI ionization process from which can be seen that the matrix-analyte crystal is bombarded with a UV laser beam exciting the matrix, and transferring the energy to the analytes. Consequently, it results in the ionization and desorption of the analytes.⁴⁶



Figure 17. MALDI ionization process

Zhang et al.⁵⁸ have integrated the solvent-free sample preparation MALDI technique with FT-ICR-MS to study the compositional and structural information of solid soot particles. Due to their limited solubility, it is difficult to achieve a comprehensive characterization of the entire solid samples by conventional organic analysis techniques, such as GC/MS,^{610, 611} HPLC, and size-exclusion chromatography (SEC).^{612, 613} Besides the soot particles, MALDI-FT-ICR-MS can be potentially suitable for the characterization of other carbonaceous materials. They introduced the modified version of the iso-abundance plot that could be of great importance when comparing the distribution differences among samples. Next, it was mentioned that the MALDI technique can minimize the possibility of ion fragmentation in the LDI source. The researchers⁵⁸ explained that the mass spectrum reflects the original state of the solid samples with high confidence, which

together with the high mass resolution and accuracy of FT-ICR-MS makes the developed method more reliable. Applying this technique, it is possible to assign the chemical formulas of the molecules in carbonaceous particles, as well as to reveal the minor components in the samples. Also, the sample preparation parameters such as matrix/analytes ratio and mixing time were optimized to minimize background signals and show good reproducibility. And the last advantage of FT-ICR-MS device is the accurate masses, which assists the exclusion of background signals in the mass spectra of samples.⁵⁸

Haya et al.⁶⁰⁷ studied different matrices for Arabian Light crude oil asphaltene at two different laser energies (40 and 80 μ J/pulse) using MALDI. They found the peaks for MWDs at about 500 amu with a high–mass tail extending up to 3000 amu, yielding average weights of about 900 amu, see Figure 18. They noticed that the signal in the low MWD range is smaller for the sample diluted in the CuSO₄ salt. Additionally, it can be seen that from the first two spectra (a and b) that the aggregation effects have become negligible even in the cw ion extraction mode.



Figure 18. MALDI spectra of the Arabian Light crude oil asphaltene diluted in dithranol matrix – a,b) dried–droplet method, c) TCNQ matrix (solvent–free method); d) CuSO4 salt (solvent–free method). Delayed and cw ion extraction and 40μ J or 80μ J laser pulse energies (266 nm) were employed as indicated. The lower laser energy spectra have been scaled by the factors indicated in each panel for direct comparison with the higher energy ones. Reproduced with permission from ⁶⁰⁷, Copyright 2007 John Wiley and Sons.

Further on, MALDI coupled to TOF-MS showed that the presence of a low-molecular-weight crystalline matrix with a photo-absorption maximum which is matching the wavelength of the laser pulse may allow the desorption and ionization of intact proteins.⁵⁰ It was reported that the matrix can efficiently absorb UV laser radiation, which could result in its rapid ionization and dissociation into the gas phase. This may rapidly expand gas phase entrains intact analyte ions.³⁹⁵ Since matrix absorbs most of the laser radiation, and not the analyte. Primary, MALDI has been utilized for analysis of high MW biomolecules, such as peptides and proteins,^{42, 43, 395} however, recent studies focus more on the characterization of polymers,^{48, 614, 615} and heavy fossil fuels.^{51, 616}



Figure 19. MALDI-TOF chromatogram of heavy oils. Reproduced with permission from ⁵¹, Copyright 2016 Elsevier.

Recently, Kim et al.⁵¹ published a short communication about the characterization of petroleum-based heavy oil via MALDI-TOF. They performed vis-breaking of various heavy oils such as vacuum residue, bitumen and pyrolyzed fuel oil was carried out at 350 °C, 400 °C and 450 °C to investigate the fractions based on MWD. A decrease in MWD range from vacuum residue to bitumen and again to pyrolyzed fuel oil have been noticed (Figure 19), however, it was expected due to their origins and chemical compositions. The highest signal at 400m/z was detected for the vacuum residue, while for the bitumen a peak was found at approximately 300 m/z. The narrowest MWD was reported for the pyrolyzed fuel oil, which indicated a lighter chemical composition in that sample. Obviously, determination of the MWD range for heavy oils is possible via MALDI-TOF due to the complexity of the calculation and spectral separation process, still, comparisons of the feed and product following the reaction may contribute to a better understanding of the MWD.



Figure 20. ET-MALDI-FT-ICR spectra resulting from the direct analysis of the (A) L-L ACN extract and (B) HPTLC band (corresponding to porphyrins) from a Middle-Eastern crude oil sample.⁵⁵

Further on, it is known that vanadium and nickel are the two most abundant trace metals in petroleum, which may occur in two forms - metalloporphyrins (petroporphyrins) and metallononporphyrins. Analytic techniques such as ultraviolet-visible (UV-Vis) spectroscopy and MS are of huge importance for the characterization of petroporphyrins, and generally, MS has been used to study the MWD of petroporphyrin mixtures. However, the electron impact (EI) MS has been used widely. Hence, the MS with molecular ion production which has a high sensitivity is found as a promising technique in this field. ⁶⁰⁶

Ramírez-Pradilla and his co-workers⁶¹⁷ have developed a MALDI matrix that can promote selective ionization of petroporphyrins via electron transfer reactions. After an HPTLC step, they used a novel type of matrix for the characterization of the asphaltenes. Their results showed the selective ionization of petroporphyrins, as well as the increment in several molecular formulas when compared to those reported in previous studies. Another study done by Pradilla et al.⁵⁵ has shown that the compound α -CNPV-CH3 can be effectively used as a matrix for the electron transfer (ET) process in MALDI-MS for the selective ionization and detection of nickel and vanadyl porphyrins present in ACN extracts, and HPTLC-purified fractions from a Middle-Eastern crude oil. They have taken an advantage of the low ionization potential of petroporphyrins to develop a MALDI matrix that is capable to selectively ionize molecules in a complex mixture. This contributed to simplified sample preparation and increased the number of identified porphyrins per sample. Figure 20 is shown the selectivity of their new matrices with an increased porphyrin signal in both liquid and TLC extractions. The advantage of minimizing and enhancing the sensitivity of the MALDI by limiting ion types to a single class is paramount for porphyrin analysis. This study has proven that the combination of the high selectivity of ET reactions in MALDI (+) with the high mass accuracy, and resolution of FT-ICR ensures an additional tool for porphyrin analysis by mass spectrometry. Continuous progress within the separation technologies will enable cleaner fractions for petroporphyrin analysis.

For example, for the different MS ionization methods, biochemical matrices may be challenging due to their imparted ion signal suppression,⁶¹⁸ which can impede the crystallization in the case of MALDI. However, Chandler et al.⁶¹⁹ have studied the suitability of commonly used buffers for MS analysis. They showed that label-based non-MS assays can be adapted for MALDI MS analysis. Also, with the implementation of an additional MALDI spot washing step, there is a possibility to reduce buffer concentrations which may result in more assays accessible for analysis with MALDI MS.⁵⁷ Krenkel et al.⁶²⁰ reported in their recent paper

that liquid atmospheric pressure (AP) MALDI has the advantage because it combines the versatility of ESI and the analysis speed of conventional solid state MALDI under AP.

3.4.8 Field Desorption Ionization (FDI)

Field desorption ionization is used for the analysis of a variety of non-volatile analytes that are difficult to ionize by other sources.⁶⁰ FDI is considered a soft technique, which yields intact M+• molecular ions for a wide range of compound classes, such as paraffins, cycloparaffins, aromatic hydrocarbons, and non-polar sulfur, which are not possible to detect by ESI or MALDI. Despite its advantage, this analysis can be extremely difficult to perform due to the pulsed nature of the FDI source, combined with the need to reapplication of the sample after each experiment. However, the development of liquid injection field desorption/ionization (LIFDI) enabled sample application without breaking the vacuum.⁶²¹ LIFDI has been used for analyzes of different samples such as petroleum mixtures,^{61, 548, 622, 623} metal complexes,⁶²⁴⁻⁶²⁶ and fullerenes.^{627, 628}

Smith et al.^{59, 60} have reported in one of their papers about automated LIFDI-FT-ICR-MS that enabled averaging more than 200 optimized mass spectra of a South American crude oil for improved dynamic range, mass resolving power, and mass accuracy relative to a single-application experiment. With these techniques, it is possible to achieve a more detailed compositional analysis of non-polar and low-polarity species in complex mixtures.

3.4.9 Others

Although MALDI has become a powerful analytical tool for the study of thermally labile, non-volatile samples by MS, its ionization efficiency depends on the properties of the analyte and matrix, as well as the sample preparation conditions, and the deposition method. Therefore, researchers continue to look towards alternative desorption/ionization methods. Decades ago, Lindner et al.⁶²⁹ have demonstrated a laser-driven shock waves in desorption/ionization mass spectrometry. Later several studies related to laser-induced acoustic desorption (LIAD)-ionization have appeared in the literature. Authors employed various thin metal films, such as copper⁶³⁰ or mercury⁶³¹ to shield the samples from the high-intensity laser. Unfortunately, the ionization of the samples has been proved to be difficult. Generally, LIAD has not been developed as a practical desorption/ionization method because the predominant desorption of neutral molecules predicted by Lindner forced researchers to combine LIAD with ionization sources such as EI and CI. Particularly, the CI method has been observed as an attractive approach due to its wide range of ionization modes (i.e. electron transfer, atom transfer, group transfer). However, this ionization method brings along several limitations. One of them is a low ionization efficiency due to short interaction time with reagent ions due to high velocities of the molecules. Another limitation is linked to the time necessary to collect the mass spectrum. The time is much longer than the duration of the pulse of neutral molecules generated by laser desorption.⁶³² We have pointed out in the sections related to FT-ICR various advantages that it may offer over other instruments in laser desorption/chemical ionization (LD/CI) experiments. First of all, due to the simultaneously detected ions, and secondly, FT-ICR may allow the use of several consecutive reaction/ion isolation steps to form reagent ions. Those ions may be stored in the cell prior to the introduction of the neutral analyte and consequently, be exposed to a large population of neutral molecules desorbed by several laser pulses.⁶³²

Perez et al.⁶³² have studied LIAD of neutral molecules coupled with EI and CI as an analysis method for non-volatile organic and biomolecules in FT-ICR-MS. They designed the experiment for a transmission mode laser desorption, placing the sample on the opposite side of the metal foils (copper or titanium), from which LIAD produced a high-amplitude acoustic wave by laser ablation. The results indicated that LIAD coupled to post-desorption IE or CI in FT-ICR can be a practical method for the analysis of thermally labile, non-volatile molecules. The main advantage of this approach is better to control the ionization step (through a selection of reagent ions) and a broader choice of ionization modes than LDI and MALDI methods.

4 Analysis for kinetic studies

In the first part of this review, separation methods coupled to ionization techniques and analyzers are discussed with their respective advantages, disadvantages and applications. Because of their importance in petrochemical industry, many have focused on optimizing mass spectrometry for detailed identification and quantification of petroleum fractions. Besides the analysis of petroleum fractions, the analysis of detailed product composition downstream of petrochemical processes is important for the design and optimization of processes. Even though research has not focused in that much detail on the use of mass spectrometry for downstream product streams, there is tremendous potential to advance chemical process design by detailed product characterization and subsequent chemical kinetic modelling. This will only become more pronounced when we move to a more circular economy.⁶³³

In this section, we discuss the state-of-the-art of kinetic model development with applications in (petro)chemical industrial processes. The combination of GC and MS coupled to a reactive system for detailed product characterization is discussed. The advantage of using mass spectrometry compared to other conventional product quantification (e.g. GC-FID/TCD) methods is highlighted for the analysis of reactive intermediates and for direct kinetic measurements with time-resolved experimentation.

4.1 Detailed kinetic models for petrochemical processes

Kinetic models are developed to describe the mechanisms of chemical reactions in (petrochemical) processes. Understanding the chemistry on a fundamental level is a crucial step in the development and upscaling of those processes. Kinetic models provide physical insights in the complex conversion of feedstock molecules to a broad spectrum of products. Besides the specific reactions between species, kinetic models also have information on the thermodynamics of the species and the rate coefficients of the reactions. Advances in theoretical calculations ⁶³⁴ and computer science (e.g. machine learning^{635, 636}), have shifted to use of fitted empirical data for thermodynamics and kinetics to more fundamental approaches. The kinetic models are further used in combination with reactor simulations or computational fluid dynamics for the design and optimization of the complete process,

With the increase in computational power, the development of kinetic models for petrochemical processes have moved from smaller kinetic models with a limited set of species and reactions to single-event detailed kinetic models. Those models contain thousands of products and reactive intermediates and up to hundreds of thousand reactions between those species. Details on how those kinetic models are built are beyond the scope of this work and can be found in dedicated review papers⁶³⁷⁻⁶⁴⁰. The complexity of single-event elementary reaction kinetic models increases logarithmically with increasing fuel complexity, specifically for kinetic models with radical intermediates (e.g. models for pyrolysis, oxidation and combustion processes). With the increasing complexity of the kinetic models for the broad product spectrum, accurate and detailed experimental quantification and identification of those products is important. For certain applications, as discussed below, the use of mass spectrometry has advantages over other conventional detectors (nitrogen- or sulfur chemiluminescence and atom emission detectors) that are coupled to gas or liquid chromatography.

In older or lumped kinetic models, the focus is on modelling the formation of the main products or cuts/fractions, e.g. ethylene and propylene in steam cracking or the naphtha yield in an fluid catalytic cracker. To validate the performance of the kinetic models, reactor simulations are performed to imitate the experimental unit and procedure. Depending on the complexity of the fuel, different lumping strategies or model reduction methods are used such that they can be employed to model steam cracking reactor design⁶⁴¹ or combustion engine performance^{642, 643} with a reasonable computational time. In those cases, the models are reduced with the focus on optimizing the model performance for a limited set of important product species for a range of experimental conditions. The more recent detailed kinetic models allow to model a

broader product spectrum. Some examples are the detailed formation of multi-ring polyaromatic hydrocarbons during pyrolysis, the decomposition of hetero-atomic impurities present in petroleum feedstocks, and the complex product spectrum during the thermal decomposition of biomass and plastic waste.

4.2 Common MS techniques for kinetic studies

When coupled to a reactor, the various configurations of ionization sources, mass spectrometers, and possible coupling to GC/LC discussed in this review can also be used for kinetic studies. In conventional apparatus, diagnostics are implemented downstream of the reactor unit for online characterization of the product stream. The ionization source and mass spectrometers are typically preceded by GC or LC for detailed analysis of a broad range of products. In those cases, MS coupled to EI is used for a qualitative assessment, while other detectors (most commonly FID) are used for quantification. For some specific measurements coupling GC or LC is not possible and MS is directly connected to the reactive system. In those cases, photoionization is preferred to reduce fragmentation and a dedicated sampling system is required. Here, we first discuss the coupling of MS to the reactor configurations i.e. for detection of reactive intermediates and for characterization of products as a function of time, are explained.

4.2.1 Reactor-GC/MS analysis

For complex reaction mixtures, downstream characterization of the broad product spectrum can be tedious. Kinetic studies require detailed quantification of all important products. For complex product streams, and even more for the conversion of renewable resources, a dual diagnostics system is required with GC or GC×GC coupled to both FID and MS. The reactor is in this case directly coupled to the GC by a sampling system. The mass spectrometer is usually preceded by EI and used for identification of the different products by their molecular fragmentation fingerprint, while the FID is used for quantification of the products. One recent example is the frontier micro-pyrolyzer experimental apparatus with a tandem reactor that can be used to study the thermal decomposition or catalytic cracking of conventional and renewable feedstocks, such as bio-oils or plastic waste^{644, 645}.

One commonly used method to characterize the chemical composition of involatile components by their thermal decomposition products is pyrolysis gas chromatography coupled to mass spectrometry (Py-GC/MS). The main difference between Py-GC/MS and conventional GC/MS is the way the sample is introduced into the gas chromatograph. Instead of direct injection of the sample, the thermal decomposition products of the sample are analyzed. The involatile components are introduced in a quartz tube with a preset temperature and in an inert atmosphere. Depending on the pyrolysis temperature and residence time, various products are introduced into the GC by decomposition of the weakest bonds in the involatile material. By analysis of the decomposition products, information on the structure of the involatile component can be revealed. Studies at different operating conditions of the Py-GC/MS allow to further study the kinetics for breakage of the weakest bonds.

Even though some research has been done for applications to heavier fractions of petroleum products⁶⁴⁶⁻⁶⁴⁸, the majority of recent research focusses on characterization of the structure and impurities of biomass⁶⁴⁹⁻⁶⁵¹ polymers⁶⁵², and plastic waste^{653, 654}. With respect to petroleum products, Riley et al.⁶⁵⁵ developed a method for the analysis of crude and heavy fuel oil asphaltenes, Calemma et al.⁶⁴⁷ studied the structural characteristics of asphaltenes, and Yin et al.⁶⁴⁸ used Py-GC×GC-MS to study the composition of coal.

4.2.2 Photoionization mass spectrometry for quantitative detection of reactive intermediates

Conventional diagnostics often fail in their ability to detect reactive intermediates, such as radicals in the case of pyrolysis or peroxides in the case of combustion processes. Those intermediates are typically present in a reactive mixture in trace amounts and at specific reactive conditions such as elevated temperatures or low pressures. Since those reactive intermediates are only stable at the studied reactive conditions, they cannot be analyzed by GC or LC. Additionally, reactive intermediates will decompose in the columns of GC or LC before they reach the detector. One common technique for detection and quantification of such species is by direct coupling of the reactor to laser absorption or fluorescence⁶⁵⁶. However, to detect a broad range of reactive intermediates, especially for large hydrocarbon radicals, mass spectrometry with probe

sampling has proven to be more successful. Careful control of the sampling system is crucial for accurate results. Some common sampling techniques include microprobes or molecular beam sampling. The use of EI with molecular beam sampling is well-known and dates back to the 1940s⁶⁵⁷. The main disadvantages of using EI are the numerous fragmentations, which limits compound identification if not preceded by GC or LC, and the difficult distinction of isomers because of the low energy resolution of the ionizing electrons. More commonly applied is photoionization induced by laser or synchrotron VUV radiation. In particular synchrotron vacuum UV photoionization mass spectrometry (SVUV-PIMS) with molecular beam sampling is an exceptionally powerful method to determine the composition of complex combustion systems^{658, 659}. Some recent reviews by Cool⁶⁶⁰, Li and Qi⁶⁶¹, Qi⁶⁶², Yang⁶⁶³ summarize the application of SVUV-PIMS to combustion systems and the subsequent use in kinetic model development. One major advantage of SVUV-PIMS compared to traditional mass spectrometry with laser induced photoionization is the tunability of the synchrotron radiation which allows for detection and quantification of isomeric structures, and control of molecular fragmentation. Laser VUV photoionization has either a fixed wavelength or a wavelength that is not easy tunable. Alternatively, REMPI has been used in several applications. This technique is limited to smaller species and aromatics, and the wavelength has to be tuned for each molecule with isomers.

One very recent example of an experimental unit with a cylindrical quartz reaction cell, molecular beam sampling, and product characterization using photo-ionization time-of-flight mass spectrometry (PI-TOF-MS) is built in the Combustion Dynamics Laboratory at Massachusetts Institute of Technology⁶⁶⁴. A scheme of the unit is given in Figure 21. Recently, several kinetic studies have been performed with the focus on the complex formation of polyaromatic hydrocarbons during pyrolysis^{665, 666}. The experimental unit allows the detection of polyaromatic hydrocarbons, unstable molecular intermediate structures, and radical species, With the use of gas chromatography, only the detection of the former would be possible.



Figure 21. Front cross-sectional view of the apparatus showing the reaction cell, the gas sampling region, and the diagnostics section. Reproduced with permissions from ⁶⁶⁴, Copyright 2018 AIP Publishing.

4.2.3 Time-resolved mass spectrometry for direct kinetic measurements

One major advantage of mass spectrometry is its ability to process ions in a millisecond time frame. The collection of data with a temporal resolution together with the separation of products and reactive intermediates based on mass-to-charge ratios allows one to differentiate between various chemical states as a function of time. Because of these features, time-resolved mass spectrometry (TRMS) has been one of the most prominent techniques in the study of dynamical systems and reaction kinetics⁶⁶⁷. Many applications of TRMS involve biochemical processes such as the study of organic reaction kinetics, the dynamics of

protein folding, biocatalysis, and metabolic profiling⁶⁶⁸⁻⁶⁷⁰. Some studies have focused on kinetics of (petro)chemical related processes^{649, 669, 671-674}, for example the pyrolysis or combustion of biomass and plastic waste or the screening of various catalysts. One specific method is TGA-MS, where a thermogravimetric analysis of involatile components, e.g. biomass or solid waste, is directly coupled to MS for direct measurement of the product composition as a function of time^{675, 676}.

Most of the existing MS techniques are optimized to have a high mass resolution for detailed composition measurements. For TRMS, on the other hand, the high temporal resolution is more important to gain information on fast changes in chemical composition or measurements of short-living chemical species. The temporal resolution depends on various factors such as the ion source, the mass analyzer, and the detector. Also decreasing the volume between the reaction zone and the ionization are crucial in time-resolved experimentation. One of the main used ionization sources for TRMS with application to biomolecules is ESI, since this technique enables efficient transfer of liquid-phase molecules to the gas phase at atmospheric pressure⁶⁶⁹. Typical mass analyzers include quadrupole, TOF, and ion traps. For pyrolysis or combustion processes, soft-ionization techniques are preferred. When coupled to gas chromatography, EI methods can provide fingerprints of molecules and allow easy identification. However, in case of time-resolved experimentation where the usage of GC is not possible, fragmentation needs to be reduced to detect a broad range of products. Heger et al.⁶⁷⁷ used REMPI-TOFMS for online measurements of polyaromatic hydrocarbons in a waste incineration plant. Later, Zimmerman et al.⁶⁷⁸⁻⁶⁸⁰ used single-photon ionization (SPI) and TOF-MS with µ-probe sampling to study the formation of products in burning cigarettes. Because of the wider applicability to all organic compound classes, SPI was preferred over REMPI⁶⁷⁸. Recently a new experimental apparatus was built at Sandia National Laboratories for direct time-resolved probing of high-pressure gas-phase chemical reactions by photoionization mass spectrometry⁶⁸¹. Ions are created by VUV photons originating from laboratory discharge lamps or from a synchrotron beamline from Lawrence Berkeley Lab's Advanced Light Source. The ions are analyzed by a custom TOF-MS. The main applications of this apparatus are hydrocarbon oxidation in low-temperature autoignition.

5 Conclusion and Outlook

Over the past decades, the characterization of crude oils and petroleum fractions has evolved from the analysis of physical-chemical and thermodynamical properties going further to compositional analysis, different instrumental methods of analysis, and molecular modeling.

Early on petroleum fractions and products were only characterized globally, focusing on characteristics that correlate with the chemical changes that occur during petroleum refining and upgrading. Advances in separation processes have made it possible to go beyond these so-called commercial indices such as boiling points, specific gravity, molecular weight, refractive index, and CHNSO, PONA, PIONA, PINA, and PNA compositional information. Applying more advanced techniques next to the progress of existing analytical tools allows to determine an unprecedented detailed compositional characterization of crude oils and related fractions.

Since society has moved towards using a wide range of energy resources, in particular, heavier crude oils, shale oil, plastic waste derived oils, and renewable biomass-derived fractions, it was and it remains essential to develop new technologies which will enable the characterization of high-boiling-point and low-solubility molecules. Gas chromatography continues playing an important role in shaping the future of R&D in the oil and gas industry. The powerful separation which can be achieved by GC in combination with mass spectrometry has contributed to easier and faster chemical identification and quantification.

So it is possible to ode SFC - $GC \times GC$ methods for the analysis of heavy petroleum fractions. Indeed, the implementation of an SFC step has contributed to the separation of the samples into saturated, unsaturated, and polar fractions. Furthermore, it was presented the ability of HPLC to be applied to high-boiling samples. LC-MS offers superior selectivity and an ability to identify conformational information based on the mass/charge ratio of the measured ions.

On the other hand, ICP-MS is an excellent technique for detecting trace elements in different sample matrices. It allows the measurement of multiple elements simultaneously in a single analysis. Apart from its numerous features, which include high sensitivity, wide linear dynamic range, and wide elemental coverage, one of the biggest disadvantages of ICP-MS is the high cost. Moreover, the use of volatile petroleum fuels in ICP-MS can make the plasma unstable.

High-resolution mass spectrometry, such as FT-ICR-MS, stands out among other analytical techniques due to its outstanding ability to determine the composition and structure of crude oil constituents. This technique may allow detection of the unique elemental formulas of thousands of molecules in a crude oil sample. Also, it can be utilized for very high-boiling and non-boiling petroleum fractions beyond the reach of $GC/GC \times$ GC. Moreover, the combination of FT-ICR-MS with different ionization sources (i.e. APPI, ESI, APCI, APLI, LDI, MALDI, and FDI) has largely contributed to the recent advances in petroleum science. APPI is an efficient ionization technique for samples containing non-polar or low polar compounds, and sulfur aromatic species, as well as APLI which is preferably applied for analysis of non-polar compounds. APCI showed the best results for aliphatic hydrocarbons, analyzing compounds with higher polarity, such as phosphoric acid esters and carbamates. Furthermore, ESI has been shown as another promising method for ionization of non-volatile and complex molecular samples bearing polar functional groups, especially nitrogen- and oxygen-containing groups. Besides these ionization methods, LDI and MALDI have extended the application of MS into solid, non-volatile petroleum products, which were often difficult to analyze by the previously mentioned approaches. LDI-MS has a mass resolution capable of discerning chemical composition, and structure in complex carbonaceous mixtures, particularly in combination with chromatographic separation. Although MALDI has been utilized often for analysis of high MW biomolecules (i.e. peptides and proteins), recent studies have been focused more on polymer characterization and heavy fossil fuels. Finally, FDI is used for the analysis of a variety of non-volatile analytes that are difficult to ionize by other sources. With this ionization technique, a wide range of compound classes, such as paraffins, cycloparaffins, aromatic hydrocarbons, and non-polar sulfur can be detected, which were not possible to detect by ESI or MALDI.

Although the petroleum era may gradually come to its end during the current century, the analytical methods have proven tremendous progress to characterize even the most complex residual oils during the past years. Nevertheless, crude oils or their fractions with a high viscosity, high melting point, and lower volatility remain difficult to analyze. Researchers continue looking towards new advanced analytical and computational techniques to assist them in these developments because process-related upsets are typically related to small amounts of impurities that are present or accidentally added to those fractions. This will become even more important now that feeds derived from plastic waste will be more and more considered that contain typically a large amount of impurities. Because of environmental concerns, the detailed analysis of hetero-atomic impurities in petroleum fraction have become more important than ever. It is expected that research on diagnostics the coming years will focus to characterize those impurities in even more detail especially when we try to move to a more circular economy.

In the coming years, the development of online sample preparation steps in multidimensional systems is expected to make a breakthrough, as it may enable the speciation and quantification of individual elemental compounds. Also, new solutions might be capable of promoting isomer separations. Next to that, future investigations should focus on the elucidation of the molecular properties that affect the stability of petroleum products. For example, insights into the role of the dominant molecular structures in the aggregation of asphaltenes. Moreover, further studies could be oriented to more automated experimental design, especially for the hyphenation of additional chromatographic separations, such as gas or liquid chromatography.

Diagnostics for analysis of petroleum products, in particular MS, have made tremendous progress for several decades. The importance of the detailed analysis of petroleum fractions remains, and has shifted to analysis of the heavier fractions such as asphaltenes. The comprehensive knowledge on MS will be extensively applied during the next decade to characterize alternative resources. The last couple of years, advanced MS

techniques have been adapted with application to several kinds of biomass (e.g. lignocellulose and algae). It is expected that this trend will continue and find new applications to alternative renewable resources such as plastic waste.

Also the advantages of using MS in kinetic studies and in the analysis of downstream product compositions are being more and more embraced. Even though MS is typically used for qualitative purposes rather than for quantification of product compositions, it can have significant advantages compared to conventional methods for detection of reactive intermediates and in time-resolved experimentation. In those cases, the use of GC or LC preceding the MS is not possible. To allow detection of a broad range of products, fragmentation needs to be minimized and soft ionization techniques are required. The last few years, tremendous progress has been made in this area, and dedicated experimental apparatus are built. Some of those are linked to a synchrotron source for ionization. It is expected that those techniques will further develop the coming years and lead to new breakthroughs in kinetic studies. One problem that remains and should be tackled is the reduced accuracy in product quantification using PI-MS compared to conventional methods such as GC-FID. In this aspect, there is a need for better predictive tools for species cross-sections, e.g. for reactive intermediates and less common molecules.

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Nomenclature

(HP)TLC	(High-performance) Thin layer chromatography
(LI)FDI	(Liquid injection) Field desorption ionization
¹³ C NMR	Carbon-13 Nuclear magnetic resonance
1D GC-MS	One-dimensional gas chromatography mass spectrometry
¹ H NMR	Proton Nuclear magnetic resonance
ACN	Acetonitrile
AI	Ambient ionization
ALCO	Arabian light crude oil
amu	Atomic mass unit
AP	Atmospheric pressure
APCI	Atmospheric pressure chemical ionization
APGC	Atmospheric Pressure Gas Chromatography
APLI	Atmospheric pressure laser <i>ionization</i>
APLI	Atmospheric pressure laser ionization
APPI	Atmospheric pressure photoionization
APSPLI	Atmospheric pressure single-photon ionization
ASAP	Atmospheric Solid Analysis Probe
ASTM	American Society for Testing and Materials
BPC	Base peak chromatogram
СЕ	Capillary electrophoresis
CHNSO	Carbon, hydrogen, nitrogen, sulfur, oxygen elemental
CI	Chemical ionization
CID	Collision-induced dissociation
Da	Dalton
DAD	Diode array detection
DAO	De-asphalted oil
DART	Direct Analysis in Real Time
DBE	Double bond equivalent
DESI	Desorption Electrospray Ionization
DIP	Direct Inlet Probe
DMSO	Dimethyl sulfoxide
EASI	Easy Ambient sonic-Spray Ionization
EI	Electron ionization
ESI	Electrospray ionization
ET	Electron transfer
ETD	Electron transfer dissociation
FAB	Fast-atom bombardment
FBP	Final boiling point
FFT	Fast Fourier transform
FID	Flame ionization detection
FPD	Flame Photometric Detection
FT-ICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
FTIR	Fourier transform infrared
GC	Gas chromatography
$GC \times GC$	Two-dimensional gas chromatography
GC-FIMS	Gas chromatography -field ionization mass spectrometry
GC-GC	Heart-cutting gas chromatography

GPC	Gel permeation chromatography
GP-MSE	Gas Purge Microsyringe Extraction
HFO	Heavy fuel oil
HPLC	High Pressure liquid chromatography
HRMS	High resolution mass spectrometry
HTGC	High temperature gas chromatography
IBP	Initial boiling point
ICP-MS	Inductively coupled plasma - Mass spectrometry
IL	Ionic liquid
IMS	Ion mobility spectrometry
IRMS	Isotope ratio mass spectrometry
KMD	Kendrick mass defect
LA	Laser ablation
LC	Liquid chromatography
LC-MS	Liquid chromatography - Mass spectrometry
LDI	Laser desorption ionization
LIAD	Laser Induced Acoustic Ionization
LSI	Laser spray ionization
LSIMS	Liquid secondary ion mass spectrometry
m/z	mass-to-charge ratio
MAI	Matrix-assisted ionization
MALDI	Matrix-assisted laser desorption ionization
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MS-MS	Tandem Mass spectrometry
NCD	Nitrogen chemiluminescence detector
NMR	Nuclear magnetic resonance
PAHs	Polycyclic aromatic hydrocarbons
PCNs	Polychlorinated naphthalenes
PINA	Paraffins, isoparaffins, naphthenes, and aromatics
PIONA	Paraffins, isoparaffins, olefins, naphthenes, and aromatics
PI-TOF-MS	Photoionization time-of-flight mass spectrometer
PNA	Paraffins, naphthenes, and aromatics
PONA	Paraffins, olefins, naphthenes, and aromatics
ppb	Parts per billion
Py-GC/MS	Pyrolysis gas chromatography coupled to mass spectrometry
Ref.	Reference
REMPI	Resonance-enhanced multiphoton ionization
RF	Radio frequency
SAI	Solvent-assisted ionization
SARA	Saturates-Aromatics-Resins-Asphaltenes
SCD	Sulfur chemiluminescence detector
SEC	Size-exclusion chromatography
SF	Sector field
SFC	Supercritical fluid chromatography
SOA	Secondary organic aerosols
SPI	Single photon ionization
SVUV-PIMS	Synchrotron vacuum ultra-violet photoionization mass spectrometry
TAS	Tri-aromatic steroid

TG	Thermogravimetry
TGA	Thermal gravimetric analysis
TIC	Total ion chromatogram
TOF-MS	Time of flight mass spectrometer
TRMS	Time-resolved mass spectrometry
UCM	Unresolved complex mixture
UV-VIS	Ultraviolet-visible spectroscopy
VGO	Vacuum gas oil
VOCs	Volatile organic compounds
XRF	X-ray fluorescence

Bibliography

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References

1. Gough, M.; Rowland, S., Characterization of unresolved complex mixtures of hydrocarbons in petroleum. *Nature* **1990**, 344, (6267), 648-650.

2. Panda, S. K.; Andersson, J. T.; Schrader, W., Characterization of Supercomplex Crude Oil Mixtures: What Is Really in There? *Angewandte Chemie International Edition* **2009**, 48, (10), 1788-1791.

3. Sorrell, S.; Speirs, J.; Bentley, R.; Brandt, A.; Miller, R., Global oil depletion: A review of the evidence. *Energy Policy* **2010**, 38, (9), 5290-5295.

4. Palacio Lozano, D. C.; Thomas, M. J.; Jones, H. E.; Barrow, M. P., Petroleomics: tools, challenges, and developments. *Annual Review of Analytical Chemistry* **2020**, 13, 405-430.

5. Rodgers, R. P.; McKenna, A. M., Petroleum analysis. *Analytical Chemistry* **2011**, 83, (12), 4665-4687.

6. Demirbas, A.; Alidrisi, H.; Balubaid, M., API gravity, sulfur content, and desulfurization of crude oil. *Petroleum Science and Technology* **2015**, 33, (1), 93-101.

7. Ryan, D. J.; Qian, K., Laser-Based Ionization: A Review on the Use of Matrix-Assisted Laser Desorption/Ionization and Laser Desorption/Ionization Mass Spectrometry in Petroleum Research. *Energy & Fuels* **2020**, 34, (10), 11887-11896.

8. Hudebine, D.; Verstraete, J. J., Reconstruction of Petroleum Feedstocks by Entropy Maximization. Application to FCC Gasolines. *Oil & Gas Science and Technology-Revue D Ifp Energies Nouvelles* **2011**, 66, (3), 437-460.

9. Van Geem, K. M.; Hudebine, D.; Reyniers, M. F.; Wahl, F.; Verstraete, J. J.; Marin, G. B., Molecular reconstruction of naphtha steam cracking feedstocks based on commercial indices. *Computers & Chemical Engineering* **2007**, 31, (9), 1020-1034.

10. Alomair, O.; Jumaa, M.; Alkoriem, A.; Hamed, M., Heavy oil viscosity and density prediction at normal and elevated temperatures. *Journal of Petroleum Exploration and Production Technology* **2016**, 6, (2), 253-263.

11. Azinfar, B.; Zirrahi, M.; Hassanzadeh, H.; Abedi, J., Characterization of heavy crude oils and residues using combined Gel Permeation Chromatography and simulated distillation. *Fuel* **2018**, 233, 885-893.

12. Alvarez-Majmutov, A.; Gieleciak, R.; Chen, J., Modeling the molecular composition of vacuum residue from oil sand bitumen. *Fuel* **2019**, 241, 744-752.

13. AlHumaidan, F. S.; Hauser, A.; Rana, M. S.; Lababidi, H. M., NMR characterization of asphaltene derived from residual oils and their thermal decomposition. *Energy & Fuels* **2017**, 31, (4), 3812-3820.

14. Chibiryaev, A. M.; Kozhevnikov, I. V.; Shalygin, A. S.; Martyanov, O. N., Transformation of petroleum asphaltenes in supercritical alcohols studied via FTIR and NMR techniques. *Energy & Fuels* **2018**, 32, (2), 2117-2127.

15. van Beek, F. T.; Edam, R.; Pirok, B. W.; Genuit, W. J.; Schoenmakers, P. J., Comprehensive twodimensional liquid chromatography of heavy oil. *Journal of Chromatography A* **2018**, 1564, 110-119.

16. Vasconcelos, G. A.; Pereira, R. C.; Santos, C. d. F.; Carvalho, V. V.; Tose, L. V.; Romão, W.; Vaz, B. G., Extraction and fractionation of basic nitrogen compounds in vacuum residue by solid-phase extraction and characterization by ultra-high resolution mass spectrometry. *International Journal of Mass Spectrometry* **2017**, 418, 67-72.

17. Picó, Y., Advanced mass spectrometry. In *Comprehensive analytical chemistry*, Elsevier: 2015; Vol. 68, pp 77-129.

18. Wall, R., Instrumentation—Mass Spectrometry in Process Control. *Industrial & Engineering Chemistry* **1957**, 49, (8), 59A-60A.

19. Trimpin, S., Novel ionization processes for use in mass spectrometry: 'Squeezing' nonvolatile analyte ions from crystals and droplets. *Rapid Communications in Mass Spectrometry* **2019**, 33, 96-120.

20. Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M., Electrospray ionization for mass spectrometry of large biomolecules. *Science* **1989**, 246, (4926), 64-71.

21. Whitehouse, C. M.; Dreyer, R. N.; Yamashita, M.; Fenn, J. B., Electrospray interface for liquid chromatographs and mass spectrometers. *Analytical Chemistry* **1985**, 57, (3), 675-679.

22. Yamashita, M.; Fenn, J. B., Electrospray ion source. Another variation on the free-jet theme. *The Journal of Physical Chemistry* **1984**, 88, (20), 4451-4459.

23. Yamashita, M.; Fenn, J. B., Negative ion production with the electrospray ion source. *The Journal of Physical Chemistry* **1984**, 88, (20), 4671-4675.

24. Abdul Jameel, A. G.; Alquaity, A. B. S.; Campuzano, F.; Emwas, A.-H.; Saxena, S.; Sarathy, S. M.; Roberts, W. L., Surrogate formulation and molecular characterization of sulfur species in vacuum residues using APPI and ESI FT-ICR mass spectrometry. *Fuel* **2021**, 293, 120471.

25. Muller, H.; Alawani, N. A.; Adam, F. M., Innate Sulfur Compounds as an Internal Standard for Determining Vacuum Gas Oil Compositions by APPI FT-ICR MS. *Energy & Fuels* **2020**, 34, (7), 8260-8273.

26. Giraldo-Dávila, D.; Chacón-Patiño, M. L.; Orrego-Ruiz, J. A.; Blanco-Tirado, C.; Combariza, M. Y., Improving compositional space accessibility in (+) APPI FT-ICR mass spectrometric analysis of crude oils by extrography and column chromatography fractionation. *Fuel* **2016**, 185, 45-58.

27. Jameel, A. G. A.; Khateeb, A.; Elbaz, A. M.; Emwas, A.-H.; Zhang, W.; Roberts, W. L.; Sarathy, S. M., Characterization of deasphalted heavy fuel oil using APPI (+) FT-ICR mass spectrometry and NMR spectroscopy. *Fuel* **2019**, 253, 950-963.

28. Huba, A. K.; Huba, K.; Gardinali, P. R., Understanding the atmospheric pressure ionization of petroleum components: The effects of size, structure, and presence of heteroatoms. *Science of the Total Environment* **2016**, 568, 1018-1025.

29. Himmelsbach, M.; Buchberger, W.; Reingruber, E., Determination of polymer additives by liquid chromatography coupled with mass spectrometry. A comparison of atmospheric pressure photoionization (APPI), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI). *Polymer Degradation and Stability* **2009**, 94, (8), 1213-1219.

30. Manheim, J.; Zhang, Y.; Viidanoja, J.; Kenttämaa, H. I., An Automated Method for Chemical Composition Analysis of Lubricant Base Oils by Using Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of The American Society for Mass Spectrometry* **2019**, 30, (10), 2014-2021.

31. Gaspar, A.; Zellermann, E.; Lababidi, S.; Reece, J.; Schrader, W., Characterization of saturates, aromatics, resins, and asphaltenes heavy crude oil fractions by atmospheric pressure laser ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **2012**, *2*6, (6), 3481-3487.

32. Zuber, J.; Kroll, M. M.; Rathsack, P.; Otto, M., Gas Chromatography/Atmospheric Pressure Chemical Ionization-Fourier Transform Ion Cyclotron Resonance Mass Spectrometry of Pyrolysis Oil from German Brown Coal. *International journal of analytical chemistry* **2016**, 2016, 5960916.

33. Panda, S. K.; Brockmann, K. J.; Benter, T.; Schrader, W., Atmospheric pressure laser ionization (APLI) coupled with Fourier transform ion cyclotron resonance mass spectrometry applied to petroleum samples analysis: comparison with electrospray ionization and atmospheric pressure photoionization methods. *Rapid Communications in Mass Spectrometry* **2011**, 25, (16), 2317-2326.

34. 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.

35. Thiäner, J. B.; Achten, C., Liquid chromatography–atmospheric pressure laser ionization–mass spectrometry (LC-APLI-MS) analysis of polycyclic aromatic hydrocarbons with 6–8 rings in the environment. *Analytical and bioanalytical chemistry* **2017**, 409, (7), 1737-1747.

36. Rizzi, A.; Cosmina, P.; Flego, C.; Montanari, L.; Seraglia, R.; Traldi, P., Laser desorption/ionization techniques in the characterization of high molecular weight oil fractions. Part 1: asphaltenes. *Journal of mass spectrometry* **2006**, 41, (9), 1232-1241.

37. Zuber, J.; Dittrich, N.; Rathsack, P.; Vogt, C., Direct mass spectrometric analysis of solid coal samples using laser desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **2020**, 34, (8), 9573-9584.

38. Apicella, B.; Alfè, M.; Amoresano, A.; Galano, E.; Ciajolo, A., Advantages and limitations of laser desorption/ionization mass spectrometric techniques in the chemical characterization of complex carbonaceous materials. *International Journal of Mass Spectrometry* **2010**, 295, (1-2), 98-102.

39. 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.

40. Smith, D. F.; McKenna, A. M.; Corilo, Y. E.; Rodgers, R. P.; Marshall, A. G.; Heeren, R. M., Direct analysis of thin-layer chromatography separations of petroleum samples by laser desorption ionization fourier transform ion cyclotron resonance mass spectrometry imaging. *Energy & Fuels* **2014**, 28, (10), 6284-6288.

41. Terra, L. A.; Filgueiras, P. R.; Tose, L. V.; Romao, W.; de Castro, E. V.; de Oliveira, L. M.; Dias, J. C.; Vaz, B. G.; Poppi, R. J., Laser desorption ionization FT-ICR mass spectrometry and CARSPLS for predicting basic nitrogen and aromatics contents in crude oils. *Fuel* **2015**, 160, 274-281.

42. Tanaka, K.; Waki, H.; Ido, Y.; Akita, S.; Yoshida, Y.; Yoshida, T.; Matsuo, T., Protein and polymer analyses up to m/z 100 000 by laser ionization time-of-flight mass spectrometry. *Rapid Communications in Mass Spectrometry* **1988**, 2, (8), 151-153.

43. Karas, M.; Hillenkamp, F., Laser desorption ionization of proteins with molecular masses exceeding 10,000 daltons. *Analytical Chemistry* **1988**, 60, (20), 2299-2301.

44. Trimpin, S.; Keune, S.; Räder, H. J.; Müllen, K., Solvent-free MALDI-MS: developmental improvements in the reliability and the potential of MALDI in the analysis of synthetic polymers and giant organic molecules. *Journal of The American Society for Mass Spectrometry* **2006**, 17, (5), 661-671.

45. Ryan, D. J.; Spraggins, J. M.; Caprioli, R. M., Protein identification strategies in MALDI imaging mass spectrometry: a brief review. *Current opinion in chemical biology* **2019**, 48, 64-72.

46. El-Aneed, A.; Cohen, A.; Banoub, J., Mass spectrometry, review of the basics: electrospray, MALDI, and commonly used mass analyzers. *Applied Spectroscopy Reviews* **2009**, 44, (3), 210-230.

47. Edwards, W. F.; Jin, L.; Thies, M. C., MALDI-TOF mass spectrometry: Obtaining reliable mass spectra for insoluble carbonaceous pitches. *Carbon* **2003**, 41, (14), 2761-2768.

48. Skelton, R.; Dubois, F.; Zenobi, R., A MALDI sample preparation method suitable for insoluble polymers. *Analytical Chemistry* **2000**, 72, (7), 1707-1710.

49. Knochenmuss, R.; Zenobi, R., MALDI ionization: the role of in-plume processes. *Chemical reviews* **2003**, 103, (2), 441-452.

50. Van Nuffel, S.; Elie, N.; Yang, E.; Nouet, J.; Touboul, D.; Chaurand, P.; Brunelle, A., Insights into the MALDI process after matrix deposition by sublimation using 3D ToF-SIMS imaging. *Analytical Chemistry* **2018**, 90, (3), 1907-1914.

51. Kim, J. G.; Kim, J. H.; Song, B.-J.; Lee, C. W.; Lee, Y.-S.; Im, J. S., Empirical approach to determine molecular weight distribution using MALDI-TOF analysis of petroleum-based heavy oil. *Fuel* **2016**, 186, 20-23.

52. Knochenmuss, R., *Electrospray and MALDI Mass Spectrometry*. John Wiley & Sons, Hoboken, NJ, USA: 2010.

53. Jackson, S. N.; Woods, A. S., The Development of Matrix-Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry. In *The Encyclopedia of Mass Spectrometry*, Gross, M. L.; Caprioli, R. M., Eds. Elsevier: Boston, 2016; pp 124-131.

54. Edwards, W. F.; Thies, M. C., Dense-gas fractionation and MALDI characterization of carbonaceous pitches. *Energy & Fuels* **2005**, 19, (3), 984-991.

55. Ramírez-Pradilla, J. S.; Blanco-Tirado, C.; Hubert-Roux, M.; Giusti, P.; Afonso, C.; Combariza, M. Y., Comprehensive petroporphyrin identification in crude oils using highly selective electron transfer reactions in MALDI-FTICR-MS. *Energy & Fuels* **2019**, 33, (5), 3899-3907.

56. Yoshimura, K.; Przybilla, L.; Ito, S.; Brand, J. D.; Wehmeir, M.; Räder, H. J.; Müllen, K., Characterization of large synthetic polycyclic aromatic hydrocarbons by MALDI-and LD-TOF mass spectrometry. *Macromolecular Chemistry and Physics* **2001**, 202, (2), 215-222.

57. Winter, M.; Ries, R.; Kleiner, C.; Bischoff, D.; Luippold, A. H.; Bretschneider, T.; Büttner, F. H., Automated MALDI target preparation concept: providing ultra-high-throughput mass spectrometry–based screening for drug discovery. *SLAS TECHNOLOGY: Translating Life Sciences Innovation* **2019**, 24, (2), 209-221.

58. Zhang, W.; Shao, C.; Sarathy, S. M., Analyzing the solid soot particulates formed in a fuel-rich flame by solvent-free matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Communications in Mass Spectrometry* **2020**, 34, (4), e8596.

59. Smith, D. F.; Rahimi, P.; Teclemariam, A.; Rodgers, R. P.; Marshall, A. G., Characterization of Athabasca Bitumen Heavy Vacuum Gas Oil Distillation Cuts by Negative/Positive Electrospray Ionization and Automated Liquid Injection Field Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2008**, 22, (5), 3118-3125.

60. Smith, D. F.; Schaub, T. M.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G., Automated liquid injection field desorption/ionization for Fourier transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* **2008**, 80, (19), 7379-7382.

61. Schaub, T. M.; Hendrickson, C. L.; Qian, K.; Quinn, J. P.; Marshall, A. G., High-resolution field desorption/ionization Fourier transform ion cyclotron resonance mass analysis of nonpolar molecules. *Analytical Chemistry* **2003**, 75, (9), 2172-2176.

62. Gross, J. H.; Vékey, K.; Dallos, A., Field desorption mass spectrometry of large multiply branched saturated hydrocarbons. *Journal of mass spectrometry* **2001**, 36, (5), 522-528.

63. Posthumus, M.; Kistemaker, P.; Meuzelaar, H.; Ten Noever de Brauw, M., Laser desorption-mass spectrometry of polar nonvolatile bio-organic molecules. *Analytical Chemistry* **1978**, 50, (7), 985-991.

64. Wilkes, J. G.; Freeman, J. P.; Heinze, T. M.; Lay Jr, J. O.; Vestal, M. L., AC corona-discharge aerosolneutralization device adapted to liquid chromatography/particle beam/mass spectrometry. *Rapid Communications in Mass Spectrometry* **1995**, 9, (2), 138-142.

65. Katta, V.; Rockwood, A. L.; Vestal, M. L., Field limit for ion evaporation from charged thermospray droplets. *International journal of mass spectrometry and ion processes* **1991**, 103, (2-3), 129-148.

66. Molin, L.; Seraglia, R.; Czarnocki, Z.; Maurin, J. K.; Pluciński, F. A.; Traldi, P., On the primary ionization mechanism (s) in matrix-assisted laser desorption ionization. *Journal of analytical methods in chemistry* **2012**, 2012, 161865-161865.

67. Creaser, C. S.; Ratcliffe, L., Atmospheric pressure matrix-assisted laser desorption/ionisation mass spectrometry: A review. *Current Analytical Chemistry* **2006**, *2*, (1), 9-15.

68. Jaskolla, T. W.; Lehmann, W.-D.; Karas, M., 4-Chloro-α-cyanocinnamic acid is an advanced, rationally designed MALDI matrix. *Proceedings of the National Academy of Sciences* **2008**, 105, (34), 12200-12205.

69. Barber, M.; Bordoli, R.; Sedgwick, R.; Tyler, A., Fast atom bombardment of solids as an ion source in mass spectrometry. *Nature* **1981**, 293, (5830), 270-275.

70. Morris, H. R.; Panico, M.; Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A., Fast atom bombardment: a new mass spectrometric method for peptide sequence analysis. *Biochemical and biophysical research communications* **1981**, 101, (2), 623-631.

71. Shackleton, C.; Straub, K., Direct analysis of steroid conjugates: the use of secondary ion mass spectrometry. *Steroids* **1982**, 40, (1), 35-51.

72. Cho, Y.; Witt, M.; Kim, Y. H.; Kim, S., Characterization of crude oils at the molecular level by use of laser desorption ionization Fourier-transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* **2012**, 84, (20), 8587-8594.

73. 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, (4), 1830-1837.

74. Cho, Y.; Ahmed, A.; Islam, A.; Kim, S., Developments in FT-ICR MS instrumentation, ionization techniques, and data interpretation methods for petroleomics. *Mass spectrometry reviews* **2015**, 34, (2), 248-263.

75. Kujawinski, E. B., Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS): characterization of complex environmental mixtures. *Environmental Forensics* **2002**, *3*, (3-4), 207-216.

76. Smith, D. F.; Podgorski, D. C.; Rodgers, R. P.; Blakney, G. T.; Hendrickson, C. L., 21 tesla FT-ICR mass spectrometer for ultrahigh-resolution analysis of complex organic mixtures. *Analytical Chemistry* **2018**, 90, (3), 2041-2047.

77. Borisov, R.; Kulikova, L.; Zaikin, V., Mass spectrometry in petroleum chemistry (petroleomics). *Petroleum Chemistry* **2019**, 59, (10), 1055-1076.

78. Tose, L. V.; Cardoso, F. M.; Fleming, F. P.; Vicente, M. A.; Silva, S. R.; Aquije, G. M.; Vaz, B. G.; Romão, W., Analyzes of hydrocarbons by atmosphere pressure chemical ionization FT-ICR mass spectrometry using isooctane as ionizing reagent. *Fuel* **2015**, 153, 346-354.

79. Artigues, A.; Puy, N.; Bartrolí, J.; Fábregas, E., Comparative assessment of internal standards for quantitative analysis of bio-oil compounds by gas chromatography/mass spectrometry using statistical criteria. *Energy & Fuels* **2014**, 28, (6), 3908-3915.

80. Masiá, A.; Blasco, C.; Picó, Y., Last trends in pesticide residue determination by liquid chromatography–mass spectrometry. *Trends in Environmental Analytical Chemistry* **2014**, *2*, 11-24.

81. Klepárník, K., Recent advances in combination of capillary electrophoresis with mass spectrometry: methodology and theory. *Electrophoresis* **2015**, 36, (1), 159-178.

82. Peters, K. E.; Walters, C. C.; Moldowan, J. M., *The biomarker guide: Volume 2, Biomarkers and isotopes in petroleum systems and earth history*. Cambridge University Press: 2007.

83. Grice, K.; Alexander, R.; Kagi, R. I., Diamondoid hydrocarbon ratios as indicators of biodegradation in Australian crude oils. *Organic Geochemistry* **2000**, 31, (1), 67-73.

84. Eiserbeck, C.; Nelson, R. K.; Grice, K.; Curiale, J.; Reddy, C. M., Comparison of GC–MS, GC–MRM-MS, and GC× GC to characterise higher plant biomarkers in Tertiary oils and rock extracts. *Geochimica et Cosmochimica Acta* **2012**, 87, 299-322.

85. Sutton, P.; Lewis, C.; Rowland, S., Isolation of individual hydrocarbons from the unresolved complex hydrocarbon mixture of a biodegraded crude oil using preparative capillary gas chromatography. *Organic Geochemistry* **2005**, 36, (6), 963-970.

86. Kallio, M.; Hyötyläinen, T., Quantitative aspects in comprehensive two-dimensional gas chromatography. *Journal of Chromatography A* **2007**, 1148, (2), 228-235.

87. Kallio, M., Comprehensive Two-Dimensional Gas Chromatography: Instrumental and Methodological Development. **2008**.

88. Djokic, M. R.; Dijkmans, T.; Yildiz, G.; Prins, W.; Van Geem, K. M., Quantitative analysis of crude and stabilized bio-oils by comprehensive two-dimensional gas-chromatography. *Journal of Chromatography A* **2012**, 1257, 131-140.

89. Vendeuvre, C.; Bertoncini, F.; Espinat, D.; Thiébaut, D.; Hennion, M.-C., Multidimensional gas chromatography for the detailed PIONA analysis of heavy naphtha: Hyphenation of an olefin trap to comprehensive two-dimensional gas chromatography. *Journal of Chromatography A* **2005**, 1090, (1-2), 116-125.

90. Adam, F.; Bertoncini, F.; Thiebaut, D.; Hennion, M. C.; Lahoutifard, N.; Addinall, A., Comprehensive 2D GC for achieving nitrogen speciation in middle distillates. *LCGC Europe* **2008**, 43.

91. Frysinger, G. S.; Gaines, R. B.; Ledford Jr, E. B., Quantitative determination of BTEX and total aromatic compounds in gasoline by comprehensive two-dimensional gas chromatography (GC× GC). *Journal of High Resolution Chromatography* **1999**, 22, (4), 195-200.

92. Harynuk, J.; Górecki, T., New liquid nitrogen cryogenic modulator for comprehensive twodimensional gas chromatography. *Journal of Chromatography A* **2003**, 1019, (1-2), 53-63.

93. Pedroso, M. P.; de Godoy, L. A. F.; Ferreira, E. C.; Poppi, R. J.; Augusto, F., Identification of gasoline adulteration using comprehensive two-dimensional gas chromatography combined to multivariate data processing. *Journal of Chromatography A* **2008**, 1201, (2), 176-182.

94. Seeley, J. V.; Libby, E. M.; Seeley, S. K.; McCurry, J. D., Comprehensive two-dimensional gas chromatography analysis of high-ethanol containing motor fuels. *Journal of separation science* **2008**, 31, (19), 3337-3346.

95. Beens, J.; Brinkman, U. A. T., The role of gas chromatography in compositional analyses in the petroleum industry. *TrAC Trends in Analytical Chemistry* **2000**, 19, (4), 260-275.

96. Adahchour, M.; Beens, J.; Vreuls, R. J.; Batenburg, A. M.; Udo, A. T., Comprehensive twodimensional gas chromatography of complex samples by using a 'reversed-type'column combination: application to food analysis. *Journal of Chromatography A* **2004**, 1054, (1-2), 47-55.

97. Vendeuvre, C.; Ruiz-Guerrero, R.; Bertoncini, F.; Duval, L.; Thiébaut, D.; Hennion, M.-C., Characterisation of middle-distillates by comprehensive two-dimensional gas chromatography (GC×GC): A powerful alternative for performing various standard analysis of middle-distillates. *Journal of Chromatography A* **2005**, 1086, (1), 21-28.

98. Adam, F.; Bertoncini, F.; Coupard, V.; Charon, N.; Thiébaut, D.; Espinat, D.; Hennion, M.-C., Using comprehensive two-dimensional gas chromatography for the analysis of oxygenates in middle distillates: I. Determination of the nature of biodiesels blend in diesel fuel. *Journal of Chromatography A* **2008**, 1186, (1-2), 236-244.

99. Wang, F. C.-Y.; Robbins, W. K.; Di Sanzo, F. P.; McElroy, F. C., Speciation of Sulfur-Containing Compounds in Diesel by Comprehensive Two-Dimensional Gas Chromatography. *Journal of Chromatographic Science* **2003**, 41, (10), 519-523.

100. Wang, F. C.-Y.; Robbins, W. K.; Greaney, M. A., Speciation of nitrogen-containing compounds in diesel fuel by comprehensive two-dimensional gas chromatography. *Journal of separation science* **2004**, 27, (5-6), 468-472.

101. Bertoncini, F.; Vendeuvre, C.; Thiebaut, D., Interest and applications of multidimensional gas chromatography for trace analysis in the petroleum industry. *Oil & gas science and technology* **2005**, 60, (6), 937-950.

102. Hamilton, J. F.; Lewis, A. C.; Millan, M.; Bartle, K. D.; Herod, A. A.; Kandiyoti, R., Comprehensive Two-Dimensional Gas Chromatography Coupled to Time-of-Flight Mass Spectrometry of Coal Liquids Produced During a Coal Liquefaction Process. *Energy & Fuels* **2007**, 21, (1), 286-294.

103. Vendeuvre, C.; Bertoncini, F.; Duval, L.; Duplan, J.-L.; Thiébaut, D.; Hennion, M.-C., Comparison of conventional gas chromatography and comprehensive two-dimensional gas chromatography for the detailed analysis of petrochemical samples. *Journal of Chromatography A* **2004**, 1056, (1), 155-162.

104. Parkash, S., *Refining processes handbook*. Elsevier: 2003.

105. Speight, J. G., *Petroleum chemistry and refining*. CRC Press: 1997.

106. Arjoon, K.; Speight, J. G., Chemical and Physical Analysis of a Petroleum Hydrocarbon Contamination on a Soil Sample to Determine Its Natural Degradation Feasibility. *Inventions* **2020**, 5, (3), 43.

107. Toraman, H. E.; Dijkmans, T.; Djokic, M. R.; Van Geem, K. M.; Marin, G. B., Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors. *Journal of Chromatography A* **2014**, 1359, 237-246.

108. Coulon, F.; Wu, G., Determination of petroleum hydrocarbon compounds from soils and sediments using ultrasonic extraction. In *Hydrocarbon and Lipid Microbiology Protocols*, Springer: 2014; pp 31-46.

Sjöblom, J.; Aske, N.; Auflem, I. H.; Brandal, Ø.; Havre, T. E.; Sæther, Ø.; Westvik, A.; Johnsen, E. E.; Kallevik, H., Our current understanding of water-in-crude oil emulsions.: Recent characterization techniques and high pressure performance. *Advances in Colloid and Interface Science* 2003, 100, 399-473.
Zahed, M. A.; Aziz, H. A.; Isa, M. H.; Mohajeri, L., Response surface analysis to improve dispersed crude oil biodegradation. *CLEAN–Soil, Air, Water* 2012, 40, (3), 262-267.

111. Fakhru'l-Razi, A.; Pendashteh, A.; Abdullah, L. C.; Biak, D. R. A.; Madaeni, S. S.; Abidin, Z. Z., Review of technologies for oil and gas produced water treatment. *Journal of hazardous materials* **2009**, 170, (2-3), 530-551.

112. Fraser, S., Distillation in refining. *Distillation* **2014**, 155-190.

113. Riazi, M., *Characterization and properties of petroleum fractions*. ASTM international: 2005; Vol.50.

114. Kaminsky, W.; Zorriqueta, I.-J. N., Catalytical and thermal pyrolysis of polyolefins. *Journal of Analytical and Applied Pyrolysis* **2007**, 79, (1-2), 368-374.

115. Almeida, D.; Marques, M. d. F., Thermal and catalytic pyrolysis of plastic waste. *Polímeros* **2016**, 26, (1), 44-51.

116. Artetxe, M.; Lopez, G.; Elordi, G.; Amutio, M.; Bilbao, J.; Olazar, M., Production of light olefins from polyethylene in a two-step process: pyrolysis in a conical spouted bed and downstream high-temperature thermal cracking. *Industrial & engineering chemistry research* **2012**, 51, (43), 13915-13923.

117. Meng, X.; Xu, C.; Gao, J.; Li, L.; Liu, Z., Catalytic and thermal pyrolysis of atmospheric residue. *Energy & Fuels* **2009**, 23, (1), 65-69.

118. Sadrameli, S.; Green, A., Systematics and modeling representations of naphtha thermal cracking for olefin production. *Journal of Analytical and Applied Pyrolysis* **2005**, 73, (2), 305-313.

119. Goual, L.; Firoozabadi, A., Measuring asphaltenes and resins, and dipole moment in petroleum fluids. *AIChE Journal* **2002**, 48, (11), 2646-2663.

120. Mansoori, G. A., Modeling of asphaltene and other heavy organic depositions. *Journal of petroleum science and engineering* **1997**, 17, (1-2), 101-111.

121. Speight, J. G., *Handbook of Petroleum Product Analysis global properties*. John Wiley & Sons: 2002.

122. Fahim, M. A.; Al-Sahhaf, T. A.; Elkilani, A., *Fundamentals of petroleum refining*. Elsevier: 2009.

123. Briker, Y.; Ring, Z.; Iacchelli, A.; McLean, N.; Rahimi, P. M.; Fairbridge, C.; Malhotra, R.; Coggiola, M. A.; Young, S. E., Diesel Fuel Analysis by GC–FIMS: Aromatics, n-Paraffins, and Isoparaffins. *Energy & Fuels* **2001**, 15, (1), 23-37.

124. Caumette, G.; Lienemann, C.-P.; Merdrignac, I.; Bouyssiere, B.; Lobinski, R., Element speciation analysis of petroleum and related materials. *Journal of Analytical Atomic Spectrometry* **2009**, 24, (3), 263-276.

125. Saravanabhavan, G.; Helferty, A.; Hodson, P. V.; Brown, R. S., A multi-dimensional high performance liquid chromatographic method for fingerprinting polycyclic aromatic hydrocarbons and their alkyl-homologs in the heavy gas oil fraction of Alaskan North Slope crude. *Journal of Chromatography A* **2007**, 1156, (1), 124-133.

126. Speight, J., Part 1: History and Terminology. *The Chemistry and Technology of Petroleum* **2014**, 3-174.

127. Altgelt, K. H., *Composition and analysis of heavy petroleum fractions*. CRC press: 1993.

128. Dutriez, T.; Courtiade, M.; Thiébaut, D.; Dulot, H.; Hennion, M.-C., Improved hydrocarbons analysis of heavy petroleum fractions by high temperature comprehensive two-dimensional gas chromatography. *Fuel* **2010**, 89, (9), 2338-2345.

129. Farenc, M.; Corilo, Y. E.; Lalli, P. M.; Riches, E.; Rodgers, R. P.; Afonso, C.; Giusti, P., Comparison of Atmospheric Pressure Ionization for the Analysis of Heavy Petroleum Fractions with Ion Mobility-Mass Spectrometry. *Energy & Fuels* **2016**, 30, (11), 8896-8903.

130. Dutriez, T.; Thiébaut, D.; Courtiade, M.; Dulot, H.; Bertoncini, F.; Hennion, M.-C., Application to SFC-GC× GC to heavy petroleum fractions analysis. *Fuel* **2013**, 104, 583-592.

131. Sama, S. G.; Barrère-Mangote, C.; Bouyssière, B.; Giusti, P.; Lobinski, R., Recent trends in element speciation analysis of crude oils and heavy petroleum fractions. *TrAC Trends in Analytical Chemistry* **2018**, 104, 69-76.

132. Giusti, P.; Lobinski, R., Recent trends in element speciation analysis of crude oils and heavy petroleum fractions. *Trends in analytical chemistry* **2017**.

133. Karlsen, D. A.; Larter, S. R., Analysis of petroleum fractions by TLC-FID: applications to petroleum reservoir description. *Organic Geochemistry* **1991**, 17, (5), 603-617.

134. Dutriez, T.; Courtiade, M.; Thiébaut, D.; Dulot, H.; Borras, J.; Bertoncini, F.; Hennion, M.-C., Advances in quantitative analysis of heavy petroleum fractions by liquid chromatography– high-temperature comprehensive two-dimensional gas chromatography: breakthrough for conversion processes. *Energy & Fuels* **2010**, 24, (8), 4430-4438.

135. Li, H.; Zhang, Y.; Xu, C.; Zhao, S.; Chung, K. H.; Shi, Q., Quantitative Molecular Composition of Heavy Petroleum Fractions: A Case Study of Fluid Catalytic Cracking Decant Oil. *Energy & Fuels* **2020**, 34, (5), 5307-5316.

136. Niessen, W. M., *Liquid chromatography-mass spectrometry*. CRC press: 2006.

137. Ardrey, R. E., *Liquid chromatography-mass spectrometry: an introduction*. John Wiley & Sons: 2003; Vol. 2.

138. Trufelli, H.; Palma, P.; Famiglini, G.; Cappiello, A., An overview of matrix effects in liquid chromatography–mass spectrometry. *Mass spectrometry reviews* **2011**, 30, (3), 491-509.

139. Holčapek, M.; Jirásko, R.; Lísa, M., Recent developments in liquid chromatography–mass spectrometry and related techniques. *Journal of Chromatography A* **2012**, 1259, 3-15.

140. Sharma, B. K.; Sarowha, S. L. S.; Bhagat, S. D., Chromatographic characterization of high-boiling petroleum fractions. *Journal of separation science* **2003**, 26, (18), 1657-1664.

141. Robb, D. B.; Covey, T. R.; Bruins, A. P., Atmospheric pressure photoionization: an ionization method for liquid chromatography– mass spectrometry. *Analytical Chemistry* **2000**, 72, (15), 3653-3659.

142. Raffaelli, A.; Saba, A., Atmospheric pressure photoionization mass spectrometry. *Mass spectrometry reviews* **2003**, 22, (5), 318-331.

143. Hanold, K. A.; Fischer, S. M.; Cormia, P. H.; Miller, C. E.; Syage, J. A., Atmospheric pressure photoionization. 1. General properties for LC/MS. *Analytical Chemistry* **2004**, *7*6, (10), 2842-2851.

144. Marchi, I.; Rudaz, S.; Veuthey, J.-L., Atmospheric pressure photoionization for coupling liquidchromatography to mass spectrometry: a review. *Talanta* **2009**, 78, (1), 1-18.

145. Kauppila, T. J.; Syage, J. A.; Benter, T., Recent developments in atmospheric pressure photoionization-mass spectrometry. *Mass spectrometry reviews* **2017**, 36, (3), 423-449.

146. Mironov, N. A.; Milordov, D. V.; Abilova, G. R.; Yakubova, S. G.; Yakubov, M. R., Methods for Studying Petroleum Porphyrins (Review). *Petroleum Chemistry* **2019**, 59, (10), 1077-1091.

147. Tose, L. V.; Murgu, M.; Vaz, B. G.; Romão, W., Application of Atmospheric Solids Analysis Probe Mass Spectrometry (ASAP-MS) in Petroleomics: Analysis of Condensed Aromatics Standards, Crude Oil, and Paraffinic Fraction. *Journal of The American Society for Mass Spectrometry* **2017**, 28, (11), 2401-2407. 148. Potgieter, H.; de Coning, P.; Bekker, R.; Rohwer, E.; Amirav, A., The pre-separation of oxygen containing compounds in oxidised heavy paraffinic fractions and their identification by GC-MS with supersonic molecular beams. *Journal of mass spectrometry* **2019**, 54, (4), 328-341.

149. Fu, J.; Kim, S.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G.; Qian, K., Nonpolar Compositional Analysis of Vacuum Gas Oil Distillation Fractions by Electron Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2006**, 20, (2), 661-667.

150. Giri, A.; Coutriade, M.; Racaud, A.; Stefanuto, P. H.; Okuda, K.; Dane, J.; Cody, R. B.; Focant, J. F., Compositional elucidation of heavy petroleum base oil by GC x GC-EI/PI/CI/FI-TOFMS. *Journal of mass spectrometry* **2019**, 54, (2), 148-157.

151. Keshet, U.; Fialkov, A. B.; Alon, T.; Amirav, A., A New Pulsed Flow Modulation GC × GC–MS with Cold El System and Its Application for Jet Fuel Analysis. *Chromatographia* **2016**, 79, (11), 741-754.

152. Fialkov, A. B.; Gordin, A.; Amirav, A., Hydrocarbons and fuels analyses with the supersonic gas chromatography mass spectrometry--the novel concept of isomer abundance analysis. *Journal of chromatography*. A **2008**, 1195, (1-2), 127-35.

153. Patkin, A., Cold El GC/MS Enhancement of High MW Hydrocarbon Molecular Weight Information. *PerkinElmer* **2015**.

154. Dagan, S.; Amirav, A., Electron impact mass spectrometry of alkanes in supersonic molecular beams. *Journal of The American Society for Mass Spectrometry* **1995**, 6, (2), 120-131.

155. Amirav, A.; Keshet, U.; Danon, A., Soft Cold EI - approaching molecular ion only with electron ionization. *Rapid communications in mass spectrometry : RCM* **2015**, 29, (21), 1954-60.

156. Linden, M. H.; Linden, H. B.; Nieth, N.; Gross, J. H., Self-Supplied Liquid Injection Field Desorption/Ionization Ion Source for an Orthogonal Time-of-Flight Instrument. *Journal of The American Society for Mass Spectrometry* **2019**, 30, (11), 2358-2368.

157. Bernhard Linden, H.; Gross, J. H., Reduced fragmentation in liquid injection field desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry by use of helium for the thermalization of molecular ions. *Rapid communications in mass spectrometry : RCM* **2012**, 26, (3), 336-44.

158. Gross, J. H., From the discovery of field ionization to field desorption and liquid injection field desorption/ionization-mass spectrometry-A journey from principles and applications to a glimpse into the future. *European journal of mass spectrometry (Chichester, England)* **2020**, 26, (4), 241-273.

159. Mead, W. L., Field ionization mass spectrometry of heavy petroleum fractions. Waxes. *Analytical Chemistry* **1968**, 40, (4), 743-747.

160. Ogawa, T., Analytical conditions for field ionization mass spectrometry of diesel fuel. *Fuel* **2005**, 84, (16), 2015-2025.

161. Wang, F. C.-Y.; Qian, K.; Green, L. A., GC×MS of Diesel: A Two-Dimensional Separation Approach. *Analytical Chemistry* **2005**, 77, (9), 2777-2785.

162. Xin-yi, Z.; Ze-long, L.; Yan-qin, X.; ying-rong, L.; Song-bai, T., Diesel detailed analysis by GC field ionization time-of-flight high-resolution mass spectrometry. *Acta Petrolei Sinica*(*Petroleum Processing Section*) **2010**, 26, (2), 277-277.

163. Yanqin, X.; Xinyi, Z.; Zelong, L.; Songbai, T., Characterization of alkenes in diesel by solid phase extraction and GC field ionization time-of-flight high-resolution mass spectrometry. *Acta Petrolei Sinica*(*Petroleum Processing Section*) **2010**, 26, (3), 431-431.

164. Genuit, W.; Chaabani, H., Comprehensive two-dimensional gas chromatography-field ionization time-of-flight mass spectrometry (GCxGC-FI-TOFMS) for detailed hydrocarbon middle distillate analysis. *International Journal of Mass Spectrometry* **2017**, 413, 27-32.

165. Beckey, H.-D., Theory of field ionization (FI) and field emission (FE). In *Field Ionization Mass Spectrometry*, Beckey, H.-D., Ed. Pergamon: 1971; Vol. 42, pp 1-10.

166. Jin, C.; Viidanoja, J.; Li, M.; Zhang, Y.; Ikonen, E.; Root, A.; Romanczyk, M.; Manheim, J.; Dziekonski, E.; Kenttämaa, H. I., Comparison of Atmospheric Pressure Chemical Ionization and Field Ionization Mass Spectrometry for the Analysis of Large Saturated Hydrocarbons. *Analytical Chemistry* **2016**, 88, (21), 10592-10598.

167. Qian, K.; Di Sanzo, F. P., Detailed Analysis of Olefins in Processed Petroleum Streams by Combined Multi-dimensional Supercritical Fluid Chromatography and Field Ionization Time-of-Flight Mass Spectrometry. *Energy & Fuels* **2016**, 30, (1), 98-103.

168. Chen, F.; Liu, Y.-R.; Tian, S.-B.; Wang, N.-X., Study on molecular compositions of hydrocracking products and changing regularity with conversion depth. *Petroleum processing and petrochemicals* **2015**, 46, (4), 103-109.

169. Herod, A. A.; Bartle, K. D.; Kandiyoti, R., Characterization of Heavy Hydrocarbons by Chromatographic and Mass Spectrometric Methods: An Overview. *Energy & Fuels* **2007**, 21, (4), 2176-2203.

170. Qian, K. N.; Wang, F. C., Compositional Analysis of Heavy Petroleum Distillates by Comprehensive Two-dimensional Gas Chromatography, Field Ionization and High-resolution Mass Spectrometry. *Journal of The American Society for Mass Spectrometry* **2019**, 30, (12), 2785-2794.

171. Shiraishi, Y.; Hirai, T.; Komasawa, I., A Novel Desulfurization Process for Fuel Oils Based on the Formation and Subsequent Precipitation of S-Alkylsulfonium Salts. 4. Desulfurization and Simultaneous Denitrogenation of Vacuum Gas Oil. *Industrial & engineering chemistry research* **2001**, 40, (15), 3398-3405.

172. Ying-Rong, L.; Ze-Long, L.; Song-Bai, T.; Xin-Yi, Z., Determination of Carbon Number Distribution of Vacuum Gas Oil by GC Field Ionization Time-of-Flight Mass Spectrometry. *Acta Petrolei Sinica(Petroleum Processing Section)* **2012**, 28, (3), 426-431.

173. Ni, H.; Hsu, C. S.; Ma, C.; Shi, Q.; Xu, C., Separation and Characterization of Olefin/Paraffin in Coal Tar and Petroleum Coker Oil. *Energy & Fuels* **2013**, 27, (9), 5069-5075.

174. Muller, H.; Saleem, Q., Saturated Compounds in Heavy Petroleum Fractions. *Energy & Fuels* **2020**, 34, (9), 10713-10723.

175. 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.

176. Alawani, N. A.; Panda, S. K.; Lajami, A. R.; Al-Qunaysi, T. A.; Muller, H., Characterization of Crude Oils through Alkyl Chain-Based Separation by Gel Permeation Chromatography and Mass Spectrometry. *Energy & Fuels* **2020**, 34, (5), 5414-5425.

177. Romão, W.; Tose, L. V.; Vaz, B. G.; Sama, S. G.; Lobinski, R.; Giusti, P.; Carrier, H.; Bouyssiere, B., Petroleomics by Direct Analysis in Real Time-Mass Spectrometry. *Journal of The American Society for Mass Spectrometry* **2016**, 27, (1), 182-185.

178. Zuppa Neto, T. d. O.; Avval, T. G.; Morais, P. A. d. O.; Ellis, W. C.; Chapman, S. C.; de Oliveira, A. E.; Linford, M. R.; Farnsworth, P. B.; Antoniosi Filho, N. R., Direct Dielectric Barrier Discharge Ionization Promotes Rapid and Simple Lubricant Oil Fingerprinting. *Journal of The American Society for Mass Spectrometry* **2020**, 31, (7), 1525-1535.

179. Da Costa, C.; Whitmarsh, S.; Lynch, T.; Creaser, C. S., The qualitative and quantitative analysis of lubricant oil additives by direct analysis in real time-mass spectrometry. *International Journal of Mass Spectrometry* **2016**, 405, 24-31.

180. Barrère, C.; Hubert-Roux, M.; Afonso, C.; Racaud, A., Rapid analysis of lubricants by atmospheric solid analysis probe–ion mobility mass spectrometry. *Journal of mass spectrometry* **2014**, 49, (8), 709-715. 181. Kassler, A.; Pittenauer, E.; Doerr, N.; Allmaier, G., Electrospray ionization and atmospheric pressure matrix-assisted laser desorption/ionization mass spectrometry of antioxidants applied in lubricants. *Rapid Communications in Mass Spectrometry* **2009**, 23, (24), 3917-3927. 182. Hourani, N.; Muller, H.; Adam, F. M.; Panda, S. K.; Witt, M.; Al-Hajji, A. A.; Sarathy, S. M., Structural Level Characterization of Base Oils Using Advanced Analytical Techniques. *Energy & Fuels* **2015**, 29, (5), 2962-2970.

183. Yang, P.; Waddell, K.; Ryddy, B. M.; Ashby, M.; Nyadong, L., Petroleum Analysis by Orbitrap Elite Mass Spectrometer with Multiple Ionization Methods. *Thermo Fish. Sci.* **2014**.

184. Purcell, J. M., Petroleum Analysis by Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *The Florida State University* **2016**.

185. Santos, J. M.; Vetere, A.; Wisniewski, A.; Eberlin, M. N.; Schrader, W., Comparing Crude Oils with Different API Gravities on a Molecular Level Using Mass Spectrometric Analysis. Part 2: Resins and Asphaltenes. *Energies* **2018**, 11, (10), 14.

186. Purcell, J. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G., Atmospheric Pressure Photoionization Proton Transfer for Complex Organic Mixtures Investigated by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Journal of The American Society for Mass Spectrometry* **2007**, 18, (9), 1682-1689.

187. Chacon-Patino, M. L.; Nelson, J.; Rogel, E.; Hench, K.; Poirier, L.; Lopez-Linares, F.; Ovalles, C., Vanadium and nickel distributions in Pentane, In-between C5-C7 Asphaltenes, and heptane asphaltenes of heavy crude oils. *Fuel* **2021**, 292, 11.

188. Chacon-Patino, M. L.; Moulian, R.; Barrere-Mangote, C.; Putman, J. C.; Weisbrod, C. R.; Blakney, G. T.; Bouyssiere, B.; Rodgers, R. P.; Giusti, P., Compositional Trends for Total Vanadium Content and Vanadyl Porphyrins in Gel Permeation Chromatography Fractions Reveal Correlations between Asphaltene Aggregation and Ion Production Efficiency in Atmospheric Pressure Photoionization. *Energy & Fuels* **2020**, 34, (12), 16158-16172.

189. Glattke, T. J.; Chacon-Patino, M. L.; Marshall, A. G.; Rodgers, R. P., Molecular Characterization of Photochemically Produced Asphaltenes via Photooxidation of Deasphalted Crude Oils. *Energy & Fuels* **2020**, 34, (11), 14419-14428.

190. Niles, S. F.; Chacon-patino, M. L.; Smith, D. F.; Rodgers, R. P.; Marshall, A. G., Comprehensive Compositional and Structural Comparison of Coal and Petroleum Asphaltenes Based on Extrography Fractionation Coupled with Fourier Transform Ion Cyclotron Resonance MS and MS/MS Analysis. *Energy & Fuels* **2020**, 34, (2), 1492-1505.

191. Chacon-Patino, M. L.; Rowland, S. M.; Rodgers, R. P., Advances in Asphaltene Petroleomics. Part 3. Dominance of Island or Archipelago Structural Motif Is Sample Dependent. *Energy & Fuels* **2018**, 32, (9), 9106-9120.

192. Witt, M.; Godejohann, M.; Oltmanns, S.; Moir, M.; Rogel, E., Characterization of Asphaltenes Precipitated at Different Solvent Power Conditions Using Atmospheric Pressure Photoionization (APPI) and Laser Desorption Ionization (LDI) Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). *Energy & Fuels* **2018**, 32, (3), 2653-2660.

193. Ruger, C. P.; Grimmer, C.; Sklorz, M.; Neumann, A.; Streibel, T.; Zimmermann, R., Combination of Different Thermal Analysis Methods Coupled to Mass Spectrometry for the Analysis of Asphaltenes and Their Parent Crude Oils: Comprehensive Characterization of the Molecular Pyrolysis Pattern. *Energy & Fuels* **2018**, 32, (3), 2699-2711.

194. Montapari, L.; Bonoldi, L.; Alessi, A.; Flego, C.; Salvalaggio, M.; Carati, C.; Bazzano, F.; Landoni, A., Molecular Evolution of Asphaltenes from Petroleum Residues after Different Severity Hydroconversion by EST Process. *Energy & Fuels* **2017**, 31, (4), 3729-3737.

195. Nascimento, P. T. H.; Santos, A. F.; Yamamoto, C. I.; Tose, L. V.; Barros, E. V.; Goncalves, G. R.; Freitas, J. C. C.; Vaz, B. G.; Romao, W.; Scheer, A. P., Fractionation of Asphaltene by Adsorption onto Silica and Chemical Characterization by Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Fourier Transform Infrared Spectroscopy Coupled to Attenuated Total Reflectance, and Proton Nuclear Magnetic Resonance. *Energy & Fuels* **2016**, 30, (7), 5439-5448. 196. Rogel, E.; Moir, M.; Witt, M., Atmospheric Pressure Photoionization and Laser Desorption Ionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry To Characterize Asphaltene Solubility Fractions: Studying the Link between Molecular Composition and Physical Behavior. *Energy & Fuels* **2015**, 29, (7), 4201-4209.

197. Chacon-Patino, M. L.; Blanco-Tirado, C.; Orrego-Ruiz, J. A.; Gomez-Escudero, A.; Combariza, M. Y., High Resolution Mass Spectrometric View of Asphaltene-SiO2 Interactions. *Energy & Fuels* **2015**, 29, (3), 1323-1331.

198. Yue, H. W.; Vieth-Hillebrand, A.; Han, Y. J.; Horsfield, B.; Schleicher, A. M.; Poetz, S., Unravelling the impact of lithofacies on the composition of NSO compounds in residual and expelled fluids of the Barnett, Niobrara and Posidonia formations. *Organic Geochemistry* **2021**, 155, 14.

199. Silva, R. C.; Snowdon, L. R.; Huang, H. P.; Larter, S., The dating of petroleum fluid residence time in subsurface reservoirs. Part 2: Tracking effects of radiolysis on crude oil by comprehensive molecular analysis. *Organic Geochemistry* **2021**, 152, 10.

200. Muller, H.; Saleem, Q.; Alawi, E. A.; Alsewdan, D. A.; Naqvi, I. A. S.; Saleh, A. H.; Rowaished, T. A., Narrow distillation cuts for an improved characterisation of crude oil: an insight on heteroatoms in heavy fraction molecules. *International Journal of Oil Gas and Coal Technology* **2021**, 26, (1), 40-59.

201. Zhao, J. M.; Liu, T.; Han, W.; Ren, L.; Zhang, L.; Dai, L. S.; Li, D. D., An insight into the molecular structure of sulfur compounds and their reactivity during residual oil hydroprocessing. *Fuel* **2021**, 283, 10. 202. Guillemant, J.; Berlioz-Barbier, A.; Chainet, F.; de Oliveira, L. P.; Lacoue-Negre, M.; Joly, J. F.; Duponchel, L., Sulfur compounds characterization using FT-ICR MS: Towards a better comprehension of vacuum gas oils hydrodesulfurization process. *Fuel Processing Technology* **2020**, 210, 9.

203. Han, Y. F.; Noah, M.; Luders, V.; Horsfield, B.; Mangelsdorf, K., NSO-compounds in oil-bearing fluid inclusions revealed by FT-ICR-MS in APPI (+) and ESI (-) modes: A new method development. *Organic Geochemistry* **2020**, 149, 14.

204. Ventura, G. T.; Rossel, P. E.; Simoneit, B. R. T.; Dittmar, T., Fourier transform ion cyclotron resonance mass spectrometric analysis of NSO-compounds generated in hydrothermally altered sediments from the Escanaba Trough, northeastern Pacific Ocean. *Organic Geochemistry* **2020**, 149, 16.

205. Guillemant, J.; Albrieux, F.; Lacoue-Negre, M.; de Oliveira, L. P.; Joly, J. F.; Duponchel, L., Chemometric Exploration of APPI(+)-FT-ICR MS Data Sets for a Comprehensive Study of Aromatic Sulfur Compounds in Gas Oils. *Analytical Chemistry* **2019**, 91, (18), 11785-11793.

206. Rodgers, R. P.; Mapolelo, M. M.; Robbins, W. K.; Chacon-Patino, M. L.; Putman, J. C.; Niles, S. F.; Rowland, S. M.; Marshall, A. G., Combating selective ionization in the high resolution mass spectral characterization of complex mixtures. *Faraday Discussions* **2019**, 218, 29-51.

207. Cho, E.; Park, M.; Hur, M.; Kang, G.; Kim, Y. H.; Kim, S., Molecular-level investigation of soils contaminated by oil spilled during the Gulf War. *Journal of hazardous materials* **2019**, 373, 271-277.

208. Thomas, M. J.; Collinge, E.; Witt, M.; Lozano, D. C. P.; Vane, C. H.; Moss-Hayes, V.; Barrow, M. P., Petroleomic depth profiling of Staten Island salt marsh soil: 2 omega detection FTICR MS offers a new solution for the analysis of environmental contaminants. *Science of The Total Environment* **2019**, 662, 852-862.

209. Kondyli, A.; Schrader, W., High-resolution GC/MS studies of a light crude oil fraction. *Journal of mass spectrometry* **2019**, 54, (1), 47-54.

210. Vetere, A.; Pröfrock, D.; Schrader, W., Qualitative and Quantitative Evaluation of Sulfur-Containing Compound Types in Heavy Crude Oil and Its Fractions. *Energy & Fuels* **2021**, 35, (10), 8723-8732.

211. Putman, J. C.; Sama, S. G.; Barrere-Mangote, C.; Rodgers, R. P.; Lobinski, R.; Marshall, A. G.; Bouyssiere, B.; Giusti, P., Analysis of Petroleum Products by Gel Permeation Chromatography Coupled Online with Inductively Coupled Plasma Mass Spectrometry and Offline with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2018**, 32, (12), 12198-12204.

212. Wang, P.; Zhang, Y. H.; Xu, C. M.; Zhang, W. L.; Zhu, G. Y.; Li, Z. Y.; Ji, H. C.; Shi, Q., Molecular Characterization of Ketones in a Petroleum Source Rock. *Energy & Fuels* **2018**, 32, (11), 11136-11142.

213. Zhao, R. B.; Sun, J. D.; Fang, Q.; Wei, Y. G.; Song, G. X.; Xu, C. M.; Hsu, C. S.; Shi, Q., Evolution of Acidic Compounds in Crude Oil during In Situ Combustion. *Energy & Fuels* **2017**, 31, (6), 5926-5932.

214. Zhang, K.; Yu, J.; Gao, S. Q.; Li, C. M.; Xu, G. W., Understanding Shale Oil Hydrotreatment with Composition Analysis Using Positive-Ion Mode Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2017**, 31, (2), 1362-1369.

215. Orrego-Ruiz, J. A.; Gomez-Escudero, A.; Rojas-Ruiz, F. A., Combination of Negative Electrospray Ionization and Positive Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry as a Quantitative Approach of Acid Species in Crude Oils. *Energy & Fuels* **2016**, 30, (10), 8209-8215.

216. Huba, A. K.; Gardinali, P. R., Characterization of a crude oil weathering series by ultrahighresolution mass spectrometry using multiple ionization modes. *Science of The Total Environment* **2016**, 563, 600-610.

217. da Silveira, G. D.; Faccin, H.; Claussen, L.; Goularte, R. B.; Do Nascimento, P. C.; Bohrer, D.; Cravo, M.; Leite, L. F. M.; de Carvalho, L. M., A liquid chromatography-atmospheric pressure photoionization tandem mass spectrometric method for the determination of organosulfur compounds in petroleum asphalt cements. *Journal of Chromatography A* **2016**, 1457, 29-40.

218. Dvorski, S. E. M.; Gonsior, M.; Hertkorn, N.; Uhl, J.; Müller, H.; Griebler, C.; Schmitt-Kopplin, P., Geochemistry of Dissolved Organic Matter in a Spatially Highly Resolved Groundwater Petroleum Hydrocarbon Plume Cross-Section. *Environmental Science & Technology* **2016**, 50, (11), 5536-5546.

219. Witt, M.; Timm, W., Determination of Simulated Crude Oil Mixtures from the North Sea Using Atmospheric Pressure Photoionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2016**, 30, (5), 3707-3713.

220. Corilo, Y. E.; Rowland, S. M.; Rodgers, R. P., Calculation of the Total Sulfur Content in Crude Oils by Positive-Ion Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2016**, 30, (5), 3962-3966.

221. Barrow, M. P.; Peru, K. M.; McMartin, D. W.; Headley, J. V., Effects of Extraction pH on the Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Profiles of Athabasca Oil Sands Process Water. *Energy & Fuels* **2016**, 30, (5), 3615-3621.

222. Wang, W.; Liu, Y. R.; Liu, Z. L.; Tian, S. B., Quantitative Analysis Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Correlation between Mass Spectrometry Data and Sulfur Content of Crude Oils. *China Petroleum Processing & Petrochemical Technology* **2015**, 17, (4), 71-80.

223. Sim, A.; Cho, Y.; Kim, D.; Witt, M.; Birdwell, J. E.; Kim, B. J.; Kim, S., Molecular-level characterization of crude oil compounds combining reversed-phase high-performance liquid chromatography with off-line high-resolution mass spectrometry. *Fuel* **2015**, 140, 717-723.

224. Gomez-Escudero, A.; Rojas-Ruiz, F. A.; Orrego-Ruiz, J. A., Characterization of vacuum gas oils using FT-ICR MS. *Ct&F-Ciencia Tecnologia Y Futuro* **2015**, 6, (1), 69-80.

225. Ayala-Cabrera, J. F.; Lipok, C.; Moyano, E.; Schmitz, O. J.; Santos, F. J., Atmospheric pressure ionization for gas chromatography-high resolution mass spectrometry determination of polychlorinated naphthalenes in marine sediments. *Chemosphere* **2021**, 263, 11.

226. Luo, R.; Schrader, W., Development of a Non-Targeted Method to Study Petroleum Polyaromatic Hydrocarbons in Soil by Ultrahigh Resolution Mass Spectrometry Using Multiple Ionization Methods. *Polycyclic Aromatic Compounds* **2020**, 1-16.

227. Panda, S. K.; Alawani, N. A.; Lajami, A. R.; Al-Qunaysi, T. A.; Muller, H., Characterization of aromatic hydrocarbons and sulfur heterocycles in Saudi Arabian heavy crude oil by gel permeation chromatography and ultrahigh resolution mass spectrometry. *Fuel* **2019**, 235, 1420-1426.

228. Kruth, C.; Czech, H.; Sklorz, M.; Passig, J.; Ehlert, S.; Cappiello, A.; Zimmermann, R., Direct Infusion Resonance-Enhanced Multiphoton Ionization Mass Spectrometry of Liquid Samples under Vacuum Conditions. *Analytical Chemistry* **2017**, 89, (20), 10917-10923.

229. Walters, C. C.; Wang, F. C.; Qian, K. N.; Wu, C. P.; Mennito, A. S.; Wei, Z. B., Petroleum alteration by thermochemical sulfate reduction - A comprehensive molecular study of aromatic hydrocarbons and polar compounds. *Geochimica et Cosmochimica Acta* **2015**, 153, 37-71.

230. De Hoffmann, E.; Stroobant, V., Mass Spectrometry: Principles and Applications, 3rd Edition. *Wiley* **2013**.

231. Saad, F.; Bounaceur, B.; Daaou, M.; Aviles-Moreno, J. R.; Martinez-Haya, B., Molecular Characterization of Nonvolatile Fractions of Algerian Petroleum with High-Resolution Mass Spectrometry. *Energy & Fuels* **2021**, 35, (10), 8699-8710.

232. Ruger, C. P.; Neumann, A.; Sklorz, M.; Schwemer, T.; Zimmermann, R., Thermal Analysis Coupled to Ultrahigh Resolution Mass Spectrometry with Collision Induced Dissociation for Complex Petroleum Samples: Heavy Oil Composition and Asphaltene Precipitation Effects. *Energy & Fuels* **2017**, 31, (12), 13144-13158.

233. Riedeman, J. S.; Kadasala, N. R.; Wei, A.; Kenttamaa, H. I., Characterization of Asphaltene Deposits by Using Mass Spectrometry and Raman Spectroscopy. *Energy & Fuels* **2016**, 30, (2), 805-809.

234. Tang, W. J.; Hurt, M. R.; Sheng, H. M.; Riedeman, J. S.; Borton, D. J.; Slater, P.; Kenttamaa, H. I., Structural Comparison of Asphaltenes of Different Origins Using Multi-stage Tandem Mass Spectrometry. *Energy & Fuels* **2015**, *2*9, (3), 1309-1314.

235. Lacroix-Andrivet, O.; Castilla, C.; Rüger, C.; Hubert-Roux, M.; Mendes Siqueira, A. L.; Giusti, P.; Afonso, C., Direct Insertion Analysis of Polymer-Modified Bitumen by Atmospheric Pressure Chemical Ionization Ultrahigh-Resolution Mass Spectrometry. *Energy & Fuels* **2021**, 35, (3), 2165-2173.

236. de Freitas, C. S.; Valencia-Davila, J. A.; Pereira, R. C. L.; Abrantes, L. T.; Kato, L.; Vaz, B. G., Isolation and characterization of sulfur-containing compounds by positive-ion electrospray ionization and online HPLC/Atmospheric pressure chemical ionization coupled to Orbitrap mass spectrometry. *Fuel* **2021**, 289, 9.

237. Zhang, Y. F.; Han, Y. H.; Wu, J. X.; Wang, Y. H.; Li, J. Y.; Shi, Q.; Xu, C. M.; Hsu, C. S., Comprehensive Composition, Structure, and Size Characterization for Thiophene Compounds in Petroleum Using Ultrahigh-Resolution Mass Spectrometry and Trapped Ion Mobility Spectrometry. *Analytical Chemistry* **2021**, 93, (12), 5089-5097.

238. Han, Y. H.; Zhang, Y. F.; Xu, C. M.; Hsu, C. S., Molecular characterization of sulfur-containing compounds in petroleum. *Fuel* **2018**, 221, 144-158.

239. Tang, W. J.; Sheng, H. M.; Jin, C. F.; Riedeman, J. S.; Kenttamaa, H. I., Characterization of aromatic organosulfur model compounds relevant to fossil fuels by using atmospheric pressure chemical ionization with CS2 and high-resolution tandem mass spectrometry. *Rapid Communications in Mass Spectrometry* **2016**, 30, (7), 953-962.

240. Elbaz, A. M.; Gani, A.; Hourani, N.; Emwas, A. H.; Sarathy, S. M.; Roberts, W. L., TG/DTG, FT-ICR Mass Spectrometry, and NMR Spectroscopy Study of Heavy Fuel Oil. *Energy & Fuels* **2015**, 29, (12), 7825-7835.

241. Souza, L. M.; Silva, S. R. C.; Filgueiras, P. R.; dos Santos, F. D.; Vasconcelos, G. A.; Lacerda, V.; Vaz, B. G.; Romao, W., Study of the Effect of Inhibitors Solutions on the Chemical Composition of Waxes by Rheology Tests and High Resolution Mass Spectrometry. *Journal of the Brazilian Chemical Society* **2020**, 31, (4), 627-637.

242. Lobodin, V. V.; Maksimova, E. V.; Rodgers, R. P., Gas Chromatography/Atmospheric Pressure Chemical Ionization Tandem Mass Spectrometry for Fingerprinting the Macondo Oil Spill. *Analytical Chemistry* **2016**, 88, (13), 6914-6922.

243. Fasya, A. G.; Millati, N.; Rahmawati, L. M.; Iyani, R.; Hanapi, A.; Ningsih, R.; Yuliani, D.; Megawati, D. S., Isolation and Bioactivity of Steroids Isolates From Petroleum Ether Fraction Of Chlorella sp. *AIP Conference Proceedings* **2020**, 2243, (1), 030005.

244. Smit, E.; De Goede, S.; Rohwer, E. R., Class Separation of the Trace Polar Species Present in Diesel Using Hydrophilic Interaction Chromatography and High Resolution Mass Spectrometry. *Energy & Fuels* **2018**, 32, (9), 8944-8954.

245. Ruger, C. P.; Miersch, T.; Schwemer, T.; Sklorz, M.; Zimmermann, R., Hyphenation of Thermal Analysis to Ultrahigh-Resolution Mass Spectrometry (Fourier Transform Ion Cyclotron Resonance Mass Spectrometry) Using Atmospheric Pressure Chemical Ionization For Studying Composition and Thermal Degradation of Complex Materials. *Analytical Chemistry* **2015**, 87, (13), 6493-6499.

246. Wu, C.; Qian, K.; Walters, C. C.; Mennito, A., Application of atmospheric pressure ionization techniques and tandem mass spectrometry for the characterization of petroleum components. *International Journal of Mass Spectrometry* **2015**, 377, 728-735.

247. Lacroix-Andrivet, O.; Hubert-Roux, M.; Siqueira, A. L. M.; Bai, Y.; Afonso, C., Comparison of Silica and Cellulose Stationary Phases to Analyze Bitumen by High-Performance Thin-Layer Chromatography Coupled to Laser Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2020**, 34, (8), 9296-9303.

248. de Mour, L. G. M.; Rosa, P., Evaluation of asphaltene precipitation in different conditions of composition, temperature, and pression. *Quimica Nova* **2018**, 41, (2), 157-162.

249. Olaitan, A. D.; Reyes, K. A.; Barnes, L. F.; Yount, J. R.; Ward, S.; Hamilton, H. S. C.; King, K. E.; Van Leeuwen, C. J.; Stepherson, J. R.; Vargas, T. K., et al., Transition metal oxide nanoparticles as surfaces for surface-assisted laser desorption/ionization mass spectrometry of asphaltenes. *Petroleum Science and Technology* **2017**, 35, (19), 1917-1924.

250. Fossen, M.; Kallevik, H.; Knudsen, K. D.; Sjöblom, J., Asphaltenes Precipitated by a Two-Step Precipitation Procedure. 2. Physical and Chemical Characteristics. *Energy & Fuels* **2011**, 25, (8), 3552-3567. 251. Acter, T.; Solihat, N. N.; Kim, S.; Uddin, N.; Mustafa, A. I.; Shamsuddin, S. M.; Kim, S., Application of silver-assisted laser desorption ionization ultrahigh-resolution mass spectrometry for the speciation of sulfur compounds. *Analytical and bioanalytical chemistry* **2020**, 412, (1), 243-255.

252. Zahraei, A.; Arisz, P. W. F.; van Bawl, A. P.; Heeren, R. M. A., Evaluation of Thin-Layer Chromatography-Laser Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometric Imaging for Visualization of Crude Oil Interactions. *Energy & Fuels* **2018**, 32, (7), 7347-7357. 253. Pomerantz, A. E.; Hammond, M. R.; Morrow, A. L.; Mullins, O. C.; Zare, R. N., Two-Step Laser Mass Spectrometry of Asphaltenes. *Journal of the American Chemical Society* **2008**, 130, (23), 7216-7217.

254. Pomerantz, A. E.; Hammond, M. R.; Morrow, A. L.; Mullins, O. C.; Zare, R. N., Asphaltene Molecular-Mass Distribution Determined by Two-Step Laser Mass Spectrometry. *Energy & Fuels* **2009**, 23, (3), 1162-1168.

255. Hurtado, P.; Gamez, F.; Martinez-Haya, B., One- and Two-Step Ultraviolet and Infrared Laser Desorption Ionization Mass Spectrometry of Asphaltenes. *Energy & Fuels* **2010**, 24, (11), 6067-6073.

256. Mukhamatdinov, II; Salih, I. S. S.; Rakhmatullin, I. Z.; Sviridenko, N. N.; Pevneva, G. S.; Sharma, R. K.; Vakhin, A. V., Transformation of Resinous Components of the Ashalcha Field Oil during Catalytic Aquathermolysis in the Presence of a Cobalt-Containing Catalyst Precursor. *Catalysts* **2021**, 11, (6), 16.

257. Moulian, R.; Chacon-Patino, M.; Lacroix-Andrivet, O.; Mounicou, S.; Siqueira, A. L. M.; Afonso, C.; Rodgers, R.; Giust, P.; Bouyssiere, B.; Barrere-Mangote, C., Speciation of Metals in Asphaltenes by High-Performance Thin-Layer Chromatography and Solid-Liquid Extraction Hyphenated with Elemental and Molecular Identification. *Energy & Fuels* **2020**, 34, (10), 12449-12456.

258. Mironov, N. A.; Sinyashin, K. O.; Abilova, G. R.; Tazeeva, E. G.; Milordov, D. V.; Yakubova, S. G.; Borisov, D. N.; Gryaznov, P. I.; Borisova, Y. Y.; Yakubov, M. R., Chromatographic isolation of vanadyl porphyrins from heavy oil resins. *Russian Chemical Bulletin* **2017**, 66, (8), 1450-1455.
259. Zhang, W.; Mullen, K., Analyzing solid fossil-fuel pitches by a combination of Soxhlet extraction and Fourier transform ion cyclotron resonance mass spectrometry. *Carbon* **2020**, 167, 414-421.

260. Ruiz-Morales, Y.; Miranda-Olvera, A. D.; Portales-Martinez, B.; Dominguez, J. M., Experimental and Theoretical Approach To Determine the Average Asphaltene Structure of a Crude Oil from the Golden Lane (Faja de Oro) of Mexico. *Energy & Fuels* **2020**, 34, (7), 7985-8006.

261. Duan, C. T.; Zheng, D. F.; Liu, J. Q.; Wang, Q. S.; Liang, P.; Gong, X. Y.; Song, H. H., Research progress on the characterization of mesophase pitch. *New Carbon Materials* **2018**, 33, (3), 193-202.

262. Fan, X. H.; Fei, Y. Q.; Chen, L.; Lit, W., Distribution and Structural Analysis of Polycyclic Aromatic Hydrocarbons Abundant in Coal Tar Pitch. *Energy & Fuels* **2017**, 31, (5), 4694-4704.

263. Zhang, W.; Andersson, J. T.; Rader, H. J.; Mullen, K., Molecular characterization of large polycyclic aromatic hydrocarbons in solid petroleum pitch and coal tar pitch by high resolution MALDI ToF MS and insights from ion mobility separation. *Carbon* **2015**, 95, 672-680.

264. Lee, H.; Abarghani, A.; Liu, B.; Shokouhimehr, M.; Ostadhassan, M., Molecular weight variations of kerogen during maturation with MALDI-TOF-MS. *Fuel* **2020**, 269, 8.

265. Borisova, Y. Y.; Minzagirova, A. M.; Gilmanova, A. R.; Galikhanov, M. F.; Borisov, D. N.; Yakubov, M. R., Heavy Oil Residues: Application as a Low-Cost Filler in Polymeric Materials. *Civil Engineering Journal-Tehran* **2019**, *5*, (12), 2554-2568.

266. Kim, H.; Lee, Y. S., A Study on Fire Explosion Characteristics via Physico-chemical Analysis of Petroleum Residues. *Applied Chemistry for Engineering* **2019**, 30, (5), 556-561.

267. Zhong, Q. F.; Mao, Q. Y.; Zhang, L. Y.; Xiang, J. H.; Xiao, J.; Mathews, J. P., Structural features of Qingdao petroleum coke from HRTEM lattice fringes: Distributions of length, orientation, stacking, curvature, and a large-scale image-guided 3D atomistic representation. *Carbon* **2018**, 129, 790-802.

268. Cardozo, S. D.; Schulze, M.; Tykwinski, R. R.; Gray, M. R., Addition Reactions of Olefins to Asphaltene Model Compounds. *Energy & Fuels* **2015**, 29, (3), 1494-1502.

269. Borges, C. N.; Mendes, M. A.; Alves, R. M. B., Mathematical Modeling of an Industrial Delayed Coking Unit. In *12th International Symposium on Process Systems Engineering*, Gernaey, K. V.; Huusom, J. K.; Gani, R., Eds. Elsevier Science Bv: Amsterdam, 2015; Vol. 37, pp 515-520.

270. Madeira, N. C. L.; Rainha, K. P.; Mendonca, J.; Lacerda, V.; Chinelatto, L. S.; de Menezes, S. M. C.; Porto, C. F. D.; Pinto, F. E.; Filgueiras, P. R.; Romao, W., et al., Study of the Influence of Resins on the Asphaltene Aggregates by H-1 DOSY NMR. *Energy & Fuels* **2020**, 34, (5), 5679-5688.

271. Mukhamatdinov, II; Salih, I. S. S.; Rakhmatullin, I. Z.; Sitnov, S. A.; Laikov, A. V.; Klochkov, V. V.; Vakhin, A. V., Influence of Co-based catalyst on subfractional composition of heavy oil asphaltenes during aquathermolysis. *Journal of petroleum science and engineering* **2020**, 186, 9.

272. Nciri, N.; Kim, J.; Kim, N.; Cho, N., An In-Depth Investigation into the Physicochemical, Thermal, Microstructural, and Rheological Properties of Petroleum and Natural Asphalts. *Materials* **2016**, 9, (10), 20.

273. Mironov, N.; Milordov, D.; Abilova, G.; Tazeeva, E.; Yakubova, S.; Yakubov, M., Preparative-scale purification of petroleum vanadyl porphyrins by sulfuric acid loaded macroporous silica. *Journal of Porphyrins and Phthalocyanines* **2020**, 24, (4), 528-537.

274. Cho, J. H.; Im, J. S.; Kim, M. I.; Lee, Y. S.; Bai, B. C., Preparation of petroleum-based binder pitch for manufacturing thermally conductive carbon molded body and comparison with commercial coal-based binder pitch. *Carbon Letters* **2020**, *30*, (4), 373-379.

275. Seo, S. W.; Choi, Y. J.; Kim, J. H.; Cho, J. H.; Lee, Y. S.; Im, J. S., Micropore-structured activated carbon prepared by waste PET/petroleum-based pitch. *Carbon Letters* **2019**, 29, (4), 385-392.

276. Shi, J. L.; Ma, C., Preparation and characterization of spinnable mesophase pitches: A review. *New Carbon Materials* **2019**, 34, (3), 211-219.

277. Ko, S.; Choi, J. E.; Yim, H.; Miyawaki, J.; Yoon, S. H.; Jeon, Y. P., Improved understanding of the molecular structure of pyrolysis fuel oil: towards its utilization as a raw material for mesophase pitch synthesis. *Carbon Letters* **2019**, 29, (3), 307-317.

278. Seo, S. W.; Kim, J. H.; Lee, Y. S.; Im, J. S., Identification of Synthesized Pitch Derived from Pyrolyzed Fuel Oil (PFO) by Pressure. *Applied Chemistry for Engineering* **2018**, 29, (6), 652-656.

279. Kim, J. G.; Kim, J. H.; Im, J. S.; Lee, Y. S.; Bae, T. S., Empirical study of petroleum-based pitch production via pressure- and temperature-controlled thermal reactions. *Journal of Industrial and Engineering Chemistry* **2018**, 62, 176-184.

280. Kim, K. H.; Lee, S.; Kim, M. I.; Lee, Y. S., The effect of carbon black on reforming of pyrolysis fuel oil for a binder pitch. *Fuel* **2017**, 206, 58-63.

281. Lee, S.; Kim, K. H.; Lee, Y. S., Preparation of carbon discs using petroleum-based binder pitch reformed with carbon black. *Carbon Letters* **2017**, 23, (1), 84-87.

282. Kim, J.; Im, U. S.; Lee, B.; Peck, D. H.; Yoon, S. H.; Jung, D. H., Pitch-based carbon fibers from coal tar or petroleum residue under the same processing condition. *Carbon Letters* **2016**, 19, (1), 72-78.

283. Kim, J. G.; Kim, J. H.; Song, B. J.; Jeon, Y. P.; Lee, C. W.; Lee, Y. S.; Im, J. S., Characterization of pitch derived from pyrolyzed fuel oil using TLC-FID and MALDI-TOF. *Fuel* **2016**, 167, 25-30.

284. Valencia-Davila, J. A.; Blanco-Tirado, C.; Combariza, M. Y., Analysis of naphthenic acids by matrix assisted laser desorption ionization time of flight mass spectrometry. *Fuel* **2017**, 193, 168-177.

285. Valencia-Davila, J. A.; Witt, M.; Blanco-Tirado, C.; Combariza, M. Y., Molecular characterization of naphthenic acids from heavy crude oils using MALDI FT-ICR mass spectrometry. *Fuel* **2018**, 231, 126-133.

286. Duan, P.; Qian, K.; Habicht, S. C.; Pinkston, D. S.; Fu, M.; Kenttämaa, H. I., Analysis of base oil fractions by ClMn(H2O)+ chemical ionization combined with laser-induced acoustic desorption/fourier transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* **2008**, 80, (6), 1847-53.

287. Dow, A. M.; Wittrig, A. R.; Kenttamaa, H. I., Laser-induced acoustic desorption mass spectrometry. *European Journal of Mass Spectrometry* **2012**, 18, (2), 77-92.

288. Crawford, K. E.; Campbell, J. L.; Fiddler, M. N.; Duan, P.; Qian, K.; Gorbaty, M. L.; Kenttämaa, H. I., Laser-Induced Acoustic Desorption/Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for Petroleum Distillate Analysis. *Analytical Chemistry* **2005**, 77, (24), 7916-7923.

289. Chen, J.; Jia, L. Y.; Zhao, L. M.; Lu, X. Q.; Guo, W. Y.; Weng, J. J.; Qi, F., Analysis of Petroleum Aromatics by Laser-Induced Acoustic Desorption/Tunable Synchrotron Vacuum Ultraviolet Photoionization Mass Spectrometry. *Energy & Fuels* **2013**, 27, (4), 2010-2017.

290. Nyadong, L.; Quinn, J. P.; Hsu, C. S.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G., Atmospheric Pressure Laser-Induced Acoustic Desorption Chemical Ionization Mass Spectrometry for Analysis of Saturated Hydrocarbons. *Analytical Chemistry* **2012**, 84, (16), 7131-7137.

291. Pinkston, D. S.; Duan, P.; Gallardo, V. A.; Habicht, S. C.; Tan, X. L.; Qian, K. N.; Gray, M.; Mullen, K.; Kenttamaa, H. I., Analysis of Asphaltenes and Asphaltene Model Compounds by Laser-Induced Acoustic Desorption/Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2009**, 23, (11), 5564-5570.

292. Gao, J. S.; Borton, D. J.; Owen, B. C.; Jin, Z. C.; Hurt, M.; Amundson, L. M.; Madden, J. T.; Qian, K. N.; Kenttamaa, H. I., Laser-Induced Acoustic Desorption/Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of The American Society for Mass Spectrometry* **2011**, 22, (3), 531-538.

293. 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.

294. Leider, A.; Richter-Brockmann, S.; Nettersheim, B. J.; Achten, C.; Hallmann, C., Low-femtogram sensitivity analysis of polyaromatic hydrocarbons using GC-APLI-TOF mass spectrometry: Extending the target window for aromatic steroids in early Proterozoic rocks. *Organic Geochemistry* **2019**, 129, 77-87.

295. 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, (7), 867-869.

296. Liu, T. L.; Lu, J. C.; Zhao, X.; Zhou, Y. S.; Wei, Q.; Xu, C. M.; Zhang, Y. H.; Ding, S. J.; Zhang, T.; Tao, X. J., et al., Distribution of Vanadium Compounds in Petroleum Vacuum Residuum and Their Transformations in Hydrodemetallization. *Energy & Fuels* **2015**, 29, (4), 2089-2096.

297. Lu, J. C.; Zhang, Y. H.; Shi, Q., Ionizing Aromatic Compounds in Petroleum by Electrospray with HCOONH4 as Ionization Promoter. *Analytical Chemistry* **2016**, 88, (7), 3471-3475.

298. Degtyareva, E. S.; Burykina, J. V.; Ananikov, V. P., ESI-MS Analysis of Thiol-yne Click Reaction in Petroleum Medium. *Molecules* **2021**, 26, (10), 9.

299. Wang, M.; Zhao, S. Q.; Liu, X. X.; Shi, Q., Molecular Characterization of Thiols in Fossil Fuels by Michael Addition Reaction Derivatization and Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry* **2016**, 88, (19), 9837-9842.

300. Chen, X.; Li, H. D.; Zhang, L. Z.; Shi, Q.; Zhao, S. Q.; Xu, C. M., CYHPO oxidation followed by methylation for selective characterization of thiophenic and sulfidic compounds in petroleum via ESI FT-ICR MS. *Fuel* **2020**, 265.

301. Li, H. D.; Chen, X.; Wu, J. X.; Zhang, Y. H.; Liu, X. X.; Shi, Q.; Zhao, S. Q.; Xu, C. M.; Hsu, C. S., Selective Methylation of Sulfides in Petroleum for Electrospray Ionization Mass Spectrometry Analysis. *Energy & Fuels* **2019**, 33, (3), 1797-1802.

302. Porto, C. F. C.; Pinto, F. E.; Souza, L. M.; Madeira, N. C. L.; Neto, A. C.; de Menezes, S. M. C.; Chinelatto, L. S.; Freitas, C. S.; Vaz, B. G.; Lacerda, V., et al., Characterization of organosulfur compounds in asphalt cement samples by ESI(+)FT-ICR MS and C-13 NMR spectroscopy. *Fuel* **2019**, 256.

303. Guillemant, J.; Lacoue-Negre, M.; Berlioz-Barbier, A.; Albrieux, F.; de Oliveira, L. P.; Joly, J. F.; Duponchel, L., Towards a new pseudo-quantitative approach to evaluate the ionization response of nitrogen compounds in complex matrices. *Scientific Reports* **2021**, 11, (1), 13.

304. Pontes, N. S.; Silva, R. V. S.; Ximenes, V. L.; Pinho, A. R.; Azevedo, D. A., Chemical speciation of petroleum and bio-oil coprocessing products: Investigating the introduction of renewable molecules in refining processes. *Fuel* **2021**, 288, 13.

305. Lima, B. D.; Martins, L. L.; de Souza, E. S.; Pudenzi, M. A.; da Cruz, G. F., Monitoring chemical compositional changes of simulated spilled Brazilian oils under tropical climate conditions by multiple analytical techniques. *Marine Pollution Bulletin* **2021**, 164, 12.

306. Mahlstedt, N.; Horsfield, B.; Wilkes, H.; Poetz, S., Tracing the Impact of Fluid Retention on Bulk Petroleum Properties Using Nitrogen-Containing Compounds. *Energy & Fuels* **2016**, 30, (8), 6290-6305.

307. Janusson, E.; McGarvey, G. B.; Islam, F.; Rowan, C.; McIndoe, J. S., Selective mass spectrometric analysis of thiols using charge-tagged disulfides. *Analyst* **2016**, 141, (19), 5520-5526.

308. Maleki, H.; Kondalaji, S. G.; Khakinejad, M.; Valentine, S. J., Structural Assignments of Sulfur-Containing Compounds in Crude Oil Using Ion Mobility Spectrometry-Mass Spectrometry. *Energy & Fuels* **2016**, 30, (11), 9150-9161.

309. Kostyukevich, Y.; Solovyov, S.; Kononikhin, A.; Popov, I.; Nikolaev, E., The investigation of the bitumen from ancient Greek amphora using FT ICR MS, H/D exchange and novel spectrum reduction approach. *Journal of mass spectrometry* **2016**, 51, (6), 430-436.

310. Hu, M.; Guo, C.; Zhang, L. Z.; Zhao, S. Q.; Chung, K. H.; Xu, C. M.; Shi, Q., Petroleum heteroatom compounds in various commercial delayed coking liquids: characterized by FT-ICR MS and GC techniques. *SCIENCE CHINA-CHEMISTRY* **2017**, 60, (2), 284-292.

311. Jarvis, J. M.; Billing, J. M.; Hallen, R. T.; Schmidt, A. J.; Schaub, T. M., Hydrothermal Liquefaction Biocrude Compositions Compared to Petroleum Crude and Shale Oil. *Energy & Fuels* **2017**, 31, (3), 2896-2906. 312. Zuber, J.; Rathsack, P.; Otto, M., Characterization of a pyrolysis liquid from a German brown coal by use of negative and positive ion mode electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry and collision-induced dissociation. *Fuel* **2017**, 200, 113-123.

313. Hosseini, S. H.; Horsfield, B.; Poetz, S.; Wilkes, H.; Yalcin, M. N.; Kavak, O., Role of Maturity in Controlling the Composition of Solid Bitumens in Veins and Vugs from SE Turkey as Revealed by Conventional and Advanced Geochemical Tools. *Energy & Fuels* **2017**, 31, (3), 2398-2413.

314. Wan, Z. H.; Li, S. M.; Pang, X. Q.; Dong, Y. X.; Wang, Z. J.; Chen, X. F.; Meng, X. B.; Shi, Q., Characteristics and geochemical significance of heteroatom compounds in terrestrial oils by negative-ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Organic Geochemistry* **2017**, 111, 34-55.

315. Pinto, F. E.; Silva, C.; Tose, L. V.; Figueiredo, M. A. G.; Souza, W. C.; Vaz, B. G.; Romao, W., Evaluation of Adsorbent Materials for the Removal of Nitrogen Compounds in Vacuum Gas Oil by Positive and Negative Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2017**, 31, (4), 3454-3464.

316. Ruddy, B. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G., Positive Ion Electrospray Ionization Suppression in Petroleum and Complex Mixtures. *Energy & Fuels* **2018**, 32, (3), 2901-2907.

317. Moustafa, N. E.; Mahmoud, K., Novel caped Pd nanoparticles-liquid chromatography-tandem mass spectrometry for the identification of oxygenates in Saudi Arabian crude oil. *CHINESE JOURNAL OF CHROMATOGRAPHY* **2018**, 36, (4), 362-369.

318. Li, X. H.; Yuan, H. Y.; Yin, J. J.; Wu, B. C., Compositional Characterization of Nitrogen Compounds in Changqing Crude Oil and Its Heavy Distillates. *China Petroleum Processing & Petrochemical Technology* **2018**, 20, (4), 51-59.

319. Liu, M.; Zhang, L. Z.; Zhang, C.; Yuan, S. H.; Zhao, D. Z.; Duan, L. H., Transformation of nitrogencontaining compounds in atmospheric residue by hydrotreating. *KOREAN JOURNAL OF CHEMICAL ENGINEERING* **2018**, 35, (2), 375-382.

320. Han, Y. J.; Poetz, S.; Mahlstedt, N.; Karger, C.; Horsfield, B., Fractionation of Pyrrolic Nitrogen Compounds Compounds during Primary Migration of Petroleum within the Barnett Shale Sequence of Marathon 1 Mesquite Well, Texas. *Energy & Fuels* **2018**, 32, (4), 4638-4650.

321. Santos, J. M.; Wisniewski, A.; Eberlin, M. N.; Schrader, W., Comparing Crude Oils with Different API Gravities on a Molecular Level Using Mass Spectrometric Analysis. Part 1: Whole Crude Oil. *Energies* **2018**, 11, (10).

322. Wang, P.; Xu, C. M.; Zhang, Y. H.; Wang, M.; Shi, Q., Identification of Artifacts in the Methylation Process of Sulfur Compounds in Petroleum. *Energy & Fuels* **2018**, 32, (10), 10571-10579.

323. Wang, X. W.; Cai, T.; Wen, W. T.; Zhang, Z. H., Effect of biosurfactant on biodegradation of heteroatom compounds in heavy oil. *Fuel* **2018**, 230, 418-429.

324. Ji, H.; Li, S. M.; Greenwood, P.; Zhang, H. G.; Pang, X. Q.; Xu, T. W.; He, N. N.; Shi, Q., Geochemical characteristics and significance of heteroatom compounds in lacustrine oils of the Dongpu Depression (Bohai Bay Basin, China) by negative-ion Fourier transform ion cyclotron resonance mass spectrometry. *MARINE AND PETROLEUM GEOLOGY* **2018**, 97, 568-591.

325. Ni, H. X.; Xu, C. M.; Wang, R.; Guo, X. F.; Long, Y. H.; Ma, C.; Yan, L. L.; Liu, X. X.; Shi, Q., Composition and Transformation of Sulfur-, Oxygen-, and Nitrogen-Containing Compounds in the Hydrotreating Process of a Low-Temperature Coal Tar. *Energy & Fuels* **2018**, 32, (3), 3077-3084.

326. Han, Y. J.; Poetz, S.; Mahlstedt, N.; Karger, C.; Horsfield, B., Fractionation and origin of NyOx and O-x compounds in the Barnett Shale sequence of the Marathon 1 Mesquite well, Texas. *MARINE AND PETROLEUM GEOLOGY* **2018**, 97, 517-524.

327. Leshuk, T.; Peru, K. M.; Livera, D. D.; Tripp, A.; Bardo, P.; Headley, J. V.; Gu, F., Petroleomic analysis of the treatment of naphthenic organics in oil sands process-affected water with buoyant photocatalysts. *WATER RESEARCH* **2018**, 141, 297-306.

328. Chen, X.; Xu, C. M.; Zhang, W. L.; Ma, C.; Liu, X. X.; Zhao, S. Q.; Shi, Q., Separation and Molecular Characterization of Ketones in a Low-Temperature Coal Tar. *Energy & Fuels* **2018**, 32, (4), 4662-4670.

329. Kostyukevich, Y.; Vlaskin, M.; Zherebker, A.; Grigorenko, A.; Borisova, L.; Nikolaev, E., High-Resolution Mass Spectrometry Study of the Bio-Oil Samples Produced by Thermal Liquefaction of Microalgae in Different Solvents. *Journal of The American Society for Mass Spectrometry* **2019**, 30, (4), 605-614.

330. Pan, Y. H.; Li, M. W.; Sun, Y. G.; Li, Z. M.; Liu, P.; Jiang, B.; Liao, Y. H., Characterization of free and bound bitumen fractions in a thermal maturation shale sequence. Part 1: Acidic and neutral compounds by negative-ion ESI FT-ICR MS. *Organic Geochemistry* **2019**, 134, 1-15.

331. Le Maitre, J.; Hubert-Roux, M.; Paupy, B.; Marceau, S.; Ruger, 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, 417-430.

332. Covas, T. R.; Rocha, Y. D.; Spigolon, A. L. D.; Pereira, R. C. L.; Valencia-Davila, J. A.; Rangel, M. D.; Vaz, B. G., Evaluation of the effects of the simulated thermal evolution of a Type-I source rock on the distribution of basic nitrogen-containing compounds. *Fuel* **2019**, 254.

333. Chen, X.; Li, H. D.; Zhang, L. Z.; Shi, Q.; Zhao, S. Q.; Xu, C. M., Direct sulfur-containing compounds analysis in petroleum via (+) ESI FT-ICR MS using HBF4 as ionization promoter. *Fuel* **2020**, 278.

334. Zhang, Y.; Chen, X.; Zhang, L. Z.; Shi, Q.; Zhao, S. Q.; Xu, C. M., Specification of the nitrogen functional group in a hydrotreated petroleum molecule using hydrogen/deuterium exchange electrospray ionization high-resolution mass spectrometry. *Analyst* **2020**, 145, (13), 4442-4451.

335. Zhang, J. K.; Cao, J.; Xia, L. W.; Xiang, B. L.; Li, E. T., Investigating biological nitrogen cycling in lacustrine systems by FT-ICR-MS analysis of nitrogen-containing compounds in petroleum. *PALAEOGEOGRAPHY PALAEOCLIMATOLOGY PALAEOECOLOGY* **2020**, 556.

336. Zhang, C.; Zhang, Y.; Liu, M.; Guan, Y. M.; Yuan, S. H., Transformation of sulfur compounds in two typical atmospheric residues in hydrotreating via ESI FT-ICR MS. *Fuel* **2020**, 281.

337. Mohler, R. E.; Ahn, S.; O'Reilly, K.; Zemo, D. A.; Devine, C. E.; Magaw, R.; Sihota, N., Towards comprehensive analysis of oxygen containing organic compounds in groundwater at a crude oil spill site using GCxGC-TOFMS and Orbitrap ESI-MS. *Chemosphere* **2020**, 244.

338. Le Maitre, J.; Paupy, B.; Hubert-Roux, M.; Marceau, S.; Ruger, C.; Afonso, C.; Giusti, P., Structural Analysis of Neutral Nitrogen Compounds Refractory to the Hydrodenitrogenation Process of Heavy Oil Fractions by High- Resolution Tandem Mass Spectrometry and Ion Mobility-Mass Spectrometry. *Energy & Fuels* **2020**, 34, (8), 9328-9338.

339. Melendez-Perez, J. J.; Oliveira, L. F. C.; Miranda, N.; Sussulini, A.; Eberlin, M. N.; Bastos, W. L.; Rangel, M. D.; Rocha, Y. D., Lacustrine versus Marine Oils: Fast and Accurate Molecular Discrimination via Electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Multivariate Statistics. *Energy & Fuels* **2020**, 34, (8), 9222-9230.

340. Castiblanco, J. E. B.; Carregosa, J. C.; Santos, J. M.; Wisniewski, A., Molecular behavior assessment on initial stages of oil spill in terrestrial environments. *ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH* **2021**, 28, (11), 13595-13604.

341. Lai, T. T.; Mao, Y. C.; Wang, W.; Wang, X. Q.; Wang, N. X.; Liu, Z. L., Characterization of basic nitrogen compounds isolated with FeCl3 in vacuum gas oil and its hydrotreated product. *Fuel* **2020**, 262.

342. Ferreira, P. S.; Madeira, N. C. L.; Folli, G. S.; Romao, W.; Filgueiras, P. R.; Kuster, R. M., SAP fractions from light, medium and heavy oils: Correlation between chemical profile and stationary phases. *Fuel* **2020**, 274.

343. Guillemant, J.; Berlioz-Barbier, A.; de Oliveira, L. P.; Albrieux, F.; Lacoue-Negre, M.; Duponchel, L.; Joly, J. F., Exploration of the Reactivity of Heteroatomic Compounds Contained in Vacuum Gas Oils during Hydrotreatment Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2020**, 34, (9), 10752-10761.

344. Orrego-Ruiz, J. A.; Marquez, R. E.; Rojas-Ruiz, F. A., New Insights on Organic Geochemistry Characterization of the Putumayo Basin Using Negative Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2020**, 34, (5), 5281-5292.

345. Lima, B. D.; Martins, L. L.; Santos, L. C.; de Souza, E. S.; Pudenzi, M. A.; Nascimento, H. L.; Eberlin, M. N.; da Cruz, G. F., Geochemical Investigation of Tar Balls Collected in a Brazilian Beach Using Biomarkers, Ni/V, delta C-13 Ratios and Ultra-High Resolution FT-ICR Mass Spectrometry. *Journal of the Brazilian Chemical Society* **2020**, 31, (4), 673-682.

346. Covas, T. R.; de Freitas, C. S.; Tose, L. V.; Valencia-Davila, J. A.; Rocha, Y. D.; Rangel, M. D.; da Silva, R. C.; Vaz, B. G., Fractionation of polar compounds from crude oils by hetero-medium pressure liquid chromatography (H-MPLC) and molecular characterization by ultrahigh-resolution mass spectrometry. *Fuel* **2020**, 267.

347. Li, P.; Zong, Z. M.; Li, Z. K.; Wang, Y. G.; Liu, F. J.; Wei, X. Y., Characterization of basic heteroatomcontaining organic compounds in liquefaction residue from Shenmu-Fugu subbituminous coal by positiveion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Fuel Processing Technology* **2015**, 132, 91-98.

348. Chen, X.; Zhang, Y.; Han, J.; Zhang, L. Z.; Zhao, S. Q.; Xu, C. M.; Shi, Q., Direct Nickel Petroporphyrin Analysis through Electrochemical Oxidation in Electrospray Ionization Ultrahigh-Resolution Mass Spectrometry. *Energy & Fuels* **2021**, 35, (7), 5748-5757.

349. Zheng, F.; Zhang, Y. F.; Zhang, Y. H.; Han, Y. H.; Zhang, L. Z.; Bouyssiere, B.; Shi, Q., Aggregation of petroporphyrins and fragmentation of porphyrin ions: Characterized by TIMS-TOF MS and FT-ICR MS. *Fuel* **2021**, 289, 7.

350. Zheng, F.; Hsu, C. S.; Zhang, Y. H.; Sun, Y. G.; Wu, Y.; Lu, H.; Sun, X.; Shi, Q., Simultaneous Detection of Vanadyl, Nickel, Iron, and Gallium Porphyrins in Marine Shales from the Eagle Ford Formation, South Texas. *Energy & Fuels* **2018**, 32, (10), 10382-10390.

351. Ramirez-Pradilla, J. S.; Blanco-Tirado, C.; Hubert-Roux, M.; Giusti, P.; Afonso, C.; Combariza, M. Y., Comprehensive Petroporphyrin Identification in Crude Oils Using Highly Selective Electron Transfer Reactions in MALDI-FTICR-MS. *Energy & Fuels* **2019**, 33, (5), 3899-3907.

352. Liu, H.; Mu, J.; Wang, Z. X.; Ji, S. F.; Shi, Q.; Guo, A. J.; Chen, K.; Lu, J. C., Characterization of Vanadyl and Nickel Porphyrins Enriched from Heavy Residues by Positive-Ion Electrospray Ionization FT-ICR Mass Spectrometry. *Energy & Fuels* **2015**, 29, (8), 4803-4813.

353. Alcazar-Vara, L. A.; Zamudio-Rivera, L. S.; Buenrostro-Gonzalez, E., Effect of Asphaltenes and Resins on Asphaltene Aggregation Inhibition, Rheological Behaviour and Waterflood Oil-Recovery. *JOURNAL OF DISPERSION SCIENCE AND TECHNOLOGY* **2016**, 37, (11), 1544-1554.

354. Wang, W.; Dong, M.; Song, C. X.; Cai, X. H.; Liu, Y. R.; Liu, Z. L.; Tian, S. B., Structural information of asphaltenes derived from petroleum vacuum residue and its hydrotreated product obtained by FT-ICR mass spectrometry with narrow ion isolation windows. *Fuel* **2018**, 227, 111-117.

355. Ren, L. M.; Han, Y. H.; Zhang, Y. H.; Zhang, Y. F.; Meng, X. H.; Shi, Q., Spray Injection Direct Analysis in Real Time (DART) Ionization for Petroleum Analysis. *Energy & Fuels* **2016**, 30, (6), 4486-4493.

356. Martins, L. L.; da Silva, P. F.; da Cruz, G. F.; Pudenzi, M. A.; Eberlin, M. N.; Riehl, C. A. D.; Souza, D., Study of Naphthenic Acidity and Corrosivity of Brazilian Crude Oils by ESI(-) FT-ICR MS. *REVISTA VIRTUAL DE QUIMICA* **2018**, 10, (3), 625-640.

357. Barros, E. V.; Dias, H. P.; Pinto, F. E.; Gomes, A. O.; Moura, R. R.; Neto, A. C.; Freitas, J. C. C.; Aquije, G.; Vaz, B. G.; Romao, W., Characterization of Naphthenic Acids in Thermally Degraded Petroleum by ESI(-)-FT-ICR MS and H-1 NMR after Solid-Phase Extraction and Liquid/Liquid Extraction. *Energy & Fuels* **2018**, 32, (3), 2878-2888.

358. Ahad, J. M. E.; Pakdel, H.; Lavoie, D.; Lefebvre, R.; Peru, K. M.; Headley, J. V., Naphthenic acids in groundwater overlying undeveloped shale gas and tight oil reservoirs. *Chemosphere* **2018**, 191, 664-672.

359. Samanipour, S.; Reid, M. J.; Rundberget, J. T.; Frost, T. K.; Thomas, K. V., Concentration and Distribution of Naphthenic Acids in the Produced Water from Offshore Norwegian North Sea Oilfields. *Environmental Science & Technology* **2020**, 54, (5), 2707-2714.

360. Wang, H.; Lu, L.; Chen, H.; McKenna, A. M.; Lu, J.; Jin, S.; Zuo, Y.; Rosario-Ortiz, F. L.; Ren, Z. J., Molecular Transformation of Crude Oil Contaminated Soil after Bioelectrochemical Degradation Revealed by FT-ICR Mass Spectrometry. *Environmental Science & Technology* **2020**, 54, (4), 2500-2509.

361. Rojas-Ruiz, F. A.; Rueda, M. F.; Pachon-Contreras, Z.; Villar-Garcia, A.; Gomez-Escudero, A.; Orrego-Ruiz, J. A., Composition to Interfacial Activity Relationship Approach of Petroleum Sulfonates by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2016**, 30, (6), 4717-4724.

362. Rojas-Ruiz, F. A.; Gomez-Escudero, A.; Pachon-Contreras, Z.; Villar-Garcia, A.; Orrego-Ruiz, J. A., Detailed Characterization of Petroleum Sulfonates by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2016**, 30, (4), 2714-2720.

363. Li, S. K.; Peng, B.; Liu, D.; Sunt, C., Resolution and Identification of Petroleum Sulfonate by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2016**, 30, (4), 2751-2759.

364. Ren, L. M.; Wu, J. X.; Qian, Q.; Liu, X. X.; Meng, X. H.; Zhang, Y. H.; Shi, Q., Separation and Characterization of Sulfoxides in Crude Oils. *Energy & Fuels* **2019**, 33, (2), 796-804.

365. Lu, Y.; Wu, J., The distribution of corrosive acidic compounds in petroleum fractions. *Petroleum Science and Technology* **2016**, 34, (23), 1880-1886.

366. Pan, Y. H.; Liao, Y. H.; Shi, Q., Variations of Acidic Compounds in Crude Oil during Simulated Aerobic Biodegradation: Monitored by Semiquantitative Negative-Ion ESI FT-ICR MS. *Energy & Fuels* **2017**, 31, (2), 1126-1135.

367. Handle, F.; Harir, M.; Fussl, J.; Kosyun, A. N.; Grossegger, D.; Hertkorn, N.; Eberhardsteiner, L.; Hofko, B.; Hospodka, M.; Blab, R., et al., Tracking Aging of Bitumen and Its Saturate, Aromatic, Resin, and Asphaltene Fractions Using High-Field Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2017**, 31, (5), 4771-4779.

368. Clingenpeel, A. C.; Fredriksen, T. R.; Qian, K.; Harper, M. R., Comprehensive Characterization of Petroleum Acids by Distillation, Solid Phase Extraction Separation, and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2018**, 32, (9), 9271-9279.

369. Wang, M.; Zhu, G. Y., Characterization of Acidic Compounds in Ancient Shale of Cambrian Formation Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Tarim Basin, China. *Energy & Fuels* **2019**, 33, (2), 1083-1089.

370. Abib, G. A. P.; Martins, L. L.; De Araujo, L.; Isidorio, T. V.; Pudenzi, M. A.; Santos, V. H.; Da Cruz, G. F., Assessing raw materials as potential adsorbents to remove acidic compounds from Brazilian crude oils by ESI (-) FT-ICR MS. *ANAIS DA ACADEMIA BRASILEIRA DE CIENCIAS* **2020**, 92, (3).

371. Silva, J. D.; Pinto, F. E.; Souza, L. M.; Romao, W.; Loh, W.; Lucas, E. F., Chemical Characterization and Interfacial Activity of Molecules Isolated from Brazilian Oils by Adsorption onto Wet Silica Particles. *Energy & Fuels* **2020**, 34, (11), 13552-13565.

372. Bhosale, S.; Manigiri, R.; Choudhury, R. P.; Bhakthavatsalam, V., High Resolution Mass Spectrometry and Principal Component Analysis for an Exhaustive Understanding of Acidic Species Composition in Vacuum Gas Oil Samples. *Energy & Fuels* **2020**, 34, (3), 2800-2806.

373. Wang, X.; Zhang, R. Y.; Liu, L.; Qiao, P. Q.; Simon, S.; Sjoblom, J.; Xu, Z. H.; Jiang, B., Interactions of Polyaromatic Compounds. Part 2. Flocculation Probed by Dynamic Light Scattering and Molecular Dynamics Simulation. *Energy & Fuels* **2017**, 31, (9), 9201-9212.

374. Petrukhina, N. N.; Maksimov, A. A., Physicochemical Properties and Performance Characteristics of Naphthenoaromatic Jet and Diesel Fuels Obtained by Hydrotreating of Highly Aromatic Fractions. *Petroleum Chemistry* **2018**, 58, (5), 347-374.

375. Kim, S.; Rodgers, R. P.; Blakney, G. T.; Hendrickson, C. L.; Marshall, A. G., Automated Electrospray Ionization FT-ICR Mass Spectrometry for Petroleum Analysis. *Journal of The American Society for Mass Spectrometry* **2009**, 20, (2), 263-268.

376. Alberici, R. M.; Simas, R. C.; de Souza, V.; de Sá, G. F.; Daroda, R. J.; Eberlin, M. N., Analysis of fuels via easy ambient sonic-spray ionization mass spectrometry. *Analytica Chimica Acta* **2010**, 659, (1), 15-22.

377. Godoy, A. T.; Pereira, G. G.; Ferreira, L. L.; Cunha, I. B. S.; Barrera-Arellano, D.; Daroda, R. J.; Eberlin, M. N.; Alberici, R. M., Biodiesel Oxidation Monitored by Ambient Desorption/Ionization Mass Spectrometry. *Energy & Fuels* **2013**, 27, (12), 7455-7459.

378. Wu, C. P.; Qian, K. N.; Nefliu, M.; Cooks, R. G., Ambient Analysis of Saturated Hydrocarbons Using Discharge-Induced Oxidation in Desorption Electrospray Ionization. *Journal of The American Society for Mass Spectrometry* **2010**, 21, (2), 261-267.

379. Da Costa, C.; Reynolds, J. C.; Whitmarsh, S.; Lynch, T.; Creaser, C. S., The quantitative surface analysis of an antioxidant additive in a lubricant oil matrix by desorption electrospray ionization mass spectrometry. *Rapid Communications in Mass Spectrometry* **2013**, 27, (21), 2420-2424.

380. Eckert, P. A.; Roach, P. J.; Laskin, A.; Laskin, J., Chemical Characterization of Crude Petroleum Using Nanospray Desorption Electrospray Ionization Coupled with High-Resolution Mass Spectrometry. *Analytical Chemistry* **2012**, 84, (3), 1517-1525.

381. Hortal, A. R.; Hurtado, P.; Martínez-Haya, B.; Mullins, O. C., Molecular-Weight Distributions of Coal and Petroleum Asphaltenes from Laser Desorption/Ionization Experiments. *Energy & Fuels* **2007**, 21, (5), 2863-2868.

382. Mitchell, M.; Mali, S.; King, C. C.; Bark, S. J., Enhancing MALDI Time-Of-Flight Mass Spectrometer Performance through Spectrum Averaging. *PLOS ONE* **2015**, 10, (3), e0120932.

383. Comisarow, M. B.; Marshall, A. G., Fourier transform ion cyclotron resonance spectroscopy. *Chemical Physics Letters* **1974**, 25, (2), 282-283.

384. Liu, Z.; Phillips, J. B., Comprehensive Two-Dimensional Gas Chromatography using an On-Column Thermal Modulator Interface. *Journal of Chromatographic Science* **1991**, 29, (6), 227-231.

385. Adahchour, M.; Beens, J.; Vreuls, R.; Brinkman, U. T., Recent developments in comprehensive twodimensional gas chromatography (GC× GC): I. Introduction and instrumental set-up. *TrAC Trends in Analytical Chemistry* **2006**, 25, (5), 438-454.

386. Adahchour, M.; Beens, J.; Brinkman, U. A. T., Recent developments in the application of comprehensive two-dimensional gas chromatography. *Journal of Chromatography A* **2008**, 1186, (1), 67-108.

387. Cortes, H. J.; Winniford, B.; Luong, J.; Pursch, M., Comprehensive two dimensional gas chromatography review. *Journal of separation science* **2009**, 32, (5-6), 883-904.

388. Marsman, J.; Wildschut, J.; Evers, P.; De Koning, S.; Heeres, H., Identification and classification of components in flash pyrolysis oil and hydrodeoxygenated oils by two-dimensional gas chromatography and time-of-flight mass spectrometry. *Journal of Chromatography A* **2008**, 1188, (1), 17-25.

389. Dijkmans, T.; Djokic, M. R.; Van Geem, K. M.; Marin, G. B., Comprehensive compositional analysis of sulfur and nitrogen containing compounds in shale oil using GC×GC – FID/SCD/NCD/TOF-MS. *Fuel* **2015**, 140, 398-406.

390. Mamyrin, B., Time-of-flight mass spectrometry (concepts, achievements, and prospects). *International Journal of Mass Spectrometry* **2001**, 206, (3), 251-266.

391. Schlag, E. W., *Time-of-flight mass spectrometry and its applications*. Newnes: 2012.

392. Ibáñez, M.; Sancho, J. V.; Pozo, Ó. J.; Niessen, W.; Hernández, F., Use of quadrupole time-of-flight mass spectrometry in the elucidation of unknown compounds present in environmental water. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry* **2005**, 19, (2), 169-178.

393. Petrovic, M.; Barceló, D., Application of liquid chromatography/quadrupole time-of-flight mass spectrometry (LC-QqTOF-MS) in the environmental analysis. *Journal of mass spectrometry* **2006**, 41, (10), 1259-1267.

394. Ferrer, I.; Thurman, E. M., Liquid chromatography/time-of-flight/mass spectrometry (LC/TOF/MS) for the analysis of emerging contaminants. *TrAC Trends in Analytical Chemistry* **2003**, 22, (10), 750-756.

395. Cotter, R. J., Time-of-flight mass spectrometry for the structural analysis of biological molecules. *Analytical Chemistry* **1992**, 64, (21), 1027A-1039A.

396. Plumb, R. S.; Stumpf, C. L.; Granger, J. H.; Castro-Perez, J.; Haselden, J. N.; Dear, G. J., Use of liquid chromatography/time-of-flight mass spectrometry and multivariate statistical analysis shows promise for the detection of drug metabolites in biological fluids. *Rapid Communications in Mass Spectrometry* **2003**, 17, (23), 2632-2638.

397. Tsutsui, H.; Maeda, T.; Min, J. Z.; Inagaki, S.; Higashi, T.; Kagawa, Y.; Toyo'oka, T., Biomarker discovery in biological specimens (plasma, hair, liver and kidney) of diabetic mice based upon metabolite profiling using ultra-performance liquid chromatography with electrospray ionization time-of-flight mass spectrometry. *Clinica chimica acta* **2011**, 412, (11-12), 861-872.

398. Beens, J.; Boelens, H.; Tijssen, R.; Blomberg, J., Quantitative Aspects of Comprehensive Two-Dimensional Gas Chromatography (GC×GC). *Journal of High Resolution Chromatography* **1998**, 21, (1), 47-54.

Beens, J.; Tijssen, R.; Blomberg, J., Comprehensive two-dimensional gas chromatography (GC x GC) as a diagnostic tool. *HRC. Journal of high resolution chromatography* **1998**, 21, (1), 63-64.

400. Bansal, V.; Vatsala, S.; Kapur, G. S.; Basu, B.; Sarpal, A. S., Hydrocarbon-Type Analysis of Middle Distillates by Mass Spectrometry and NMR Spectroscopy TechniquesA Comparison. *Energy & Fuels* **2004**, 18, (5), 1505-1511.

401. Beens, J.; Brinkman, U. A. T., Comprehensive two-dimensional gas chromatography—a powerful and versatile technique. *Analyst* **2005**, 130, (2), 123-127.

402. Pedroso, M. P.; Godoy, L. A. F. d.; Fidélis, C. H. d. V.; Ferreira, E. C.; Poppi, R. J.; Augusto, F., Comprehensive two-dimensional gas chromatography (GC × GC) - Cromatografia gasosa bidimensional abrangente (GC × GC). $Qu\tilde{A}$ -mica Nova **2009**, 32, 422-430.

403. Hamilton, J. F.; Lewis, A. C.; Bartle, K. D., Peak amplitude and resolution in comprehensive gas chromatography using valve modulation. *Journal of separation science* **2003**, 26, (6-7), 578-584.

404. Frysinger, G. S.; Gaines, R. B., Forensic analysis of ignitable liquids in fire debris by comprehensive two-dimensional gas chromatography. *Journal of Forensic Science* **2002**, 47, (3), 471-482.

405. Fraga, C. G.; Prazen, B. J.; Synovec, R. E., Comprehensive two-dimensional gas chromatography and chemometrics for the high-speed quantitative analysis of aromatic isomers in a jet fuel using the standard addition method and an objective retention time alignment algorithm. *Analytical Chemistry* **2000**, 72, (17), 4154-4162.

406. Hua, R.; Li, Y.; Liu, W.; Zheng, J.; Wei, H.; Wang, J.; Lu, X.; Kong, H.; Xu, G., Determination of sulfurcontaining compounds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector. *Journal of Chromatography A* **2003**, 1019, (1), 101-109.

407. Wang, F. C.-Y.; Walters, C. C., Pyrolysis Comprehensive Two-Dimensional Gas Chromatography Study of Petroleum Source Rock. *Analytical Chemistry* **2007**, 79, (15), 5642-5650.

408. Pursch, M.; Eckerle, P.; Biel, J.; Streck, R.; Cortes, H.; Sun, K.; Winniford, B., Comprehensive twodimensional gas chromatography using liquid nitrogen modulation: set-up and applications. *Journal of Chromatography A* **2003**, 1019, (1-2), 43-51.

409. Johnson, K. J.; Prazen, B. J.; Young, D. C.; Synovec, R. E., Quantification of naphthalenes in jet fuel with GC× GC/Tri-PLS and windowed rank minimization retention time alignment. *Journal of separation science* **2004**, 27, (5-6), 410-416.

410. van Deursen, M.; Beens, J.; Reijenga, J.; Lipman, P.; Cramers, C.; Blomberg, J., Group-type identification of oil samples using comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (GC× GC-TOF). *Journal of High Resolution Chromatography* **2000**, 23, (7-8), 507-510.

411. Blomberg, J.; Schoenmakers, P. J.; Beens, J.; Tijssen, R., Compehensive two-dimensional gas chromatography (GC×GC) and its applicability to the characterization of complex (petrochemical) mixtures. *Journal of High Resolution Chromatography* **1997**, 20, (10), 539-544.

412. van Stee, L. L. P.; Beens, J.; Vreuls, R. J. J.; Brinkman, U. A. T., Comprehensive two-dimensional gas chromatography with atomic emission detection and correlation with mass spectrometric detection: principles and application in petrochemical analysis. *Journal of Chromatography A* **2003**, 1019, (1), 89-99. 413. Hua, R.-X.; Ruan, C.-H.; Wang, J.-H.; Lu, X.; Liu, J.; Xiao, K.; Kong, H.-W.; Xu, G.-W., Research of group separation of petroleum fractions by comprehensive two-dimensional gas chromatography. *ACTA*

CHIMICA SINICA-CHINESE EDITION- **2002**, 60, (12), 2185-2191. 414. Sun, K.; Winniford, W.; Griffith, J.; Colura, K.; Green, S.; Pursch, M.; Luong, J., Comprehensive twodimensional gas chromatography for fast screening of wash oils. *Journal of Chromatographic Science* **2003**, 41, (10), 506-518.

415. Hua, R. X.; Wang, J. H.; Kong, H. W.; Liu, J.; Lu, X.; Xu, G. W., Analysis of sulfur-containing compounds in crude oils by comprehensive two-dimensional gas chromatography with sulfur chemiluminescence detection. *Journal of separation science* **2004**, 27, (9), 691-698.

416. Reddy, C. M.; Eglinton, T. I.; Hounshell, A.; White, H. K.; Xu, L.; Gaines, R. B.; Frysinger, G. S., The West Falmouth oil spill after thirty years: the persistence of petroleum hydrocarbons in marsh sediments. *Environmental Science & Technology* **2002**, 36, (22), 4754-4760.

417. Frysinger, G. S.; Gaines, R. B., Separation and identification of petroleum biomarkers by comprehensive two-dimensional gas chromatography. *Journal of separation science* **2001**, 24, (2), 87-96.

418. Reichenbach, S. E.; Ni, M.; Kottapalli, V.; Visvanathan, A., Information technologies for comprehensive two-dimensional gas chromatography. *Chemometrics and Intelligent Laboratory Systems* **2004**, 71, (2), 107-120.

419. Hyötyläinen, T.; Kallio, M.; Hartonen, K.; Jussila, M.; Palonen, S.; Riekkola, M.-L., Modulator design for comprehensive two-dimensional gas chromatography: quantitative analysis of polyaromatic hydrocarbons and polychlorinated biphenyls. *Analytical Chemistry* **2002**, 74, (17), 4441-4446.

420. Ong, R.; Lundstedt, S.; Haglund, P.; Marriott, P., Pressurised liquid extraction–comprehensive twodimensional gas chromatography for fast-screening of polycyclic aromatic hydrocarbons in soil. *Journal of Chromatography A* **2003**, 1019, (1-2), 221-232.

421. Frysinger, G. S.; Gaines, R. B.; Xu, L.; Reddy, C. M., Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science & Technology* **2003**, 37, (8), 1653-1662.

422. Hao, C.; Headley, J. V.; Peru, K. M.; Frank, R.; Yang, P.; Solomon, K. R., Characterization and pattern recognition of oil–sand naphthenic acids using comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry. *Journal of Chromatography A* **2005**, 1067, (1), 277-284.

423. Gaines, R. B.; Frysinger, G. S.; Hendrick-Smith, M. S.; Stuart, J. D., Oil spill source identification by comprehensive two-dimensional gas chromatography. *Environmental Science & Technology* **1999**, 33, (12), 2106-2112.

424. Gaines, R. B.; Ledford Jr, E. B.; Stuart, J. D., Analysis of water samples for trace levels of oxygenate and aromatic compounds using headspace solid-phase microextraction and comprehensive twodimensional gas chromatography. *Journal of Microcolumn Separations* **1998**, 10, (7), 597-604.

425. Beens, J.; Dallüge, J.; Adahchour, M.; Vreuls, R. J.; Brinkman, U. A. T., Moving cryogenic modulator for the comprehensive two-dimensional gas chromatography (GC× GC) of surface water contaminants. *Journal of Microcolumn Separations* **2001**, 13, (3), 134-140.

426. Xu, X.; Stee, L.; Williams, J.; Beens, J.; Adahchour, M.; Vreuls, R.; Brinkman, U.; Lelieveld, J., Comprehensive two-dimensional gas chromatography (GC× GC) measurements of volatile organic compounds in the atmosphere. *Atmospheric Chemistry and Physics* **2003**, *3*, (3), 665-682.

427. ASTM, A. I., *Annual Book of Standards, Section Five, Petroleum Products, Lubricants, and Fossil Fuels.* West Conshohocken, PA, 2009.

428. McCurry, J. D.; Quimby, B. D., Two-Dimensional Gas Chromatography Analysis of Components in Fuel and Fuel Additives Using a Simplified Heart-Cutting GC System. *Journal of Chromatographic Science* **2003**, 41, (10), 524-527.

429. Dumont, E.; Tienpont, B.; Higashi, N.; Mitsui, K.; Ochiai, N.; Kanda, H.; David, F.; Sandra, P., Heartcutting two-dimensional gas chromatography in combination with isotope ratio mass spectrometry for the characterization of the wax fraction in plant material. *Journal of Chromatography A* **2013**, 1317, 230-238. 430. Ruiz-Guerrero, R.; Vendeuvre, C.; Thiébaut, D.; Bertoncini, F.; Espinat, D., Comparison of Comprehensive Two-Dimensional Gas Chromatography Coupled with Sulfur-Chemiluminescence Detector to Standard Methods for Speciation of Sulfur-Containing Compounds in Middle Distillates. *Journal of Chromatographic Science* **2006**, 44, (9), 566-573.

431. Reymond, C.; Le Masle, A.; Colas, C.; Charon, N., Input of an Off-Line, Comprehensive, Three-Dimensional Method (CPC×SFC/HRMS) to Quantify Polycyclic Aromatic Hydrocarbons in Vacuum Gas Oils. *Analytical Chemistry* **2020**, 92, (9), 6684-6692.

432. Dufour, A.; Thiebaut, D.; Loriau, M.; Ligiero, L.; Vial, J., Impact of the Oil Matrix on Anionic and Nonionic Surfactant Separation Using Ultra-High-Performance Liquid Chromatography Hyphenated to High-Resolution Mass Spectrometry. *Energy & Fuels* **2020**, 34, (11), 13943-13953.

433. Guan, D.; Chen, Z.; Chen, X.; Zhang, Y.; Qi, Q.; Shi, Q.; Zhao, S.; Xu, C.; Zhang, L., Molecular-level heavy petroleum hydrotreating modeling and comparison with high-resolution mass spectrometry. *Fuel* **2021**, 297, 120792.

434. Rüger, C. P.; Le Maître, J.; Maillard, J.; Riches, E.; Palmer, M.; Afonso, C.; Giusti, P., Exploring Complex Mixtures by Cyclic Ion Mobility High-Resolution Mass Spectrometry: Application Toward Petroleum. *Analytical Chemistry* **2021**, 93, (14), 5872-5881.

435. Giles, K.; Ujma, J.; Wildgoose, J.; Pringle, S.; Richardson, K.; Langridge, D.; Green, M., A cyclic ion mobility-mass spectrometry system. *Analytical Chemistry* **2019**, 91, (13), 8564-8573.

436. Hsu, C. S.; Green, M., Fragment-free accurate mass measurement of complex mixture components by gas chromatography/field ionization-orthogonal acceleration time-of-flight mass spectrometry: an unprecedented capability for mixture analysis. *Rapid Communications in Mass Spectrometry* **2001**, 15, (3), 236-239.

437. Qian, K.; Dechert, G. J., Recent Advances in Petroleum Characterization by GC Field Ionization Time-of-Flight High-Resolution Mass Spectrometry. *Analytical Chemistry* **2002**, 74, (16), 3977-3983.

438. Qian, K.; Diehl, J. W.; Dechert, G. J.; DiSanzo, F. P., The coupling of supercritical fluid chromatography and field ionization time-of-flight high-resolution mass spectrometry for rapid and quantitative analysis of petroleum middle distillates. *European journal of mass spectrometry (Chichester, England)* **2004**, 10, (2), 187-96.

439. Qian, K.; Dechert, G. J.; Edwards, K. E., Deducing molecular compositions of petroleum products using GC-field ionization high resolution time of flight mass spectrometry. *International Journal of Mass Spectrometry* **2007**, 265, (2), 230-236.

440. Ha, H. Z.; Ring, Z.; Liu, S., Data Reconciliation Among PIONA, GC-FIMS, and SimDis Measurements for Petroleum Fractions. *Petroleum Science and Technology* **2008**, 26, (1), 7-28.

441. Bansal, V.; Krishna, G. J.; Chopra, A.; Sarpal, A. S., Detailed Hydrocarbon Characterization of RFCC Feed Stocks by NMR Spectroscopic Techniques. *Energy & Fuels* **2007**, 21, (2), 1024-1029.

442. Boswell, H. A.; Edwards, M.; Gorecki, T., Comparison of Thermal and Flow-Based Modulation in Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry (GC x GC-TOFMS) for the Analysis of Base Oils. *Separations* **2020**, *7*, (4), 17.

443. Ávila, B. M. F.; Aguiar, A.; Gomes, A. O.; Azevedo, D. A., Characterization of extra heavy gas oil biomarkers using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. *Organic Geochemistry* **2010**, 41, (9), 863-866.

444. Ávila, B. M. F.; Pereira, R.; Gomes, A. O.; Azevedo, D. A., Chemical characterization of aromatic compounds in extra heavy gas oil by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. *Journal of Chromatography A* **2011**, 1218, (21), 3208-3216.

445. Parastar, H.; Radović, J. R.; Jalali-Heravi, M.; Diez, S.; Bayona, J. M.; Tauler, R., Resolution and quantification of complex mixtures of polycyclic aromatic hydrocarbons in heavy fuel oil sample by means of GC × GC-TOFMS combined to multivariate curve resolution. *Analytical Chemistry* **2011**, 83, (24), 9289-97.

446. von Mühlen, C.; de Oliveira, E. C.; Zini, C. A.; Caramao, E. B.; Marriott, P. J., Characterization of nitrogen-containing compounds in heavy gas oil petroleum fractions using comprehensive twodimensional gas chromatography coupled to time-of-flight mass spectrometry. *Energy & Fuels* **2010**, 24, (6), 3572-3580.

447. Mostafapour, S.; Parastar, H., N-way partial least squares with variable importance in projection combined to GC × GC-TOFMS as a reliable tool for toxicity identification of fresh and weathered crude oils. *Analytical and bioanalytical chemistry* **2015**, 407, (1), 285-295.

448. Radović, J. R.; Thomas, K. V.; Parastar, H.; Díez, S.; Tauler, R.; Bayona, J. M., Chemometrics-Assisted Effect-Directed Analysis of Crude and Refined Oil Using Comprehensive Two-Dimensional Gas Chromatography–Time-of-Flight Mass Spectrometry. *Environmental Science & Technology* **2014**, 48, (5), 3074-3083.

449. Cappelli Fontanive, F.; Souza-Silva, É. A.; Macedo da Silva, J.; Bastos Caramão, E.; Alcaraz Zini, C., Characterization of sulfur and nitrogen compounds in Brazilian petroleum derivatives using ionic liquid capillary columns in comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection. *Journal of Chromatography A* **2016**, 1461, 131-143.

450. Wang, M.; Zhu, G.; Milkov, A. V.; Chi, L., Comprehensive Molecular Compositions and Origins of DB301 Crude Oil from Deep Strata, Tarim Basin, China. *Energy & Fuels* **2020**, 34, (6), 6799-6810.

451. Zhu, G.; Wang, M.; Zhang, Y.; Zhang, Z., Higher Ethanodiamondoids in Petroleum. *Energy & Fuels* **2018**, 32, (4), 4996-5000.

452. Ristic, N. D.; Djokic, M. R.; Delbeke, E.; Gonzalez-Quiroga, A.; Stevens, C. V.; Van Geem, K. M.; Marin, G. B., Compositional Characterization of Pyrolysis Fuel Oil from Naphtha and Vacuum Gas Oil. *Energy & Fuels* **2018**, 32, (2), 1276-1286.

453. Alam, M. S.; Stark, C.; Harrison, R. M., Using Variable Ionization Energy Time-of-Flight Mass Spectrometry with Comprehensive GC×GC To Identify Isomeric Species. *Analytical Chemistry* **2016**, 88, (8), 4211-4220.

454. Eschner, M. S.; Welthagen, W.; Gröger, T. M.; Gonin, M.; Fuhrer, K.; Zimmermann, R., Comprehensive multidimensional separation methods by hyphenation of single-photon ionization time-of-flight mass spectrometry (SPI-TOF-MS) with GC and GC× GC. *Analytical and bioanalytical chemistry* **2010**, 398, (3), 1435-1445.

455. Welthagen, W.; Mitschke, S.; Mühlberger, F.; Zimmermann, R., One-dimensional and comprehensive two-dimensional gas chromatography coupled to soft photo ionization time-of-flight mass spectrometry: a two-and three-dimensional separation approach. *Journal of Chromatography A* **2007**, 1150, (1-2), 54-61.

456. Giri, A.; Coutriade, M.; Racaud, A.; Okuda, K.; Dane, J.; Cody, R. B.; Focant, J.-F., Molecular Characterization of Volatiles and Petrochemical Base Oils by Photo-Ionization GC×GC-TOF-MS. *Analytical Chemistry* **2017**, 89, (10), 5395-5403.

457. Eschner, M. S.; Welthagen, W.; Gröger, T. M.; Gonin, M.; Fuhrer, K.; Zimmermann, R., Comprehensive multidimensional separation methods by hyphenation of single-photon ionization time-of-flight mass spectrometry (SPI-TOF-MS) with GC and GCxGC. *Analytical and bioanalytical chemistry* **2010**, 398, (3), 1435-1445.

458. Mitschke, S.; Welthagen, W.; Zimmermann, R., Comprehensive gas chromatography-time-of-flight mass spectrometry using soft and selective photoionization techniques. *Analytical Chemistry* **2006**, 78, (18), 6364-75.

459. Cheng, B.; Wang, T. G.; Huang, H. P.; Wang, G. L.; Simoneit, B. R. T., Ratios of low molecular weight alkylbenzenes (C-0-C-4) in Chinese crude oils as indicators of maturity and depositional environment. *Organic Geochemistry* **2015**, 88, 78-90.

460. Li, S. F.; Cao, J.; Hu, S. Z., Analyzing hydrocarbon fractions in crude oils by two-dimensional gas chromatography/time-of-flight mass spectrometry under reversed-phase column system. *Fuel* **2015**, 158, 191-199.

461. Li, S. F.; Cao, J.; Hu, S. Z.; Luo, G. M., Characterization of compounds in unresolved complex mixtures (UCM) of a Mesoproterzoic shale by using GC x GC-TOFMS. *MARINE AND PETROLEUM GEOLOGY* **2015**, 66, 791-800.

462. Wang, H. T.; Zhang, S. C.; Weng, N.; Zhang, B.; Zhu, G. Y.; Liu, L. Y., Discovery and identification of a series of alkyl decalin isomers in petroleum geological samples. *Analyst* **2015**, 140, (13), 4694-4701.

463. Zhang, W. F.; Zhu, S. K.; He, S.; Wang, Y. X., Screening of oil sources by using comprehensive twodimensional gas chromatography/time-of-flight mass spectrometry and multivariate statistical analysis. *Journal of Chromatography A* **2015**, 1380, 162-170.

464. Weng, N.; Wan, S.; Wang, H. T.; Zhang, S. C.; Zhu, G. Y.; Liu, J. F.; Cai, D.; Yang, Y. X., Insight into unresolved complex mixtures of aromatic hydrocarbons in heavy oil via two-dimensional gas chromatography coupled With time-of-flight mass spectrometry analysis. *Journal of Chromatography A* **2015**, 1398, 94-107.

465. Zhu, G. Y.; Wang, H. T.; Weng, N.; Yang, H. J.; Zhang, K.; Liao, F. R.; Neng, Y., Geochemistry, origin and accumulation of continental condensate in the ultra-deep-buried Cretaceous sandstone reservoir, Kuqa Depression, Tarim Basin, China. *MARINE AND PETROLEUM GEOLOGY* **2015**, 65, 103-113.

466. Zhu, G. Y.; Weng, N.; Wang, H. T.; Yang, H. J.; Zhang, S. C.; Su, J.; Liao, F. R.; Zhang, B.; Ji, Y. G., Origin of diamondoid and sulphur compounds in the Tazhong Ordovician condensate, Tarim Basin, China: Implications for hydrocarbon exploration in deep-buried strata. *MARINE AND PETROLEUM GEOLOGY* **2015**, 62, 14-27.

467. Araujo, B. Q.; Azevedo, D. D., Uncommon steranes in Brazilian marginal crude oils: Dinoflagellate molecular fossils in the Sergipe-Alagoas Basin, Brazil. *Organic Geochemistry* **2016**, 99, 38-52.

468. Gao, X. B.; Zhu, S. K.; Zhang, W. F.; Li, D. H.; Dai, W.; He, S., Analysis of crude oils using gas purge microsyringe extraction coupled to comprehensive two dimensional gas chromatography-time-of-flight mass spectrometry. *Fuel* **2016**, 182, 788-797.

469. Parsons, B. A.; Pinkerton, D. K.; Wright, B. W.; Synovec, R. E., Chemical characterization of the acid alteration of diesel fuel: Non-targeted analysis by two-dimensional gas chromatography coupled with time-of-flight mass spectrometry with tile-based Fisher ratio and combinatorial threshold determination. *Journal of Chromatography A* **2016**, 1440, 179-190.

470. Ristic, N. D.; Djokic, M. R.; Van Geem, K. M.; Marin, G. B., On-line Analysis of Nitrogen Containing Compounds in Complex Hydrocarbon Matrixes. *Jove-Journal of Visualized Experiments* **2016**, (114).

471. Potgieter, H.; Bekker, R.; Govender, A.; Rohwer, E., Two-dimensional gas chromatography-online hydrogenation for improved characterization of petrochemical samples. *Journal of Chromatography A* **2016**, 1445, 118-125.

472. Qiao, L.; Xia, D.; Gao, L. R.; Huang, H. T.; Zheng, M. H., Occurrences, sources and risk assessment of short- and medium-chain chlorinated paraffins in sediments from the middle reaches of the Yellow River, China. *Environmental Pollution* **2016**, 219, 483-489.

473. Chattopadhyay, K.; Yadav, A.; Singh, D.; Chopra, A.; Rai, K.; Pandey, J. N.; Kagdiyal, V.; Saxena, D., Detailed Hydrocarbon Class Composition Analysis and Trace Level BTEX Estimation in Raffinate Column Bottom (RCB) Using GCxGC-TOFMS. *Chromatographia* **2017**, 80, (1), 145-150.

474. Jennerwein, M. K.; Eschner, M. S.; Wilharm, T.; Zimmermann, R.; Groger, T. M., Proof of Concept of High-Temperature Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry for Two-Dimensional Simulated Distillation of Crude Oils. *Energy & Fuels* **2017**, 31, (11), 11651-11659.

475. Kulsing, C.; Rawson, P.; Webster, R. L.; Evans, D. J.; Marriott, P. J., Group-Type Analysis of Hydrocarbons and Sulfur Compounds in Thermally Stressed Merox Jet Fuel Samples. *Energy & Fuels* **2017**, 31, (9), 8978-8984.

476. Laakia, J.; Casilli, A.; Araujo, B. Q.; Goncalves, F. T. T.; Marotta, E.; Oliveira, C. J. F.; Carbonezi, C. A.; Loureiro, M. R. B.; Azevedo, D. A.; Neto, F. R. A., Characterization of unusual tetracyclic compounds and possible novel maturity parameters for Brazilian crude oils using comprehensive two-dimensional gas chromatography-time of flight mass spectrometry. *Organic Geochemistry* **2017**, 106, 93-104.

477. Hu, S. Z.; Li, S. F.; Wang, J. H.; Cao, J., Origin of unresolved complex mixtures (UCMs) in biodegraded oils: Insights from artificial biodegradation experiments. *Fuel* **2018**, 231, 53-60.

478. Liang, Z. R.; Chen, L. F.; Alam, M. S.; Rezaei, S. Z.; Stark, C.; Xu, H. M.; Harrison, R. M., Comprehensive chemical characterization of lubricating oils used in modern vehicular engines utilizing GC x GC-TOFMS. *Fuel* **2018**, 220, 792-799.

479. Lin, C. H.; Wang, J. Q.; Chen, S. Y.; Wang, Z. X.; Liu, H.; Chen, K.; Guo, A. J., Thermal Treatment of Fluid Catalytic Cracking Slurry Oil: Determination of the Thermal Stability and its Correlation with the Quality of Derived Cokes. *Journal of Analytical and Applied Pyrolysis* **2018**, 135, 406-414.

480. Vale, D. L.; de Aguiar, P. F.; de Oliveira, L.; Vanini, G.; Pereira, V. B.; Alexandre, L. O.; da Silva, G. S. C.; Mendes, L. A.; Gomes, A. O.; Azevedo, D. A., Comprehensive and multidimensional tools for crude oil property prediction and petrochemical industry refinery inferences. *Fuel* **2018**, 223, 188-197.

481. Vanini, G.; Pereira, V. B.; Romao, W.; Gomes, A. O.; Oliveira, L.; Dias, J. C. M.; Azevedo, D. A., Analytical advanced techniques in the molecular-level characterization of Brazilian crude oils. *Microchemical Journal* **2018**, 137, 111-118.

482. Walters, C. C.; Wang, F. C.; Higgins, M. B.; Madincea, M. E., Universal biomarker analysis using GC×GC with dual FID and ToF-MS (EI/FI) detection. *Organic Geochemistry* **2018**, 115, 57-66.

483. Jennerwein, M.; Eschner, M.; Wilharm, T.; Groger, T.; Zimmermann, R., Evaluation of reversed phase versus normal phase column combination for the quantitative analysis of common commercial available middle distillates using GC x GC-TOFMS and Visual Basic Script. *Fuel* **2019**, 235, 336-338.

484. Scarlett, A. G.; Despaigne-Diaz, A. I.; Wilde, S. A.; Grice, K., An examination by GC x GC-TOFMS of organic molecules present in highly degraded oils emerging from Caribbean terrestrial seeps of Cretaceous age. *Geoscience Frontiers* **2019**, 10, (1), 5-15.

485. Scarlett, A. G.; Holman, A. I.; Georgiev, S. V.; Stein, H. J.; Summons, R. E.; Grice, K., Multispectroscopic and elemental characterization of southern Australian asphaltites. *Organic Geochemistry* **2019**, 133, 77-91.

486. Zhang, Z. Y.; Zhang, Y. J.; Zhu, G. Y.; Han, J. F.; Chi, L. X., Variations of diamondoids distributions in petroleum fluids during migration induced phase fractionation: A case study from the Tazhong area, NW China. *Journal of petroleum science and engineering* **2019**, 179, 1012-1022.

487. Zhang, Z. Y.; Zhang, Y. J.; Zhu, G. Y.; Han, J. F.; Chi, L. X., Geochemical and Isotopic Evidence of the Genesis of a Condensate in the Eastern Tarim Basin, China: Implications for Petroleum Exploration. *Energy* & *Fuels* **2019**, 33, (6), 4849-4856.

488. Ljesevic, M.; Gojgic-Cvijovic, G.; leda, T.; Hashimoto, S.; Nakano, T.; Bulatovic, S.; Ilic, M.; Beskoski, V., Biodegradation of the aromatic fraction from petroleum diesel fuel by Oerskovia sp. followed by comprehensive GC x GC-TOF MS. *Journal of hazardous materials* **2019**, 363, 227-232.

489. Kafer, U.; Groger, T. M.; Rohbogner, C.; Struckmeier, D.; Saraji-Bozorgzad, M. R.; Wilharm, T.; Zimmermann, R., Detailed Chemical Characterization of Bunker Fuels by High-Resolution Time-of-Flight Mass Spectrometry Hyphenated to GC x GC and Thermal Analysis. *Energy & Fuels* **2019**, 33, (11), 10745-10755.

490. Bowman, D. T.; Warren, L. A.; Slater, G. F., Isomer-specific monitoring of naphthenic acids at an oil sands pit lake by comprehensive two-dimensional gas chromatography-mass spectrometry. *Science of The Total Environment* **2020**, 746.

491. Gieleciak, R.; Litz, K. E.; Rankin, J. P.; De Crisci, A.; Chen, J. W., Analysis of Hydrocarbon Compositional Changes during Oxidative Desulfurization of Bitumen-Derived Gas Oil. *Energy & Fuels* **2020**, 34, (10), 12088-12102.

492. Karakhanov, E.; Maximov, A.; Kulikov, L.; Makeeva, D.; Kalinina, M.; Kardasheva, Y.; Glotov, A., Evaluation of sulfide catalysts performance in hydrotreating of oil fractions using comprehensive gas chromatography time-of-flight mass spectrometry. *Pure and Applied Chemistry* **2020**, 92, (6), 941-948.

493. Spaak, G.; Edwards, D. S.; Grosjean, E.; Scarlett, A. G.; Rollet, N.; Grice, K., Identifying multiple sources of petroleum fluids in Browse Basin accumulations using diamondoids and semi-volatile aromatic compounds. *MARINE AND PETROLEUM GEOLOGY* **2020**, 113.

494. Tong, R. L.; Zhang, H. Y.; Lin, X. C.; Wang, Y. G.; Meng, X. K., Analysis of distillate product in the direct coal liquefaction of a Chinese bituminous coal. *International Journal of Oil Gas and Coal Technology* **2020**, 23, (3), 375-394.

495. Trinklein, T. J.; Schoneich, S.; Sudol, P. E.; Warren, C. G.; Gough, D. V.; Synovec, R. E., Total-transfer comprehensive three-dimensional gas chromatography with time-of-flight mass spectrometry. *Journal of Chromatography A* **2020**, 1634.

496. Xu, J. J.; Jin, Q., Hydrocarbon potential and polycyclic aromatic compounds differences of Carboniferous-Permian coaly source rocks, Bohai Bay Basin: An implication for different sources of gas condensate and oils. *Journal of petroleum science and engineering* **2020**, 195.

497. Zhang, Z. Y.; Zhu, G. Y.; Chi, L. X.; Wang, P. J.; Zhou, L.; Li, J. F.; Wu, Z. H., Discovery of the high - yield well GT1 in the deep strata of the southern margin of the Junggar Basin, China: Implications for liquid petroleum potential in deep assemblage. *Journal of petroleum science and engineering* **2020**, 191.

498. Zhu, G. Y.; Li, J. F.; Chi, L. X.; Zhang, Z. Y.; Li, T. T.; Zhou, L.; Wu, Z. H., The Influence of Gas Invasion on the Composition of Crude Oil and the Controlling Factors for the Reservoir Fluid Phase. *Energy & Fuels* **2020**, 34, (3), 2710-2725.

499. Zhu, G. Y.; Li, J. F.; Zhang, Z. Y.; Wang, M.; Xue, N.; He, T.; Zhao, K., Stability and cracking threshold depth of crude oil in 8000 m ultra-deep reservoir in the Tarim Basin. *Fuel* **2020**, 282.

500. Franca, D.; Coutinho, D. M.; Barra, T. A.; Xavier, R. S.; Azevedo, D. A., Molecular-level characterization of Brazilian pre-salt crude oils by advanced analytical techniques. *Fuel* **2021**, 293.

501. Jencik, J.; Honig, V.; Obergruber, M.; Hajek, J.; Vrablik, A.; Cerny, R.; Schlehofer, D.; Herink, T., Advanced Biofuels Based on Fischer-Tropsch Synthesis for Applications in Diesel Engines. *Materials* **2021**, 14, (11).

502. Jiao, S. H.; Guo, A. J.; Wang, F.; Yu, Y. Y.; Biney, B. W.; Liu, H.; Chen, K.; Liu, D.; Wang, Z. X.; Sun, L. Y., Sequential pretreatments of an FCC slurry oil sample for preparation of feedstocks for high-value solid carbon materials. *Fuel* **2021**, 285.

503. Kumar, S.; Dutta, S., Utility of comprehensive GC x GC-TOFMS in elucidation of aromatic hydrocarbon biomarkers. *Fuel* **2021**, 283.

504. Li, J. F.; Zhang, Z. Y.; Zhu, G. Y.; Zhao, K.; Chi, L. X.; Wang, P. J.; Chen, Y. J., Geochemical Characteristics and the Origin of Superdeep Condensates in Tarim Basin, China. *Acs Omega* **2021**, 6, (11), 7275-7285.

505. Liang, M.; Liang, H. D.; Gao, P.; Rao, Z.; Liang, Y. C., Characterization and risk assessment of polycyclic aromatic hydrocarbon emissions by coal fire in northern China. *Environmental Geochemistry and Health* **2021**.

506. Zhu, G. Y.; Milkov, A. V.; Li, J. F.; Xue, N.; Chen, Y. Q.; Hu, J. F.; Li, T. T.; Zhang, Z. Y.; Chen, Z. Y., Deepest oil in Asia: Characteristics of petroleum system in the Tarim basin, China. *Journal of petroleum science and engineering* **2021**, 199.

507. Lewis, A. C.; Carslaw, N.; Marriott, P. J.; Kinghorn, R. M.; Morrison, P.; Lee, A. L.; Bartle, K. D.; Pilling, M. J., A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature* **2000**, 405, (6788), 778-781.

508. Wang, Y.; Xu, X.; Yin, L.; Cheng, H.; Mao, T.; Zhang, K.; Lin, W.; Meng, Z.; Palasota, J. A., Coupling of comprehensive two-dimensional gas chromatography with quadrupole mass spectrometry: Application to the identification of atmospheric volatile organic compounds. *Journal of Chromatography A* **2014**, 1361, 229-239.

509. Edwards, S. J.; Lewis, A. C.; Andrews, S. J.; Lidster, R. T.; Hamilton, J. F.; Rhodes, C. N., A compact comprehensive two-dimensional gas chromatography (GC× GC) approach for the analysis of biogenic VOCs. *Analytical Methods* **2013**, *5*, (1), 141-150.

510. Guan, X.; Zhao, Z.; Cai, S.; Wang, S.; Lu, H., Analysis of volatile organic compounds using cryogenfree thermal modulation based comprehensive two-dimensional gas chromatography coupled with quadrupole mass spectrometry. *Journal of Chromatography A* **2019**, 1587, 227-238.

511. Wolfender, J.-L.; Rodriguez, S.; Hostettmann, K., Liquid chromatography coupled to mass spectrometry and nuclear magnetic resonance spectroscopy for the screening of plant constituents. *Journal of Chromatography A* **1998**, 794, (1-2), 299-316.

512. Loegel, T. N.; Danielson, N. D.; Borton, D. J.; Hurt, M. R.; Kenttämaa, H. I., Separation of asphaltenes by reversed-phase liquid chromatography with fraction characterization. *Energy & Fuels* **2012**, 26, (5), 2850-2857.

513. Kruve, A.; Rebane, R.; Kipper, K.; Oldekop, M.-L.; Evard, H.; Herodes, K.; Ravio, P.; Leito, I., Tutorial review on validation of liquid chromatography–mass spectrometry methods: Part II. *Analytica Chimica Acta* **2015**, 870, 8-28.

514. Kruve, A.; Rebane, R.; Kipper, K.; Oldekop, M.-L.; Evard, H.; Herodes, K.; Ravio, P.; Leito, I., Tutorial review on validation of liquid chromatography–mass spectrometry methods: Part I. *Analytica Chimica Acta* **2015**, 870, 29-44.

515. Hamilton, R. J.; Sewell, P. A., Introduction to high performance liquid chromatography. In *Introduction to high performance liquid chromatography*, Springer: 1982; pp 1-12.

516. Xiao, W.; Oefner, P. J., Denaturing high-performance liquid chromatography: A review. *Human mutation* **2001**, 17, (6), 439-474.

517. Meyer, V. R., *Practical high-performance liquid chromatography*. John Wiley & Sons: 2013.

518. Horváth, C., High-performance liquid chromatography: advances and perspectives. **2013**.

519. Islas-Flores, C.; Buenrostro-Gonzalez, E.; Lira-Galeana, C., Comparisons between open column chromatography and HPLC SARA fractionations in petroleum. *Energy & Fuels* **2005**, 19, (5), 2080-2088.

520. Barman, B. N.; Cebolla, V. L.; Membrado, L., Chromatographic Techniques for Petroleum and Related Products. *Critical Reviews in Analytical Chemistry* **2000**, 30, (2-3), 75-120.

521. Magi, E.; Ianni, C.; Rivaro, P.; Frache, R., Determination of porphyrins and metalloporphyrins using liquid chromatography–diode array detection and mass spectrometry. *Journal of Chromatography A* **2001**, 905, (1-2), 141-149.

522. Encinas, D.; Gómez-de-Balugera, Z., Fullerene C 60 in Atmospheric Aerosol and Its Relationship to Combustion Processes. *Archives of environmental contamination and toxicology* **2018**, 75, (4), 616-624.

523. Sanchís, J.; Oliveira, L. F. S.; De Leão, F. B.; Farré, M.; Barceló, D., Liquid chromatography– atmospheric pressure photoionization–Orbitrap analysis of fullerene aggregates on surface soils and river sediments from Santa Catarina (Brazil). *Science of The Total Environment* **2015**, 505, 172-179.

524. Mketo, N.; Nomngongo, P. N.; Ngila, J. C., An innovative microwave-assisted digestion method with diluted hydrogen peroxide for rapid extraction of trace elements in coal samples followed by inductively coupled plasma-mass spectrometry. *Microchemical Journal* **2016**, 124, 201-208.

525. Lu, C.-W.; Hung, H.-Y.; Sung, H.-C.; Sheu, Y.-S.; Lin, W.-L.; Wu, S.-P., Total sulfur determination in petroleum fuels for routine quality control by sector field inductively coupled plasma mass spectrometry after dilution treatment. *Journal of Analytical Atomic Spectrometry* **2019**, 34, (3), 570-576.

526. Houk, R. S.; Fassel, V. A.; Flesch, G. D.; Svec, H. J.; Gray, A. L.; Taylor, C. E., Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Analytical Chemistry* **1980**, 52, (14), 2283-2289.

527. Wilschefski, S. C.; Baxter, M. R., Inductively coupled plasma mass spectrometry: introduction to analytical aspects. *The Clinical Biochemist Reviews* **2019**, 40, (3), 115.

528. Moulian, R. m.; Sama, S. G.; Garnier, C.; Mounicou, S.; Enrico, M.; Jaurand, X.; Lobinski, R.; Giusti, P.; Bouyssiere, B.; Barrère-Mangote, C., Speciation of Metals in Asphaltenes by High-Performance Thin-Layer Chromatography and Laser Ablation Inductively Coupled Plasma-Mass Spectrometry. *Energy & Fuels* **2019**, 33, (7), 6060-6068.

529. González, G. n.; Acevedo, S.; Castillo, J.; Villegas, O.; Ranaudo, M. a. A.; Guzmán, K.; Orea, M.; Bouyssiere, B., Study of Very High Molecular Weight Cluster Presence in THF Solution of Asphaltenes and Subfractions A1 and A2, by Gel Permeation Chromatography with Inductively Coupled Plasma Mass Spectrometry. *Energy & Fuels* **2020**, 34, (10), 12535-12544.

530. Caumette, G.; Lienemann, C.-P.; Merdrignac, I.; Bouyssiere, B.; Lobinski, R., Fractionation and speciation of nickel and vanadium in crude oils by size exclusion chromatography-ICP MS and normal phase HPLC-ICP MS. *Journal of Analytical Atomic Spectrometry* **2010**, 25, (7), 1123-1129.

531. Vargas, V.; Castillo, J.; Torres, R. O.; Bouyssière, B.; Lienemann, C.-P., Development of a chromatographic methodology for the separation and quantification of V, Ni and S compounds in petroleum products. *Fuel Processing Technology* **2017**, 162, 37-44.

532. Vargas, V.; Castillo, J.; Ocampo-Torres, R.; Lienemann, C.-P.; Bouyssiere, B., Surface modification of SiO2 nanoparticles to increase asphaltene adsorption. *Petroleum Science and Technology* **2018**, 36, (8), 618-624.

533. Gascon, G.; Negrin, J.; Garcia-Montoto, V.; Acevedo, S.; Lienemann, C.-P.; Bouyssiere, B., Simplification of heavy matrices by liquid–liquid extraction: part I—how to separate LMW, MMW, and HMW compounds in maltene fractions of V, Ni, and S compounds. *Energy & Fuels* **2019**, 33, (3), 1922-1927.

534. Boduszynski, M. M., Composition of heavy petroleums. 1. Molecular weight, hydrogen deficiency, and heteroatom concentration as a function of atmospheric equivalent boiling point up to 1400.degree.F (760.degree.C). *Energy & Fuels* **1987**, 1, (1), 2-11.

535. Marshall, A. G.; Rodgers, R. P., Petroleomics: The Next Grand Challenge for Chemical Analysis. *Accounts of Chemical Research* **2004**, 37, (1), 53-59.

536. Sage, E. New concept of mass spectrometer based on arrays of resonating nanostructures. Université de Grenoble, 2013.

537. Hsu, C. S.; Liang, Z.; Campana, J. E., Hydrocarbon Characterization by UltraHigh Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry* **1994**, 66, (6), 850-855.

538. Kim, S.; Rodgers, R. P.; Marshall, A. G., Truly "exact" mass: Elemental composition can be determined uniquely from molecular mass measurement at \sim 0.1mDa accuracy for molecules up to \sim 500Da. *International Journal of Mass Spectrometry* **2006**, 251, (2), 260-265.

539. Marshall, A. G.; Hendrickson, C. L., Fourier transform ion cyclotron resonance detection: principles and experimental configurations. *International Journal of Mass Spectrometry* **2002**, 215, (1), 59-75.

540. Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S., Fourier transform ion cyclotron resonance mass spectrometry: A primer. *Mass spectrometry reviews* **1998**, 17, (1), 1-35.

541. Podgorski, D. C.; Corilo, Y. E.; Nyadong, L.; Lobodin, V. V.; Bythell, B. J.; Robbins, W. K.; McKenna, A. M.; Marshall, A. G.; Rodgers, R. P., Heavy petroleum composition. 5. Compositional and structural continuum of petroleum revealed. *Energy & Fuels* **2013**, *2*7, (3), 1268-1276.

542. Qian, K.; Edwards, K. E.; Mennito, A. S.; Freund, H.; Saeger, R. B.; Hickey, K. J.; Francisco, M. A.; Yung, C.; Chawla, B.; Wu, C., Determination of structural building blocks in heavy petroleum systems by collision-induced dissociation Fourier transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* **2012**, 84, (10), 4544-4551.

543. Wei, W.; Yingrong, L.; Zelong, L.; Huandi, H.; Songbai, T., Linkage of aromatic ring structures in saturates, aromatics, resins and asphaltenes fractions of vacuum residues determined by collision-induced dissociation technology. *China Petroleum Processing & Petrochemical Technology* **2016**, 18, (1), 59-65.

544. Håkansson, K.; Chalmers, M. J.; Quinn, J. P.; McFarland, M. A.; Hendrickson, C. L.; Marshall, A. G., Combined electron capture and infrared multiphoton dissociation for multistage MS/MS in a Fourier transform ion cyclotron resonance mass spectrometer. *Analytical Chemistry* **2003**, 75, (13), 3256-3262.

545. Purcell, J. M.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G., Atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry for complex mixture analysis. *Analytical Chemistry* **2006**, 78, (16), 5906-5912.

546. Rodgers, R. P.; Marshall, A. G., Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). In *Asphaltenes, Heavy Oils, and Petroleomics,* Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G., Eds. Springer New York: New York, NY, 2007; pp 63-93.

547. Guan, S.; Marshall, A. G.; Scheppele, S. E., Resolution and Chemical Formula Identification of Aromatic Hydrocarbons and Aromatic Compounds Containing Sulfur, Nitrogen, or Oxygen in Petroleum Distillates and Refinery Streams. *Analytical Chemistry* **1996**, 68, (1), 46-71.

548. Fu, J.; Klein, G. C.; Smith, D. F.; Kim, S.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G., Comprehensive compositional analysis of hydrotreated and untreated nitrogen-concentrated fractions from syncrude oil by electron ionization, field desorption ionization, and electrospray ionization ultrahigh-resolution FT-ICR mass spectrometry. *Energy & Fuels* **2006**, 20, (3), 1235-1241.

549. Miyabayashi, K.; Naito, Y.; Tsujimoto, K.; Miyake, M., Structure characterization of petroleum vacuum residues by in-beam EI Fourier transform ion cyclotron resonance mass spectrometry. *International Journal of Mass Spectrometry* **2002**, 221, (2), 93-105.

550. Miyabayashi, K.; Naito, Y.; Miyake, M., Characterization of Heavy Oil by FT-ICR MS Coupled with Various Ionization Techniques. *Journal of the Japan Petroleum Institute* **2009**, 52, (4), 159-171.

551. Kondyli, A.; Schrader, W., Evaluation of the combination of different atmospheric pressure ionization sources for the analysis of extremely complex mixtures. *Rapid Communications in Mass Spectrometry* **2020**, 34, (8), e8676.

552. Muller, H.; Adam, F. M.; Panda, S. K.; Al-Jawad, H. H.; Al-Hajji, A. A., Evaluation of Quantitative Sulfur Speciation in Gas Oils by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Validation by Comprehensive Two-Dimensional Gas Chromatography. *Journal of The American Society for Mass Spectrometry* **2012**, 23, (5), 806-815.

553. Ware, R. L.; Rodgers, R. P.; Marshall, A. G.; Mante, O. D.; Dayton, D. C.; Verdier, S.; Gabrielsen, J.; Rowland, S. M., Tracking Elemental Composition through Hydrotreatment of an Upgraded Pyrolysis Oil Blended with a Light Gas Oil. *Energy & Fuels* **2020**, 34, (12), 16181-16186.

554. Putman, J. C.; Moulian, R.; Barrère-Mangote, C.; Rodgers, R. P.; Bouyssiere, B.; Giusti, P.; Marshall, A. G., Probing Aggregation Tendencies in Asphaltenes by Gel Permeation Chromatography. Part 1: Online Inductively Coupled Plasma Mass Spectrometry and Offline Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2020**, 34, (7), 8308-8315.

555. Chacón-Patiño, M. L.; Smith, D. F.; Hendrickson, C. L.; Marshall, A. G.; Rodgers, R. P., Advances in Asphaltene Petroleomics. Part 4. Compositional Trends of Solubility Subfractions Reveal that Polyfunctional Oxygen-Containing Compounds Drive Asphaltene Chemistry. *Energy & Fuels* **2020**, 34, (3), 3013-3030.

556. Djokic, M. R.; Muller, H.; Ristic, N. D.; Akhras, A. R.; Symoens, S. H.; Marin, G. B.; Van Geem, K. M., Combined characterization using HT-GC× GC-FID and FT-ICR MS: A pyrolysis fuel oil case study. *Fuel Processing Technology* **2018**, 182, 15-25.

557. Dutriez, T.; Courtiade, M.; Thiébaut, D.; Dulot, H.; Bertoncini, F.; Vial, J.; Hennion, M.-C., High-temperature two-dimensional gas chromatography of hydrocarbons up to nC60 for analysis of vacuum gas oils. *Journal of Chromatography A* **2009**, 1216, (14), 2905-2912.

558. Sessions, A. L.; Zhang, L.; Welander, P. V.; Doughty, D.; Summons, R. E.; Newman, D. K., Identification and quantification of polyfunctionalized hopanoids by high temperature gas chromatography–mass spectrometry. *Organic Geochemistry* **2013**, 56, 120-130.

559. Sutton, P.; Rowland, S., High temperature gas chromatography–time-of-flight-mass spectrometry (HTGC–ToF-MS) for high-boiling compounds. *Journal of Chromatography A* **2012**, 1243, 69-80.

560. Netzel, D. A.; Rovani, J. F., Direct separation and quantitative determination of (n-, iso-) alkanes in neat asphalt using urea adduction and high-temperature gas chromatography (HTGC). *Energy & Fuels* **2007**, 21, (1), 333-338.

561. Rodrigues, É. V.; Silva, S. R.; Romão, W.; Castro, E. V.; Filgueiras, P. R., Determination of crude oil physicochemical properties by high-temperature gas chromatography associated with multivariate calibration. *Fuel* **2018**, 220, 389-395.

562. Page, J. S.; Kelly, R. T.; Tang, K.; Smith, R. D., Ionization and transmission efficiency in an electrospray ionization—mass spectrometry interface. *Journal of The American Society for Mass Spectrometry* **2007**, 18, (9), 1582-1590.

563. Honarvar, E.; Venter, A. R., Comparing the effects of additives on protein analysis between desorption electrospray (DESI) and electrospray ionization (ESI). *Journal of The American Society for Mass Spectrometry* **2018**, 29, (12), 2443-2455.

564. Chen, L.; Bertolini, A.; Dubost, F.; Achourov, V.; Betancourt, S.; Cañas, J. A.; Dumont, H.; Pomerantz, A. E.; Mullins, O. C., Yen–Mullins Model Applies to Oilfield Reservoirs. *Energy & Fuels* **2020**, 34, (11), 14074-14093.

565. Oss, M.; Kruve, A.; Herodes, K.; Leito, I., Electrospray ionization efficiency scale of organic compounds. *Analytical Chemistry* **2010**, 82, (7), 2865-2872.

566. Cui, D.; Chang, H.; Zhang, X.; Pan, S.; Wang, Q., Pyrolysis temperature effect on compositions of neutral nitrogen and acidic species in shale oil using negative-ion ESI FT-ICR MS. *Acs Omega* **2020**, 5, (37), 23940-23950.

567. Cui, D.; Li, J.; Zhang, X.; Zhang, L.; Chang, H.; Wang, Q., Pyrolysis temperature effect on compositions of basic nitrogen species in Huadian shale oil using positive-ion ESI FT-ICR MS and GC-NCD. *Journal of Analytical and Applied Pyrolysis* **2021**, 153, 104980.

568. Pinto, F. E.; Barros, E. V.; Tose, L. V.; Souza, L. M.; Terra, L. A.; Poppi, R. J.; Vaz, B. G.; Vasconcelos, G.; Subramanian, S.; Simon, S., Fractionation of asphaltenes in n-hexane and on adsorption onto CaCO3 and characterization by ESI (+) FT-ICR MS: Part I. *Fuel* **2017**, 210, 790-802.

569. Trubetskaya, A.; Johnson, R.; Monaghan, R. F. D.; Ramos, A. S.; Brunsvik, A.; Wittgens, B.; Han, Y.; Pisano, I.; Leahy, J. J.; Budarin, V., Combined analytical strategies for chemical and physical characterization of tar from torrefaction of olive stone. *Fuel* **2021**, 291, 120086.

570. Xiong, Z.; Han, H.; Azis, M. M.; Hu, X.; Wang, Y.; Su, S.; Hu, S.; Xiang, J., Formation of the heavy tar during bio-oil pyrolysis: A study based on Fourier transform ion cyclotron resonance mass spectrometry. *Fuel* **2019**, 239, 108-116.

571. Xiong, Z.; Guo, J.; Chaiwat, W.; Deng, W.; Hu, X.; Han, H.; Chen, Y.; Xu, K.; Su, S.; Hu, S., et al., Assessing the chemical composition of heavy components in bio-oils from the pyrolysis of cellulose, hemicellulose and lignin at slow and fast heating rates. *Fuel Processing Technology* **2020**, 199, 106299.

572. Xiong, Z.; Guo, J.; Han, H.; Xu, J.; Jiang, L.; Su, S.; Hu, S.; Wang, Y.; Xiang, J., Effects of AAEMs on formation of heavy components in bio-oil during pyrolysis at various temperatures and heating rates. *Fuel Processing Technology* **2021**, 213, 106690.

573. Terrell, E.; Garcia-Perez, M., Novel Strategy To Analyze Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Data of Biomass Pyrolysis Oil for Oligomeric Structure Assignment. *Energy & Fuels* **2020**, 34, (7), 8466-8481.

574. Neumann, A.; Kafer, U.; Groger, T.; Wilharm, T.; Zimmermann, R.; Ruger, C. P., Investigation of Aging Processes in Bitumen at the Molecular Level with High-Resolution Fourier-Transform Ion Cyclotron Mass Spectrometry and Two-Dimensional Gas Chromatography Mass Spectrometry. *Energy & Fuels* **2020**, 34, (9), 10641-10654.

575. 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.

576. Thiäner, J. B.; Nett, L.; Zhou, S.; Preibisch, Y.; Hollert, H.; Achten, C., Identification of 7–9 ring polycyclic aromatic hydrocarbons in coals and petrol coke using High performance liquid chromatography– Diode array detection coupled to Atmospheric pressure laser ionization–Mass spectrometry (HPLC-DAD-APLI-MS). *Environmental Pollution* **2019**, 252, 723-732.

577. Bagley, S. P.; Wornat, M. J., Identification of six-to nine-ring polycyclic aromatic hydrocarbons from the supercritical pyrolysis of n-decane. *Energy & Fuels* **2013**, 27, (3), 1321-1330.

578. McClaine, J. W.; Oña, J. O.; Wornat, M. J., Identification of a new C28H14 polycyclic aromatic hydrocarbon as a product of supercritical fuel pyrolysis: Tribenzo [cd, ghi, lm] perylene. *Journal of Chromatography A* **2007**, 1138, (1-2), 175-183.

579. Rüger, C. P.; Neumann, A.; Sklorz, M.; Zimmermann, R., Atmospheric Pressure Single Photon Laser Ionization (APSPLI) Mass Spectrometry Using a 157 nm Fluorine Excimer Laser for Sensitive and Selective Detection of Non-to Semipolar Hydrocarbons. *Analytical Chemistry* **2021**, 93, (8), 3691-3697.

580. Hortal, A. R.; Martínez-Haya, B.; Lobato, M. D.; Pedrosa, J. M.; Lago, S., On the determination of molecular weight distributions of asphaltenes and their aggregates in laser desorption ionization experiments. *Journal of mass spectrometry* **2006**, 41, (7), 960-968.

581. Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G.; Yen, A.; Asomaning, S., Mass spectral analysis of asphaltenes. I. Compositional differences between pressure-drop and solvent-drop asphaltenes determined by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **2006**, 20, (5), 1965-1972.

582. Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G.; Yen, A., Mass spectral analysis of asphaltenes. II. Detailed compositional comparison of asphaltenes deposit to its crude oil counterpart for two geographically different crude oils by ESI FT-ICR MS. *Energy & Fuels* **2006**, 20, (5), 1973-1979.

583. Millan, M.; Behrouzi, M.; Karaca, F.; Morgan, T. J.; Herod, A. A.; Kandiyoti, R., Characterising high mass materials in heavy oil fractions by size exclusion chromatography and MALDI-mass spectrometry. *Catalysis today* **2005**, 109, (1-4), 154-161.

584. Apicella, B.; Millan, M.; Herod, A.; Carpentieri, A.; Pucci, P.; Ciajolo, A., Separation and measurement of flame-formed high molecular weight polycyclic aromatic hydrocarbons by size-exclusion chromatography and laser desorption/ionization time-of-flight mass spectrometry. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry* **2006**, 20, (7), 1104-1108.

585. Qian, K.; Edwards, K. E.; Siskin, M.; Olmstead, W. N.; Mennito, A. S.; Dechert, G. J.; Hoosain, N. E., Desorption and ionization of heavy petroleum molecules and measurement of molecular weight distributions. *Energy & Fuels* **2007**, 21, (2), 1042-1047.

586. Sheu, E. Y., Petroleum asphaltene properties, characterization, and issues. *Energy & Fuels* **2002**, 16, (1), 74-82.

587. Robins, C.; Limbach, P. A., The use of nonpolar matrices for matrix-assisted laser desorption/ionization mass spectrometric analysis of high boiling crude oil fractions. *Rapid Communications in Mass Spectrometry* **2003**, 17, (24), 2839-2845.

588. Miller, J.; Fisher, R.; Thiyagarajan, P.; Winans, R.; Hunt, J., Subfractionation and characterization of Mayan asphaltene. *Energy & Fuels* **1998**, 12, (6), 1290-1298.

589. Strausz, O. P.; Peng, P. a.; Murgich, J., About the colloidal nature of asphaltenes and the MW of covalent monomeric units. *Energy & Fuels* **2002**, 16, (4), 809-822.

590. Domin, M.; Herod, A.; Kandiyoti, R.; Larsen, J.; Lazaro, M.; Li, S.; Rahimi, P., Enery Fuels 1999, 13, 552-557. *For a detailed recent review on MALDI-TDF-MS cf. Nielen, MWF Mass Spectrosc. Rev* **1999**, 18, 309-344.

591. Badre, S.; Goncalves, C. C.; Norinaga, K.; Gustavson, G.; Mullins, O. C., Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen. *Fuel* **2006**, 85, (1), 1-11.

592. Lobodin, V. V.; Nyadong, L.; Ruddy, B. M.; Curtis, M.; Jones, P. R.; Rodgers, R. P.; Marshall, A. G., DART Fourier transform ion cyclotron resonance mass spectrometry for analysis of complex organic mixtures. *International Journal of Mass Spectrometry* **2015**, 378, 186-192.

593. Ren, L.; Han, Y.; Zhang, Y.; Zhang, Y.; Meng, X.; Shi, Q., Spray injection direct analysis in real time (DART) ionization for petroleum analysis. *Energy & Fuels* **2016**, 30, (6), 4486-4493.

594. Oldenburg, T. B.; Brown, M.; Bennett, B.; Larter, S. R., The impact of thermal maturity level on the composition of crude oils, assessed using ultra-high resolution mass spectrometry. *Organic Geochemistry* **2014**, 75, 151-168.

595. Smith, D.; Španěl, P., SIFT-MS and FA-MS methods for ambient gas phase analysis: developments and applications in the UK. *Analyst* **2015**, 140, (8), 2573-2591.

596. Mennito, A. S.; Qian, K., Characterization of Heavy Petroleum Saturates by Laser Desorption Silver Cationization and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **2013**, 27, (12), 7348-7353.

597. Cho, Y.; Witt, M.; Jin, J. M.; Kim, Y. H.; Nho, N.-S.; Kim, S., Evaluation of laser desorption ionization coupled to fourier transform ion cyclotron resonance mass spectrometry to study metalloporphyrin complexes. *Energy & Fuels* **2014**, 28, (11), 6699-6706.

598. Klein, G. C.; Angström, A.; Rodgers, R. P.; Marshall, Α. G., Use of saturates/aromatics/resins/asphaltenes (SARA) fractionation to determine matrix effects in crude oil analysis by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy* & Fuels 2006, 20, (2), 668-672.

599. Gaspar, A.; Schrader, W., Expanding the data depth for the analysis of complex crude oil samples by Fourier transform ion cyclotron resonance mass spectrometry using the spectral stitching method. *Rapid Communications in Mass Spectrometry* **2012**, 26, (9), 1047-1052.

600. McKenna, A. M.; Purcell, J. M.; Rodgers, R. P.; Marshall, A. G., Heavy Petroleum Composition. 1. Exhaustive Compositional Analysis of Athabasca Bitumen HVGO Distillates by Fourier Transform Ion

Cyclotron Resonance Mass Spectrometry: A Definitive Test of the Boduszynski Model. *Energy & Fuels* **2010**, 24, (5), 2929-2938.

601. Andreatta, G.; Bostrom, N.; Mullins, O. C., High-Q ultrasonic determination of the critical nanoaggregate concentration of asphaltenes and the critical micelle concentration of standard surfactants. *Langmuir* **2005**, 21, (7), 2728-2736.

602. Buch, L.; Groenzin, H.; Buenrostro-Gonzalez, E.; Andersen, S. I.; Lira-Galeana, C.; Mullins, O. C., Molecular size of asphaltene fractions obtained from residuum hydrotreatment☆. *Fuel* **2003**, 82, (9), 1075-1084.

603. Ruiz-Morales, Y.; Wu, X.; Mullins, O. C., Electronic absorption edge of crude oils and asphaltenes analyzed by molecular orbital calculations with optical spectroscopy. *Energy & Fuels* **2007**, 21, (2), 944-952.

604. Ruiz-Morales, Y.; Mullins, O. C., Polycyclic aromatic hydrocarbons of asphaltenes analyzed by molecular orbital calculations with optical spectroscopy. *Energy & Fuels* **2007**, 21, (1), 256-265.

605. Groenzin, H.; Mullins, O. C., Molecular size and structure of asphaltenes from various sources. *Energy & Fuels* **2000**, 14, (3), 677-684.

606. Xu, H.; Que, G.; Yu, D.; Lu, J. R., Characterization of Petroporphyrins Using Ultraviolet– Visible Spectroscopy and Laser Desorption Ionization Time-of-Flight Mass Spectrometry. *Energy & Fuels* **2005**, 19, (2), 517-524.

607. Martínez-Haya, B.; Hortal, A. R.; Hurtado, P.; Lobato, M. D.; Pedrosa, J. M., Laser desorption/ionization determination of molecular weight distributions of polyaromatic carbonaceous compounds and their aggregates. *Journal of mass spectrometry* **2007**, 42, (6), 701-713.

608. Nguyen, H. P.; Ortiz, I. P.; Temiyasathit, C.; Kim, S. B.; Schug, K. A., Laser desorption/ionization mass spectrometry fingerprinting of complex hydrocarbon mixtures: application to crude oils using data mining techniques. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry* **2008**, 22, (14), 2220-2226.

609. Wu, Q.; Pomerantz, A. E.; Mullins, O. C.; Zare, R. N., Laser-Based Mass Spectrometric Determination of Aggregation Numbers for Petroleum- and Coal-Derived Asphaltenes. *Energy & Fuels* **2014**, 28, (1), 475-482.

610. Rissanen, T.; Hyötyläinen, T.; Kallio, M.; Kronholm, J.; Kulmala, M.; Riekkola, M.-L., Characterization of organic compounds in aerosol particles from a coniferous forest by GC–MS. *Chemosphere* **2006**, 64, (7), 1185-1195.

611. Sánchez, N. E.; Salafranca, J.; Callejas, A.; Millera, Á.; Bilbao, R.; Alzueta, M. U., Quantification of polycyclic aromatic hydrocarbons (PAHs) found in gas and particle phases from pyrolytic processes using gas chromatography–mass spectrometry (GC–MS). *Fuel* **2013**, 107, 246-253.

612. Herod, A. A.; Zhuo, Y.; Kandiyoti, R., Size-exclusion chromatography of large molecules from coal liquids, petroleum residues, soots, biomass tars and humic substances. *Journal of biochemical and biophysical methods* **2003**, 56, (1-3), 335-361.

613. Alfè, M.; Apicella, B.; Barbella, R.; Tregrossi, A.; Ciajolo, A., Distribution of soot molecular weight/size along premixed flames as inferred by size exclusion chromatography. *Energy & Fuels* **2007**, 21, (1), 136-140.

614. Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F., Characterization of polymers by matrixassisted laser desorption/ionization time-of-flight mass spectrometry: Molecular weight estimates in samples of varying polydispersity. *Rapid Communications in Mass Spectrometry* **1995**, 9, (5), 453-460.

615. Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F., Characterization of polymers by matrixassisted laser desorption ionization-time of flight mass spectrometry. End group determination and molecular weight estimates in poly (ethylene glycols). *Macromolecules* **1995**, 28, (13), 4562-4569.

616. Herod, A.; Lazaro, M.-J.; Domin, M.; Islas, C.; Kandiyoti, R., Molecular mass distributions and structural characterisation of coal derived liquids. *Fuel* **2000**, 79, (3-4), 323-337.

617. Ramírez-Pradilla, J. S.; Blanco-Tirado, C.; Combariza, M. Y., Electron-Transfer Ionization of Nanoparticles, Polymers, Porphyrins, and Fullerenes Using Synthetically Tunable α -Cyanophenylenevinylenes as UV MALDI-MS Matrices. *ACS applied materials & interfaces* **2019**, 11, (11), 10975-10987.

618. Sinclair, I.; Bachman, M.; Addison, D.; Rohman, M.; Murray, D. C.; Davies, G.; Mouchet, E.; Tonge, M. E.; Stearns, R. G.; Ghislain, L., Acoustic mist ionization platform for direct and contactless ultrahigh-throughput mass spectrometry analysis of liquid samples. *Analytical Chemistry* **2019**, 91, (6), 3790-3794.

619. Chandler, J.; Haslam, C.; Hardy, N.; Leveridge, M.; Marshall, P., A systematic investigation of the best buffers for use in screening by maldi–mass spectrometry. *SLAS DISCOVERY: Advancing Life Sciences R&D* **2017**, 22, (10), 1262-1269.

620. Krenkel, H.; Hartmane, E.; Piras, C.; Brown, J.; Morris, M.; Cramer, R., Advancing liquid atmospheric pressure matrix-assisted laser desorption/ionization mass spectrometry toward ultrahigh-throughput analysis. *Analytical Chemistry* **2020**, 92, (4), 2931-2936.

621. Linden, H. B., Liquid injection field desorption ionization: a new tool for soft ionization of samples including air-sensitive catalysts and non-polar hydrocarbons. *European Journal of Mass Spectrometry* **2004**, 10, (4), 459-468.

622. Stanford, L. A.; Kim, S.; Klein, G. C.; Smith, D. F.; Rodgers, R. P.; Marshall, A. G., Identification of water-soluble heavy crude oil organic-acids, bases, and neutrals by electrospray ionization and field desorption ionization Fourier transform ion cyclotron resonance mass spectrometry. *Environmental Science & Technology* **2007**, 41, (8), 2696-2702.

623. Stanford, L. A.; Rodgers, R. P.; Marshall, A. G.; Czarnecki, J.; Wu, X. A., Compositional characterization of bitumen/water emulsion films by negative-and positive-ion electrospray ionization and field desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* **2007**, 21, (2), 963-972.

624. Gross, J. H.; Nieth, N.; Linden, H. B.; Blumbach, U.; Richter, F. J.; Tauchert, M. E.; Tompers, R.; Hofmann, P., Liquid injection field desorption/ionization of reactive transition metal complexes. *Analytical and bioanalytical chemistry* **2006**, 386, (1), 52-58.

625. Monillas, W. H.; Yap, G. P.; Theopold, K. H., A Tale of Two Isomers: A Stable Phenyl Hydride and a High-Spin (S= 3) Benzene Complex of Chromium. *Angewandte Chemie International Edition* **2007**, 46, (35), 6692-6694.

626. Heinze, K.; Fischer, A., Polymer-Supported Dioxido-MoVI Complexes as Truly Functional Molybdenum Oxotransferase Model Systems. *European Journal of Inorganic Chemistry* **2007**, 2007, (7), 1020-1026.

627. Talyzin, A. V.; Tsybin, Y. O.; Peera, A. A.; Schaub, T. M.; Marshall, A. G.; Sundqvist, B.; Mauron, P.; Züttel, A.; Billups, W., Synthesis of C59H x and C58H x Fullerenes Stabilized by Hydrogen. *The Journal of Physical Chemistry B* **2005**, 109, (12), 5403-5405.

628. Talyzin, A. V.; Tsybin, Y. O.; Schaub, T. M.; Mauron, P.; Shulga, Y. M.; Züttel, A.; Sundqvist, B.; Marshall, A. G., Composition of hydrofullerene mixtures produced by C60 reaction with hydrogen gas revealed by high-resolution mass spectrometry. *The Journal of Physical Chemistry B* **2005**, 109, (26), 12742-12747.

629. Lindner, B.; Seydel, U., Laser desorption mass spectrometry of nonvolatiles under shock wave conditions. *Analytical Chemistry* **1985**, 57, (4), 895-899.

630. Lindner, B., On the desorption of electrosprayed organic compounds from supporting metal foils by laser induced pressure waves. *International journal of mass spectrometry and ion processes* **1991**, 103, (2-3), 203-218.

631. Golovlev, V.; Allman, S.; Garrett, W.; Taranenko, N.; Chen, C., Laser-induced acoustic desorption. *International journal of mass spectrometry and ion processes* **1997**, 169, 69-78.

632. Pérez, J.; Ramírez-Arizmendi, L. E.; Petzold, C. J.; Guler, L. P.; Nelson, E. D.; Kenttämaa, H. I., Laserinduced acoustic desorption/chemical ionization in Fourier-transform ion cyclotron resonance mass spectrometry. *International Journal of Mass Spectrometry* **2000**, 198, (3), 173-188.

633. Ragaert, K.; Delva, L.; Van Geem, K., Mechanical and chemical recycling of solid plastic waste. *Waste Management* **2017**, 69, 24-58.

634. Sabbe, M. K.; Saeys, M.; Reyniers, M.-F.; Marin, G. B.; Van Speybroeck, V.; Waroquier, M., Group Additive Values for the Gas Phase Standard Enthalpy of Formation of Hydrocarbons and Hydrocarbon Radicals. *The Journal of Physical Chemistry A* **2005**, 109, (33), 7466-7480.

635. Dobbelaere, M. R.; Plehiers, P. P.; Van de Vijver, R.; Stevens, C. V.; Van Geem, K. M., Machine Learning in Chemical Engineering: Strengths, Weaknesses, Opportunities, and Threats. *Engineering* **2021**.

636. Vermeire, F. H.; Green, W. H., Transfer learning for solvation free energies: From quantum chemistry to experiments. *Chemical Engineering Journal* **2021**, 418, 129307.

637. Green, W. H., Moving from postdictive to predictive kinetics in reaction engineering. *AIChE Journal* **2020**, 66, (11), e17059.

638. Van de Vijver, R.; Vandewiele, N. M.; Bhoorasingh, P. L.; Slakman, B. L.; Seyedzadeh Khanshan, F.; Carstensen, H.-H.; Reyniers, M.-F.; Marin, G. B.; West, R. H.; Van Geem, K. M., Automatic Mechanism and Kinetic Model Generation for Gas- and Solution-Phase Processes: A Perspective on Best Practices, Recent Advances, and Future Challenges. *International Journal of Chemical Kinetics* **2015**, 47, (4), 199-231.

639. Liu, M.; Grinberg Dana, A.; Johnson, M. S.; Goldman, M. J.; Jocher, A.; Payne, A. M.; Grambow, C. A.; Han, K.; Yee, N. W.; Mazeau, E. J., et al., Reaction Mechanism Generator v3.0: Advances in Automatic Mechanism Generation. *Journal of Chemical Information and Modeling* **2021**, 61, (6), 2686-2696.

640. Dogu, O.; Pelucchi, M.; Van de Vijver, R.; Van Steenberge, P. H. M.; D'Hooge, D. R.; Cuoci, A.; Mehl, M.; Frassoldati, A.; Faravelli, T.; Van Geem, K. M., The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Progress in Energy and Combustion Science* **2021**, 84, 100901.

641. De Bruycker, R.; Amghizar, I.; Vermeire, F. H.; Nyman, T.; Hakola, M.; Van Geem, K. M., Steam cracking of bio-derived normal and branched alkanes: Influence of branching on product distribution and formation of aromatics. *Journal of Analytical and Applied Pyrolysis* **2016**, 122, 468-478.

642. Ranzi, E.; Frassoldati, A.; Stagni, A.; Pelucchi, M.; Cuoci, A.; Faravelli, T., Reduced Kinetic Schemes of Complex Reaction Systems: Fossil and Biomass-Derived Transportation Fuels. *International Journal of Chemical Kinetics* **2014**, 46, (9), 512-542.

643. Wang, K.; Xu, R.; Parise, T.; Shao, J.; Movaghar, A.; Lee, D. J.; Park, J.-W.; Gao, Y.; Lu, T.; Egolfopoulos, F. N., et al., A physics-based approach to modeling real-fuel combustion chemistry – IV. HyChem modeling of combustion kinetics of a bio-derived jet fuel and its blends with a conventional Jet A. *Combustion and Flame* **2018**, 198, 477-489.

644. Eschenbacher, A.; Myrstad, T.; Bech, N.; Thi, H. D.; Auersvald, M.; Van Geem, K. M.; Jensen, A. D., Fluid catalytic co-processing of bio-oils with petroleum intermediates: Comparison of vapour phase low pressure hydrotreating and catalytic cracking as pretreatment. *Fuel* **2021**, 302, 121198.

645. Eschenbacher, A.; Varghese, R. J.; Abbas-Abadi, M. S.; Van Geem, K. M., Maximizing light olefins and aromatics as high value base chemicals via single step catalytic conversion of plastic waste. *Chemical Engineering Journal* **2022**, 428, 132087.

646. Seeley, M. E.; Wang, Q.; Bacosa, H.; Rosenheim, B. E.; Liu, Z., Environmental petroleum pollution analysis using ramped pyrolysis-gas chromatography–mass spectrometry. *Organic Geochemistry* **2018**, 124, 180-189.

647. Calemma, V.; Rausa, R., Thermal decomposition behaviour and structural characteristics of asphaltenes. *Journal of Analytical and Applied Pyrolysis* **1997**, 40-41, 569-584.

648. Yin, H.; Lu, J.; Liu, G.; Niu, Z.; Zha, X.; Wu, D.; Feng, A.; Hu, Y., Application of Chemometrics for Coal Pyrolysis Products by Online py-GC×GC–MS. *Acs Omega* **2021**, *6*, (5), 3763-3770.

649. Gorugantu, S.; Carstensen, H.-H.; Van Geem, K. M.; Marin, G. B., Measuring biomass fast pyrolysis kinetics: State of the art. *WIREs Energy and Environment* **2019**, 8, (2), e326.

650. He, Y.; Zhao, Y.; Chai, M.; Zhou, Z.; Sarker, M.; Li, C.; Liu, R.; Cai, J.; Liu, X., Comparative study of fast pyrolysis, hydropyrolysis and catalytic hydropyrolysis of poplar sawdust and rice husk in a modified Py-GC/MS microreactor system: Insights into product distribution, quantum description and reaction mechanism. *Renewable and Sustainable Energy Reviews* **2020**, 119, 109604.

651. Wang, G.; Dai, Y.; Yang, H.; Xiong, Q.; Wang, K.; Zhou, J.; Li, Y.; Wang, S., A Review of Recent Advances in Biomass Pyrolysis. *Energy & Fuels* **2020**, 34, (12), 15557-15578.

652. Rial-Otero, R.; Galesio, M.; Capelo, J.-L.; Simal-Gándara, J., A Review of Synthetic Polymer Characterization by Pyrolysis–GC–MS. *Chromatographia* **2009**, 70, (3), 339-348.

653. Menares, T.; Herrera, J.; Romero, R.; Osorio, P.; Arteaga-Pérez, L. E., Waste tires pyrolysis kinetics and reaction mechanisms explained by TGA and Py-GC/MS under kinetically-controlled regime. *Waste Management* **2020**, 102, 21-29.

654. Akoueson, F.; Chbib, C.; Monchy, S.; Paul-Pont, I.; Doyen, P.; Dehaut, A.; Duflos, G., Identification and quantification of plastic additives using pyrolysis-GC/MS: A review. *Science of The Total Environment* **2021**, 773, 145073.

655. Riley, B. J.; Lennard, C.; Fuller, S.; Spikmans, V., Pyrolysis-GC-MS analysis of crude and heavy fuel oil asphaltenes for application in oil fingerprinting. *Environmental Forensics* **2018**, 19, (1), 14-26.

656. Kohse-Höinghaus, K., Laser techniques for the quantitative detection of reactive intermediates in combustion systems. *Progress in Energy and Combustion Science* **1994**, 20, (3), 203-279.

657. Eltenton, G. C., The Study of Reaction Intermediates by Means of a Mass Spectrometer Part I. Apparatus and Method. *The Journal of Chemical Physics* **1947**, 15, (7), 455-481.

658. Battin-Leclerc, F.; Herbinet, O.; Glaude, P.-A.; Fournet, R.; Zhou, Z.; Deng, L.; Guo, H.; Xie, M.; Qi, F., Experimental Confirmation of the Low-Temperature Oxidation Scheme of Alkanes. *Angewandte Chemie International Edition* **2010**, 49, (18), 3169-3172.

659. Hansen, N.; Klippenstein, S. J.; Taatjes, C. A.; Miller, J. A.; Wang, J.; Cool, T. A.; Yang, B.; Yang, R.; Wei, L.; Huang, C., et al., Identification and Chemistry of C4H3 and C4H5 Isomers in Fuel-Rich Flames. *The Journal of Physical Chemistry A* **2006**, 110, (10), 3670-3678.

660. Cool, T. A.; McIlroy, A.; Qi, F.; Westmoreland, P. R.; Poisson, L.; Peterka, D. S.; Ahmed, M., Photoionization mass spectrometer for studies of flame chemistry with a synchrotron light source. *Review of Scientific Instruments* **2005**, *7*6, (9), 094102.

661. Li, Y.; Qi, F., Recent Applications of Synchrotron VUV Photoionization Mass Spectrometry: Insight into Combustion Chemistry. *Accounts of Chemical Research* **2010**, 43, (1), 68-78.

662. Qi, F., Combustion chemistry probed by synchrotron VUV photoionization mass spectrometry. *Proceedings of the Combustion Institute* **2013**, 34, (1), 33-63.

663. Yang, B., Towards predictive combustion kinetic models: Progress in model analysis and informative experiments. *Proceedings of the Combustion Institute* **2021**, 38, (1), 199-222.

664. Middaugh, J. E.; Buras, Z. J.; Matrat, M.; Chu, T.-C.; Kim, Y.-S.; Alecu, I. M.; Vasiliou, A. K.; Goldsmith, C. F.; Green, W. H., A combined photoionization time-of-flight mass spectrometry and laser absorption spectrometry flash photolysis apparatus for simultaneous determination of reaction rates and product branching. *Review of Scientific Instruments* **2018**, 89, (7), 074102.

665. Smith, M. C.; Liu, G.; Buras, Z. J.; Chu, T.-C.; Yang, J.; Green, W. H., Direct Measurement of Radical-Catalyzed C6H6 Formation from Acetylene and Validation of Theoretical Rate Coefficients for C2H3 + C2H2 and C4H5 + C2H2 Reactions. *The Journal of Physical Chemistry A* **2020**, 124, (14), 2871-2884.

666. Yang, J.; Smith, M. C.; Prendergast, M. B.; Chu, T.-C.; Green, W. H., C14H10 polycyclic aromatic hydrocarbon formation by acetylene addition to naphthalenyl radicals observed. *Physical Chemistry Chemical Physics* **2021**, 23, (26), 14325-14339.

667. Urban, P. L.; Chen, Y.-C.; Wang, Y.-S., *Time-Resolved Mass Spectrometry: From Concept to Applications*. Wiley: 2016.

668. Rob, T.; Wilson, D. J., Time-Resolved Mass Spectrometry for Monitoring Millisecond Time-Scale Solution-Phase Processes. *European Journal of Mass Spectrometry* **2012**, 18, (2), 205-214.

669. Chen, Y.-C.; Urban, P. L., Time-resolved mass spectrometry. *TrAC Trends in Analytical Chemistry* **2013**, 44, 106-120.

670. Lee, J. K., Fast reaction kinetics with time-resolved mass spectrometry. *Nature Methods* **2015**, 12, (5), 387-387.

671. Blitz, M. A.; Goddard, A.; Ingham, T.; Pilling, M. J., Time-of-flight mass spectrometry for time-resolved measurements. *Review of Scientific Instruments* **2007**, 78, (3), 034103.

672. Ludwig, W.; Brandt, B.; Friedrichs, G.; Temps, F., Kinetics of the Reaction C2H5 + HO2 by Time-Resolved Mass Spectrometry. *The Journal of Physical Chemistry A* **2006**, 110, (9), 3330-3337.

673. Nielsen, I. E.; Eriksson, A. C.; Lindgren, R.; Martinsson, J.; Nyström, R.; Nordin, E. Z.; Sadiktsis, I.; Boman, C.; Nøjgaard, J. K.; Pagels, J., Time-resolved analysis of particle emissions from residential biomass combustion – Emissions of refractory black carbon, PAHs and organic tracers. *Atmospheric Environment* **2017**, 165, 179-190.

674. Chen, P., Electrospray Ionization Tandem Mass Spectrometry in High-Throughput Screening of Homogeneous Catalysts. *Angewandte Chemie International Edition* **2003**, 42, (25), 2832-2847.

675. Singh, S.; Wu, C.; Williams, P. T., Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques. *Journal of Analytical and Applied Pyrolysis* **2012**, 94, 99-107. 676. Saadatkhah, N.; Carillo Garcia, A.; Ackermann, S.; Leclerc, P.; Latifi, M.; Samih, S.; Patience, G. S.; Chaouki, J., Experimental methods in chemical engineering: Thermogravimetric analysis—TGA. *The Canadian Journal of Chemical Engineering* **2020**, 98, (1), 34-43.

677. Heger, H. J.; Zimmermann, R.; Dorfner, R.; Beckmann, M.; Griebel, H.; Kettrup, A.; Boesl, U., On-Line Emission Analysis of Polycyclic Aromatic Hydrocarbons down to pptv Concentration Levels in the Flue Gas of an Incineration Pilot Plant with a Mobile Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometer. *Analytical Chemistry* **1999**, **71**, (1), 46-57.

678. Adam, T.; McAughey, J.; McGrath, C.; Mocker, C.; Zimmermann, R., Simultaneous on-line size and chemical analysis of gas phase and particulate phase of cigarette mainstream smoke. *Analytical and bioanalytical chemistry* **2009**, 394, (4), 1193-1203.

679. Hanley, L.; Zimmermann, R., Light and Molecular Ions: The Emergence of Vacuum UV Single-Photon Ionization in MS. *Analytical Chemistry* **2009**, 81, (11), 4174-4182.

680. Zimmermann, R.; Hertz-Schünemann, R.; Ehlert, S.; Liu, C.; McAdam, K.; Baker, R.; Streibel, T., Highly Time-Resolved Imaging of Combustion and Pyrolysis Product Concentrations in Solid Fuel Combustion: NO Formation in a Burning Cigarette. *Analytical Chemistry* **2015**, 87, (3), 1711-1717.

681. Sheps, L.; Antonov, I.; Au, K., Sensitive Mass Spectrometer for Time-Resolved Gas-Phase Chemistry Studies at High Pressures. *The Journal of Physical Chemistry A* **2019**, 123, (50), 10804-10814.