

Review

Molecular Characterization of Hydrocarbons in Petroleum by Ultrahigh-Resolution Mass Spectrometry

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Abstract: The progress in ultrahigh-resolution mass spectrometry (UHRMS) and related technologies has significantly promoted the development of petroleomics. The study of petroleomics has greatly broadened our knowledge of the composition of petroleum at the molecular level, especially heavy fractions that cannot be analyzed by gas chromatography (GC)-based methods. To date, heteroatom-containing (O, N, S, and metal atoms) compounds in petroleum have been studied extensively by UHRMS. Nevertheless, the main components of petroleum, hydrocarbon compounds, have remained out of reach of petroleomics characterization for a long time because they are too difficult to be softly and efficiently ionized for UHRMS analysis. It is undoubtedly the case that petroleum hydrocarbons should not be the missing part of petroleomics characterization since they play important roles not only as feeding pools for various high value-added petroleum products but also as critical biomarkers for geochemistry studies. Here, the most recent breakthroughs in petroleomics characterization of hydrocarbon compounds using UHRMS rather than conventional methods have been reviewed. Innovations of soft ionization methods can transform non-polar hydrocarbon molecules into molecular ions or quasi-molecular ions that are reachable for UHRMS without fragmentation. The development of data processing methods has assisted the decoding of the complicated UHRMS data to visualize the molecular composition and structure of hydrocarbon compounds. These advances make it possible to see the whole picture of petroleum compositions, from light distillation fractions to heavy distillation fractions, and from small volatile molecules to large non-volatile ones. The applications of UHRMS-based methods for petroleomics characterization of hydrocarbon compounds in crude oils and various petroleum samples including fuel oil, slurry, and even asphaltene have made a great contribution to petrochemistry and geochemistry studies, especially in the fields of molecular refining and biomarker discovery.

Keywords: petroleomics; ultrahigh-resolution mass spectrometry; petroleum hydrocarbon; molecular characterization; ionization method; data processing



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1. Introduction

Petroleum is a highly complex organic mixture of hydrocarbons and non-hydrocarbons (heteroatom-containing compounds). Naturally existing hydrocarbons in crude oil mainly include alkanes, cycloalkanes, and aromatic hydrocarbons, with unstable olefins and alkynes hardly existing. After processing, the oil contains not only saturated but also unsaturated hydrocarbons. Non-hydrocarbons mainly include nitrogen-containing compounds, sulfur-containing compounds, oxygen-containing compounds, and metal-containing organic compounds. The comprehensive characterization of hydrocarbons in petroleum has become a challenging problem because of the variety of compound types, wide distribution range of molecular weight, and large polarity difference [1–3]. Comprehensive characterization at the molecular level is the foundation of molecular refining to obtain high-quality

clean oil and high value-added petroleum products, and is the cutting-edge direction in the petrochemical field [4–6].

Petroleum processing is a process of removing heteroatomic compounds and tailoring hydrocarbon compounds into the desired structure to obtain the ideal product [7–9]. The type, structure, and quantity of hydrocarbons decide the performance of petroleum products. For example, high-quality gasoline needs more iso-alkanes than n-alkanes because iso-alkanes have higher octane numbers and lower cetane numbers, while diesel fuel wants the exact opposite properties. Olefins affect the stability of petroleum products, and excessive aromatic hydrocarbons not only make the oil coke but also bring environmental pollution. Therefore, the content of olefins and aromatics should be strictly controlled in the oil processing process [1,10,11]. In the field of geochemical studies, the characterization of petroleum hydrocarbons contributes to a deeper understanding of source rocks and can better reveal their present-day state and evolutionary history [12–17], because biomarkers such as steranes, terpenes, and diamondoids preserve the carbon skeleton of the original biochemical components and record evidence of the evolution from living organic matter to sedimentary organic matter [18–20]. Aromatic compounds occupy a large proportion of petroleum and sedimentary organic matter. In the process of the thermal evolution of organic matter, the methylation, demethylation, and methyl rearrangement of aromatic compounds are controlled by their own thermal stability. With the increase in thermal evolution, the aromatic compounds with good thermal stability are less likely to undergo the above processes, so their relative content gradually increases, while the relative content of the aromatic compounds with poor thermal stability gradually decreases. Therefore, the ratio of the content of aromatic compounds is a good indicator of the maturity of petroleum [21–24]. In summary, comprehensive molecular characterization of hydrocarbon compounds in petroleum is very important and meaningful.

Currently, gas chromatography (GC) is the technique of choice when characterizing the molecular structure of hydrocarbon compounds in petroleum [25,26]. GC is the most efficient method for the analysis of volatile mixtures; the separation of compounds is achieved by the difference in molecular interaction between compounds in the carrier gas and the stationary phase of the column. GC can be used in conjunction with a variety of detectors, such as a flame ionization detector (FID), a thermal conductivity detector, an electron capture detector, and a mass spectrometry (MS) detector [27–31]. An FID has superior quantitative analysis capability for hydrocarbon compounds and has been more widely used, but it relies on model compounds and retention indices for structural characterization, which is a tedious process. An MS detector has superior qualitative capability, and the combination of gas chromatography and MS can achieve the identification and recognition of hydrocarbon compounds in oil [32,33]. However, conventional GC is limited by the temperature of the column used and can generally only analyze hydrocarbons below C35; the use of high-temperature resistant columns can extend the range of detectable carbon numbers to C60 [34–36]. It is worth mentioning that, due to the limitation of chromatographic separation capacity, in the middle and high carbon number region, GC cannot separate these high carbon number hydrocarbons, which form overlapping peaks in the chromatogram and an indistinguishable bulging of complex compounds appears, so GC-MS has a better separation and identification capability only when analyzing hydrocarbons in light gasoline fractions (<C15) [37,38]. Full two-dimensional gas chromatography–mass spectrometry (GC × GC-MS) has further improved the separation capability of GC, but the hydrocarbon compounds that can be analyzed only account for a small fraction of the petroleum fraction; the detection of hydrocarbons in middle distillates and heavy oils cannot be achieved [39–41].

The limitation of column temperature and the lack of separation capacity prevents GC from achieving the analytical identification of high carbon number hydrocarbons in petroleum. In recent years, scientists have proposed petroleomics approaches. Petroleomics relies on ultrahigh-resolution mass spectrometry to realize the detection of individual compounds in complex mixtures, which indirectly realizes the separation of compounds in

complex systems [42,43]. Petroleomics is a discipline that employs high-resolution mass spectrometry (HRMS) and related analytical characterization tools to systematically analyze the molecular composition of petroleum. The detailed characterization of petroleum's molecular composition is used to predict the properties of petroleum products and to discuss the correlation between petroleum's physicochemical properties and product performance, which guides the improvement of refining processes [44–46]. UHRMS is not limited by the boiling point of the sample and can achieve full-component analysis of heavy oil, relying on ultrahigh mass resolution, avoiding tedious pretreatment processes, and enabling the separation of single compounds directly in the mass spectrogram, which has become the preferred solution for analyzing the molecular composition in complex petroleum [47,48]. Compounds containing heteroatoms such as nitrogen, oxygen, and sulfur, as well as metal compounds, have a higher ionization efficiency and ionization response in an electrospray ionization source, which are more easily detected by MS [49–51]. However, the analysis of hydrocarbons by petroleomics is currently lagging far behind the heteroatomic compounds. Hydrocarbons are non-polar compounds with low ionization energies and are prone to carbon–carbon chain breakage during ionization, making it difficult to obtain accurate molecular structure information [52–55]. Soft ionization of hydrocarbons refers to the formation of charged ions without the breakage of carbon–carbon bonds in the hydrocarbon molecule, producing molecular ions or quasi-molecular ions that retain their original structure. Therefore, to apply UHRMS to the analysis of hydrocarbon compounds in petroleum, the first thing to solve is how to make the mass spectrometer “see” hydrocarbons, which is the development of soft ionization technology for hydrocarbon compounds. Secondly, data processing and analysis in a large-capacity database have always been difficult problems in the field of analytical chemistry. Presented with a petroleum system with a large and complex molecular composition, UHRMS will achieve a large-capacity molecular database, so the development of processing and analysis methods for large-capacity data to better predict the molecular structure information of target compounds is also an urgent need to solve.

In this review, we first introduce the development of soft ionization methods for hydrocarbons, followed by a discussion of the development of complex data processing methods for analyzing hydrocarbons in petroleum by UHRMS, and present cutting-edge applications for the characterization of hydrocarbons in different complex petroleum samples using UHRMS. At the end of the review, we discuss and look into the prospects and future of the UHRMS characterization of hydrocarbons in petroleum.

2. Development of Soft Ionization Methods for Hydrocarbons

UHRMS is the primary method for petroleomics characterization because petroleum compounds are too complex to be completely separated by chromatography and can only be separated by the ultrahigh mass resolution of MS. However, the limitation is that ionization requires that each compound must be softly ionized, i.e., the compound must not produce its own molecular fragments during ionization, otherwise the mass spectral peaks formed by its own fragmented molecules and the original compound will coexist and affect the identification of the original compound [56]. Non-polar hydrocarbon compounds with low ionization energies are prone to molecular fragmentation during ionization, so achieving soft ionization of hydrocarbons is the first issue to be solved. In the early stages, field ionization (FI) and field resolution (FD) were developed for the soft ionization of hydrocarbons. FI can ionize n-alkanes and cycloalkanes into molecular ions, but more severe fragmentation still occurs when ionizing isomeric alkanes with quaternary carbon atoms, so accurate molecular information cannot be obtained. FD has the same ionization principle as FI and is more suitable for ionizing large saturated hydrocarbons that are difficult to volatilize. Both methods suffer from a complicated operation, poor reproducibility, and low ionization efficiency, which greatly limit their application in hydrocarbon analysis [33,57–59]. In response to the above-mentioned drawbacks, scientists have developed more advanced soft ionization techniques for hydrocarbons in recent years. The first

is the chemical derivatization-based soft ionization technique. Chemical derivatization is based on the insertion of more polar heteroatoms such as N and O into hydrocarbon molecules through an addition reaction, which transforms non-polar hydrocarbons into strongly polar “addition molecules”, indirectly enabling the soft ionization of hydrocarbons in an electrospray ionization source. The second is the chemical ionization-based soft ionization technique, which is the application of the research results of molecular ionization reactions in analytical chemistry. Soft ionization of hydrocarbon molecules can be achieved directly within the ion source by regulating the molecular ionization reaction and ionization process. The development of these two soft ionization methods has made possible the UHRMS characterization of hydrocarbon compounds.

2.1. Chemical Derivatization-Based Soft Ionization

The chemical derivatization method uses derivatization reagents to insert specific ions or groups into hydrocarbon molecules through addition reactions to achieve soft ionization of “addition molecules”, thus indirectly achieving soft ionization of hydrocarbon molecules. Ruthenium-ion-catalyzed oxidation (RICO) is an efficient reaction for the conversion of saturated hydrocarbons to alcohols and ketones [60–62]. Zhou’s group achieved the analysis of saturated hydrocarbons indirectly using the RICO reaction, which can oxidize branched paraffins and naphthenes with tertiary C-H bonds to alcohols and n-paraffins without tertiary C-H bonds to ketones, which can be reduced by LiAlH_4 to form alcohols. Thus, n-paraffins can be discriminated from iso-paraffins. Then, negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to characterize the monohydric alcohols (O_1) in the products of the RICO and RICO- LiAlH_4 reduction reactions, enabling the ionization analysis of iso-paraffins, acyclic paraffins, and cyclic paraffins. Finally, the technique was used to characterize petroleum vacuum residue (VR)-derived saturates, and the results showed that saturated molecules in a VR contain up to 11 cyclic rings, and the maximum carbon number was up to 92 (Figure 1) [63,64]. Ag^+ can be complexed with fractions containing π -bonds through π -complexation [65–67]. Casas-Ferreira et al. proposed a new method for the detection of polycyclic aromatic hydrocarbon (PAH) isomers based on flow injection analysis, electrospray ionization, and tandem MS (FIA-ESI-MS/MS). Seven PAHs were selected as test compounds for the soft ionization of aromatic hydrocarbons indirectly by forming complexes with Ag (I). This method proved to be a suitable option for studying the ionization of PAHs, allowing rapid, non-separated quantitative analysis of complex PAH mixtures [68]. Zhang et al. used the complexation of unsaturated hydrocarbon bonds with Ag^+ in combination with (+) ESI UHRMS for the selective characterization of the molecular composition of olefins in complex hydrocarbon mixtures. A variety of hydrocarbon model compounds were selected, and the response results showed that the method could achieve efficient complexation and mass spectrometric detection of olefins. The observed results from Ag^+ complexation ESI UHRMS were in agreement with those from gas chromatography–mass spectrometry equipped with the electron impact ion source (GC-EI-MS). This method can directly molecularly characterize olefins in mixtures without time-consuming olefin pre-separation, showing good prospects for application (Figure 2) [69]. Shi’s group has recently developed a method to characterize aromatic hydrocarbons in heavy petroleum fractions. Aromatic hydrocarbons were converted into their corresponding sulfonates and then analyzed by negative-ion electrospray ionization (–ESI) MS. The sulfonation has good selectivity for aromatic hydrocarbons in saturated fractions, and the sulfonated derivatives are strongly polarized and can be easily and efficiently ionized in UHRMS. The method allows semiquantitative analysis of the molecular characterization of aromatic compounds in heavy petroleum fractions. In addition, this method can be used to distinguish monoaromatic steranes from alkyl naphthalenes, which have the same molecular composition [70]. RICO derivatization can achieve indirect soft ionization of saturated hydrocarbons through redox reactions. However, this derivatization process is complicated, tedious, and time-consuming, and the reproducibility of the results is poor. Ag^+ can only

complex with molecules containing π -bonds, and thus are only suitable for the analysis of hydrocarbons containing π -bonds such as olefins and aromatics, and cannot achieve soft ionization analysis of saturated hydrocarbons. These drawbacks largely limit the UHRMS analysis of hydrocarbons, so there is an urgent need to develop a more simple, efficient, and comprehensive soft ionization technique for hydrocarbons.

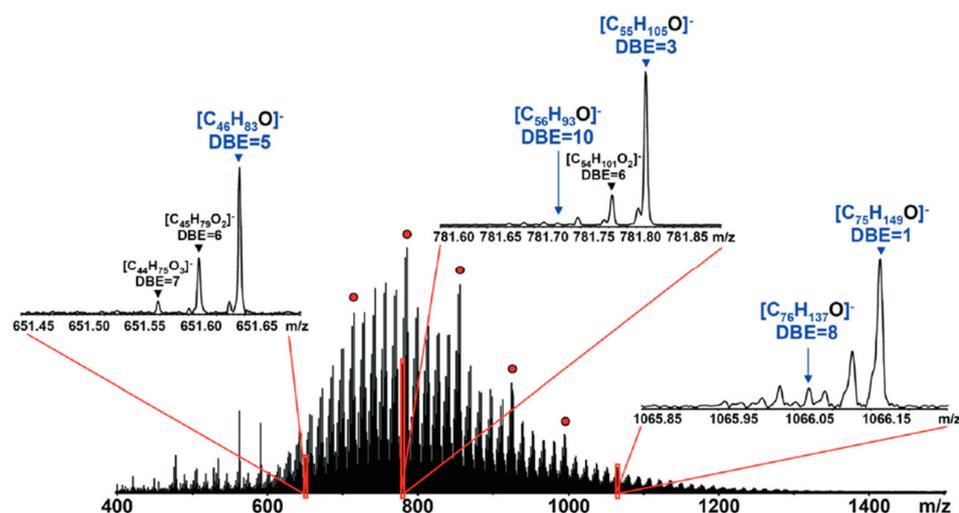


Figure 1. Broadband negative-ion ESI FT-ICR mass spectrum of the O_1 species in the product of the RICO of saturate fraction of Dagang vacuum residue. The insert shows the expanded mass scale spectrum at m/z 651, 781, and 1065. The peaks marked with an asterisk are highly abundant compared to the adjacent peaks. DBE values were calculated for the neutral states of the compounds. Reprinted with permission from Ref. [63]; Copyright 2012, American Chemical Society.

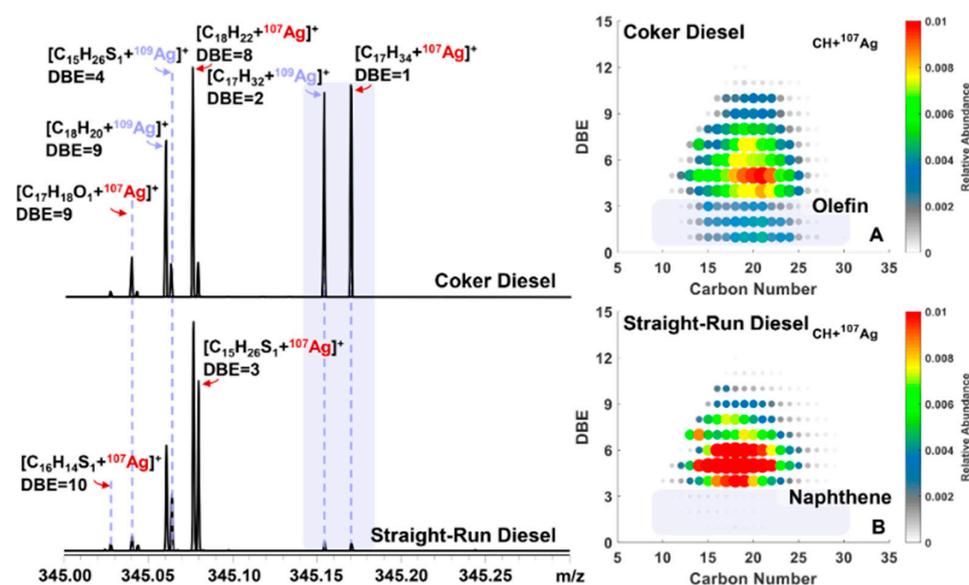


Figure 2. Expanded Ag^+ complexation (+) ESI HR mass spectra and the plots of $[CH + ^{107}Ag]^+$ DBE versus carbon number for coker diesel (A) and straight-run diesel (B). The color represents the relative abundance percentage of the sum of $[CH + ^{107}Ag]^+$ and $[CH + ^{109}Ag]^+$ peaks. Reprinted with permission from Ref. [69]; Copyright 2022, Elsevier.

2.2. Chemical Ionization-Based Soft Ionization

Atmospheric pressure chemical ionization (APCI) is a softer ionization technique that is a direct application of the results of molecular ionization reactions in analytical chemistry. In the process of APCI, electrons first bombard the reagent molecules rather than

directly ionizing the target molecules; then the reagent molecules are ionized into excited ions, and the sample molecules are subsequently ionized by the reagent ions through the molecular ion reaction. This ionization process has a low reaction thermal effect and the fragmentation of molecular ions is usually less than electron ionization [71]. APCI is a multi-factor mediated gas-phase molecular ion reaction process under corona discharge. Variations in various parameters in the ionization environment, such as ionization solvent, ion source gas, vaporizer temperature, transfer tube voltage, etc., can cause different gas-phase molecular ionization reactions of hydrocarbons in APCI, resulting in very different ionization products and different fragmentation degrees [72]. For this reason, it is hopeful that soft ionization of hydrocarbons can be achieved directly in ion sources by regulating and optimizing various parameters in the ionization environment [73]. Using a linear quadrupole ion trap (LQIT) mass spectrometer, Gao et al. successfully ionized saturated hydrocarbons, unsaturated hydrocarbons, straight-chain alkanes, branched alkanes, and cycloalkanes by APCI using small molecule hydrocarbons (pentane) as reagents. This ionization method produced different types of abundant ions ($[M + H]^+$, $M^{+\bullet}$, $[M - H]^+$ and $[M - 2H]^{+\bullet}$), but with some fragmentation. The method can be performed on any mass spectrometer equipped with an APCI source with good compatibility [74]. Kuhnert et al. presented an optimized APCI method using nitrogen as the reagent gas for the ionization analysis of 17 non-volatile non-polar hydrocarbon compounds that are not easily ionized. All of these analytes were successfully ionized into abundant and intact stable $[M - H]^+$ ions without the use of any derivatization or addition reactions, but the problem of fragmentation is still not fully resolved. This method enables the analysis of hydrocarbons in actual hydrocarbon compound mixtures such as automotive motor oil [75]. Romão et al. proposed a simple, rapid, and efficient method for the analysis of saturated hydrocarbons in hydrocarbon fraction samples and paraffin/crude oil mixtures using FT-ICR MS. Using isooctane as a reagent and nitrogen as a sheath gas, the saturated hydrocarbons in oil samples were ionized to a single $[M - H]^+$ ion using an APCI source and with a low degree of fragmentation. This method gives a new means for the ionization analysis of saturated hydrocarbons in petroleum samples (Figure 3) [76]. A fully automated method for the analysis of saturated hydrocarbons based on (+) APCI/O₂ has recently been proposed, utilizing isooctane as a reagent and oxygen as a sheath gas, reducing the formation of ions other than the required $[M - H]^+$. The method can rapidly analyze a wide range of base oils with different viscosities. Rapid measurement of the relative abundance of different hydrocarbons in base oils enables refiners to better evaluate methods for converting light distillation fractions of crude oil into the desired product [77]. The above results show that APCI can directly ionize hydrocarbon compounds, and the variation of its gas-phase molecular ion reaction conditions could significantly affect the type of hydrocarbon ionization products. In analyzing model compounds of hydrocarbons, the above-mentioned ionization techniques perform well, but in analyzing hydrocarbon compounds in middle distillate oils with complex compositions or even heavy oils, the fragmentation of hydrocarbon molecular skeletons easily occurs during ionization due to matrix effects, which makes the number of interfering peaks in the mass spectra greatly increase and makes it difficult to obtain correct characterization results of hydrocarbons in oil. To solve this challenge, Han's group proposed the concept of soft and clean ionization, where "soft" meant the whole molecular skeleton and the side chains remained unbroken during the production of ions, while "clean" meant the ionization process could be followed to generate one and only one dominant production to reduce identification interference. After systematic optimization, hexane-assisted APCI methods were developed for the analysis of diamondoids and ethanodiamondoids to obtain bridgehead carbocations of $[M - H]^+$ without any other byproduct ions, achieving accurate analysis and identification of diamondoid compounds in UHRMS (Figure 4) [78–80]. It is worth mentioning that, in addition to the currently widely used APCI ionization technique, direct analysis in real time mass spectrometry (DART-MS), which has emerged in recent years, also belongs to the category of chemical ionization. The ionization mechanism of DART is that a neutral or inert gas (e.g., nitrogen

or helium) is discharged at atmospheric pressure to generate excited atoms, which are rapidly heated and accelerated by an electric field to desorb and instantaneously ionize the compound to be measured on the sample surface. The connection of the DART source to HRMS allows direct analysis of the sample in real time [81]. Dane et al. used DART in negative-ion mode with time-of-flight MS to characterize n-alkanes with larger carbon numbers ($C > 18$), producing mainly $[M + O_2]^{-\bullet}$ and with less fragmentation, achieving soft ionization of hydrocarbons to some extent [82]. In general, DART still has disadvantages in ionizing hydrocarbons that are difficult to solve at this stage, such as poor sensitivity and strong ionization discrimination, so we highly recommend the adoption of the APCI method for the analysis of hydrocarbons.

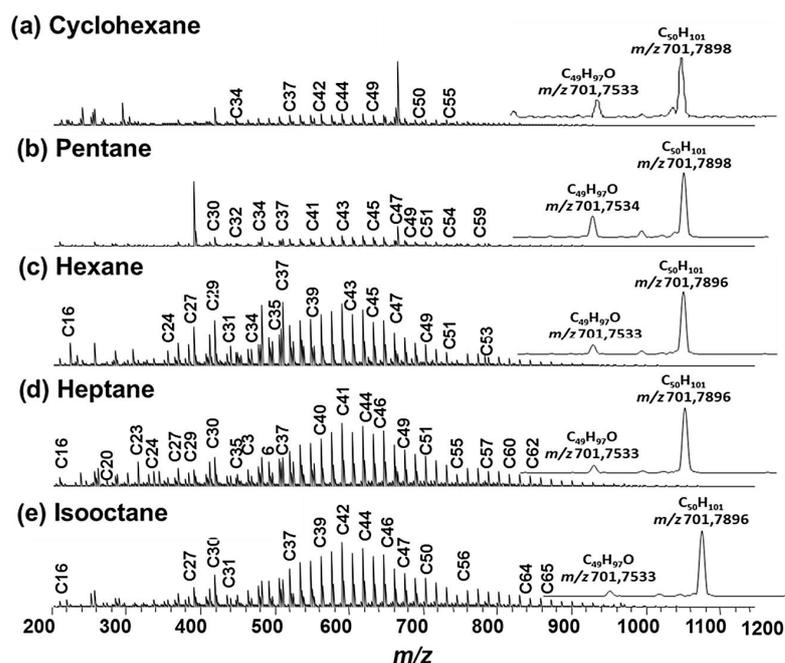


Figure 3. APCI (+) FT-ICR mass spectra for paraffin B at 0.5 mg mL^{-1} using different aliphatic solvents as APCI reagent. Reprint with permission from Ref. [76]; Copyright 2015, Elsevier.

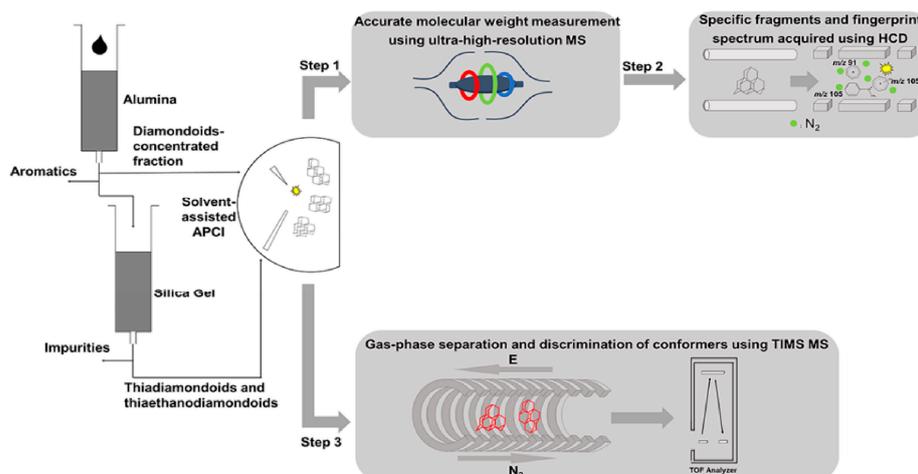


Figure 4. Workflow of the multi-dimensional mass spectrometry (MS) strategy. Step 1: Determination of the accurate molecular weight and molecular composition using solvent-assisted atmospheric pressure chemical ionization (APCI)-ultrahigh-resolution MS. Step 2: Structural identification by analyzing the specific fragments and fingerprint spectral profiles using high-energy collision dissociation (HCD). Step 3: Differentiation and identification of the conformational isomers using trapped ion mobility spectrometry MS (TIMS-MS). Reprinted with permission from Ref. [80]; Copyright 2023, Elsevier.

3. Development of Data Processing Methods for UHRMS Analysis of Petroleum Hydrocarbons

UHRMS has ultrahigh mass resolution and mass accuracy. Connected with different types of ionization sources, it can obtain the precise elemental composition of compounds in each fraction of oil, especially in heavy distillation fractions, which greatly promotes the progress of petroleomics. However, the molecular composition of petroleum is very complicated; up to 30,000 mass spectrum peaks can be obtained in UHRMS in a single analysis, which makes data processing a great challenge. In petroleomics, the more commonly used data processing methods are Kendrick Mass Defect (KMD) analysis, van Krevelen (VK) diagrams (Figure 5), and double bond equivalence (DBE) versus carbon number plot [83–86]. The two visualization methods, KMD and VK, can identify the class and type of compounds but cannot obtain the target compound's structural information. In contrast, the DBE versus carbon number distribution plot is the only data processing method that is currently relevant to the structure of a compound. DBE represents the number of double bonds plus the number of rings in a given formula. The DBE value of $C_cH_hN_nO_oS_s$ (lowercase letters represent the number of corresponding atoms) can be calculated by the following equation (c = number of carbon atoms, h = number of hydrogen atoms, n = number of nitrogen atoms):

$$DBE = c - \frac{h}{2} + \frac{n}{2} + 1$$

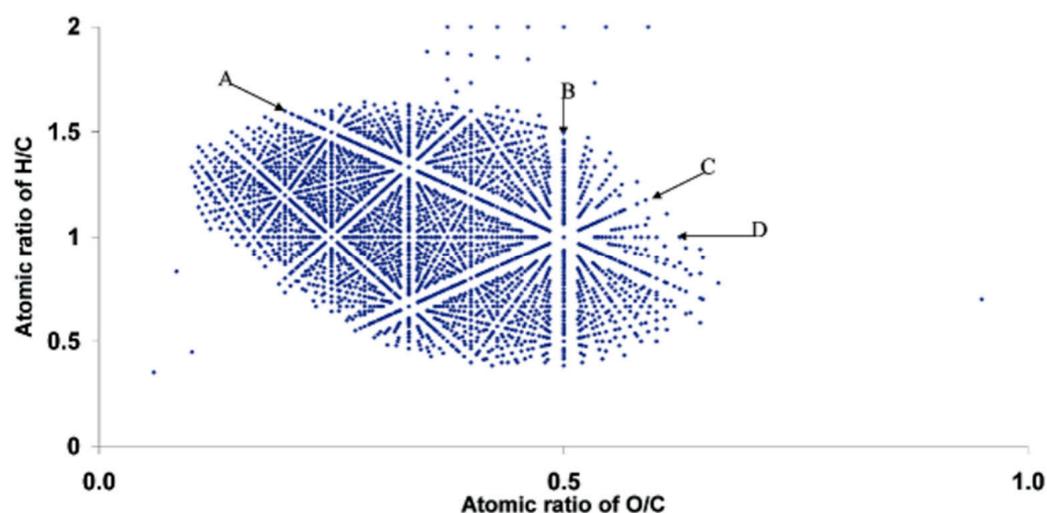


Figure 5. The van Krevelen plot for elemental data calculated from the ultrahigh-resolution mass spectrum of McDonalds Branch DOM. Distinctive lines in the plot representing chemical reactions are noted as: (A) methylation, demethylation, or alkyl chain elongation; (B) hydrogenation or dehydrogenation; (C) hydration or condensation; and (D) oxidation or reduction. Reprinted with permission from Ref. [85]; Copyright 2003, American Chemical Society.

Here, we first introduce the method of interpreting the DBE versus carbon number plot. In the plot, the abscissa represents the distribution of carbon number, and the ordinate represents the number of equivalent double bonds. The size of the dots in the plot represents the relative abundance of the compound, with larger dots indicating a higher relative abundance of the compound in the sample. Figure 6 is the DBE versus carbon number plot of saturated hydrocarbons in raw oil (using complex saturated hydrocarbon mixture simulation). In this work, straight-chain alkanes and branched alkanes are mainly ionized into $[M - H]^+$, and cycloalkanes are ionized into $[M - H]^+$ and $M^{+\bullet}$ depending on the capillary temperature. In this simulated raw oil, the carbon number of alkanes represented by $DBE = 0$ is about $C_{10}\sim C_{50}$, and the abundance of alkanes with carbon number distribution between $C_{28}\sim C_{36}$ is higher (Figure 6, left). The graph also shows higher DBE series

corresponding to cycloalkanes with increasing ring numbers (from one to eight rings). At a heated metal capillary temperature of ~ 250 °C, cycloalkanes also generate radical cations, as shown by an isoabundance-contoured plot of DBE versus carbon number (Figure 6, right). High-abundance species with carbon number C_{27} – C_{30} and DBE = 4 likely represent C_{27} – C_{30} steranes, in agreement with GC/EIMS, GC \times GC, and FIMS biomarker analysis of similar mixtures [87].

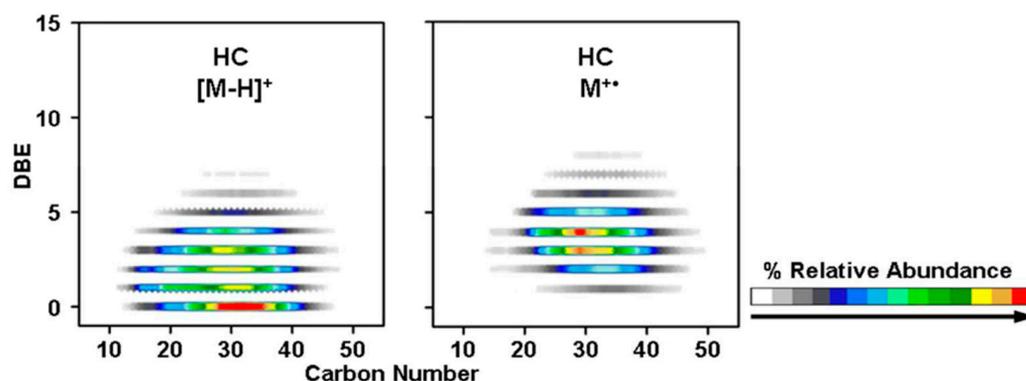


Figure 6. Isoabundance-contoured plot of double bond equivalents vs carbon number for the hydrocarbon composition. Reprinted with permission from Ref. [87]; Copyright 2012, American Chemical Society.

The identification of molecular structures of hydrocarbon compounds is essential for petroleum analysis. Nowadays, DBE versus carbon number plot has become the most widely used data processing method for hydrocarbon analysis in petroleomics. However, hydrocarbon compounds in crude oil exhibit continuous DBE distribution. Therefore, it is difficult to identify hydrocarbon structures merely by DBE value. For example, hydrocarbons with DBE = 4, 7, and 10 are usually considered aromatic hydrocarbons with 1, 2, and 3 aromatic rings, respectively [88,89]. However, this judgment ignores the contribution of cycloalkanes to the DBE values, and those with a DBE of 4 may also be tetracyclic cycloalkanes (steranes). The concept of planar limits was proposed by Cho et al. to explain the type of molecular structure in crude oil based on the DBE versus carbon number plot [90]. The planar limit was defined as the line formed by connecting the maximum DBE at each carbon number in the DBE versus carbon number plot. The slope and intercept of planar limits were related to the addition of functional groups and core structure, respectively. This method can analyze the overall structural characteristics of saturated hydrocarbon/aromatic/resin/asphaltic (SARA) fractions but cannot accurately infer the structure of individual molecular formulae. Based on this idea, a DBE linear equation describing the structure of petroleum hydrocarbons was proposed by Dong et al. It is divided into alkyl, naphthenic, and aromatic homologous equations based on the magnitude of the slope. The structure of any petroleum hydrocarbon can be represented by a combination of these three types of DBE linear equations, and the distribution map of aromatic hydrocarbons was constructed based on the DBE linear equation to visualize the ring structure of petroleum hydrocarbons. The experimental results of UHRMS validate the feasibility of the distribution map to distinguish naphthenic and aromatic rings and to classify the numbers of aromatic rings. This method provides a new idea for the determination and identification of petroleum hydrocarbon structures in complex petroleum samples (Figure 7) [79]. Due to the limitation of instruments and technology, the data analysis methods for hydrocarbon compounds in petroleum by UHRMS are still relatively limited. However, we believe that with the development of new MS and the modification of ionization technology, the data analysis methods for hydrocarbon compounds will also become more and more advanced.

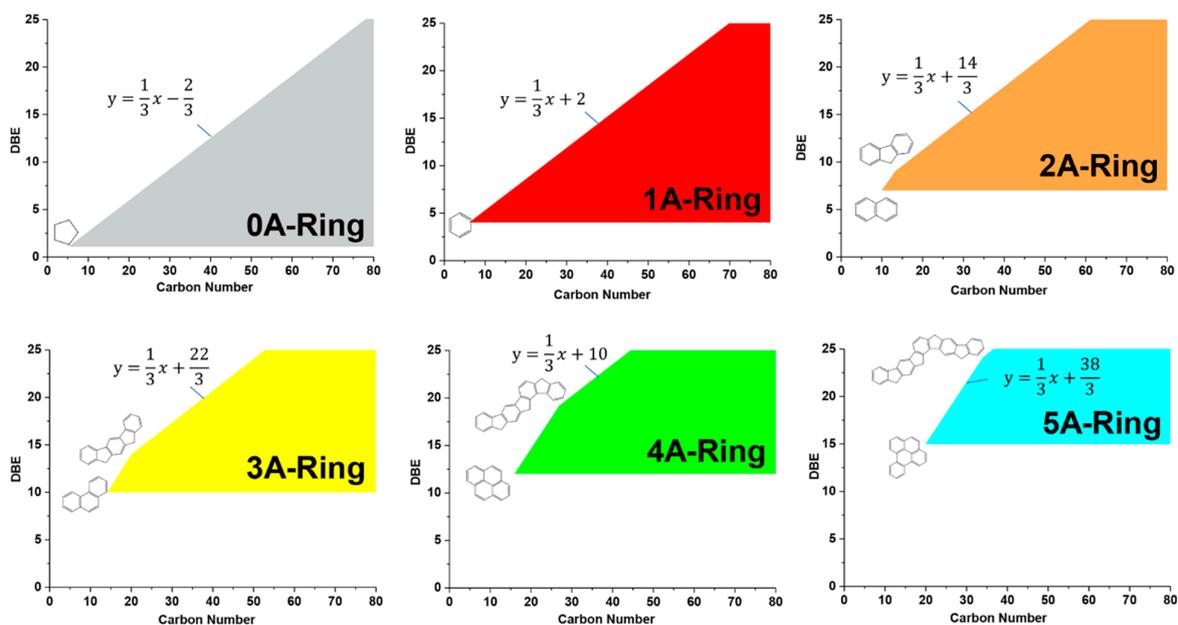


Figure 7. Distribution map of hydrocarbons with different numbers of aromatic rings. Reprinted with permission from Ref. [79]; Copyright 2023, Elsevier.

4. UHRMS Characterization of Hydrocarbons in Different Complex Petroleum Matrix

After selecting a suitable soft ionization and data processing method, it is possible to use UHRMS for detailed molecular characterization of hydrocarbons in the different oil samples. In recent years, scientists have performed much meaningful work in this field. Marshall et al. used FT-ICR MS to molecularly characterize natural crude oil from the Gulf of Mexico seep as well as crude oil from nearby reservoirs and inferred the transport routes of the seeped crude oil by detecting the presence or absence of hydrocarbon biomarkers (steranes, diasteranes, and pentacyclic triterpenes) in the crude oil, and this work highlighted that in addition to FT-ICR, MS can be used as a means to determine oil connectivity in addition to the traditional GC-MS technique [91]. Mangelsdorf's group studied fluid inclusion (FI) oil (representing expelled fluids) and hydrocarbon source rock (SR) extracts (representing retained bitumen) from calcite veins in the Hosszúhetény Calcareous Marl Formation (HCMF) (Hungary) to assess the fractionation of organic compounds during initial migration. FT-ICR-MS measurements indicate that aromatic compounds (CHs) are preferentially expelled. In-depth studies of the compound library indicate that hydrocarbons with higher aromaticity are preferentially retained in hydrocarbon source rocks during primary transport, especially for high DBE compounds with low carbon numbers. These findings confirm that the functional groups, aromaticity, and degree of alkylation of hydrocarbons and non-hydrocarbons are the main factors influencing the fractionation of petroleum components during primary transport (Figure 8) [92]. Wax deposition is a great concern in the petroleum industry because it can cause a partial or total blockage of pipelines. Romão et al. used four Brazilian crude oils (P1–P4) and five inhibitor solutions (I1–I5), combined with rheological results, to understand the characteristics of saturated fractions at the molecular level by HRMS (Orbitrap-coupled APCI source) and GC × GC-MS, and to relate the results of rheological tests to the properties of saturated fractions. The experimental results revealed that inhibitor I1 favored the inhibition process of paraffins when oils have smaller and monocyclic saturated chain hydrocarbon profiles, whereas for oils with larger amounts of polycyclic chain hydrocarbons, the inhibitor I4 appeared to be the alternative [93]. Dong et al. developed a comprehensive and in-depth UHRMS analytical method (APCI-Orbitrap Fusion MS) for the production process of Liaohe Petrochemical lubricants. The molecular composition of the raw oil and the molecular change during the process were studied at the molecular level, and it was found that after hydrotreat-

ing and isomerization/refinement, the polycyclic aromatic hydrocarbons in the raw oil would be hydrogenated and saturated, and the polycyclic cycloalkanes would undergo reactions such as ring-opening [94]. In the chapter on the development of soft ionization methods for hydrocarbons, we mentioned that Han's group used the solvent-assisted APCI ionization technique to achieve clean and soft ionization of high-molecule diamondoids. Combined with Orbitrap Fusion MS, they detected and reported for the first time naturally occurring thiaethanodiamondoids (1–7 cages) and higher ethanodiamondoids (4–7 cages). The developed method was also used to extend the previously reported presence of higher diamondoids and higher thiadiamondoids in ZS1C crude oil to seven cage species. In addition, this work introduced ion mobility resolution to differentiate isomers and established a correlation between compound structures and CCS values, which has methodological implications for mass spectrometric characterization. The discovery of new species and advanced cage species of diamondoids not only provides potential markers for the elucidation of geochemical evolution but also provides an impetus for the artificial synthesis of advanced diamondoids as functional materials (Figure 9) [80].

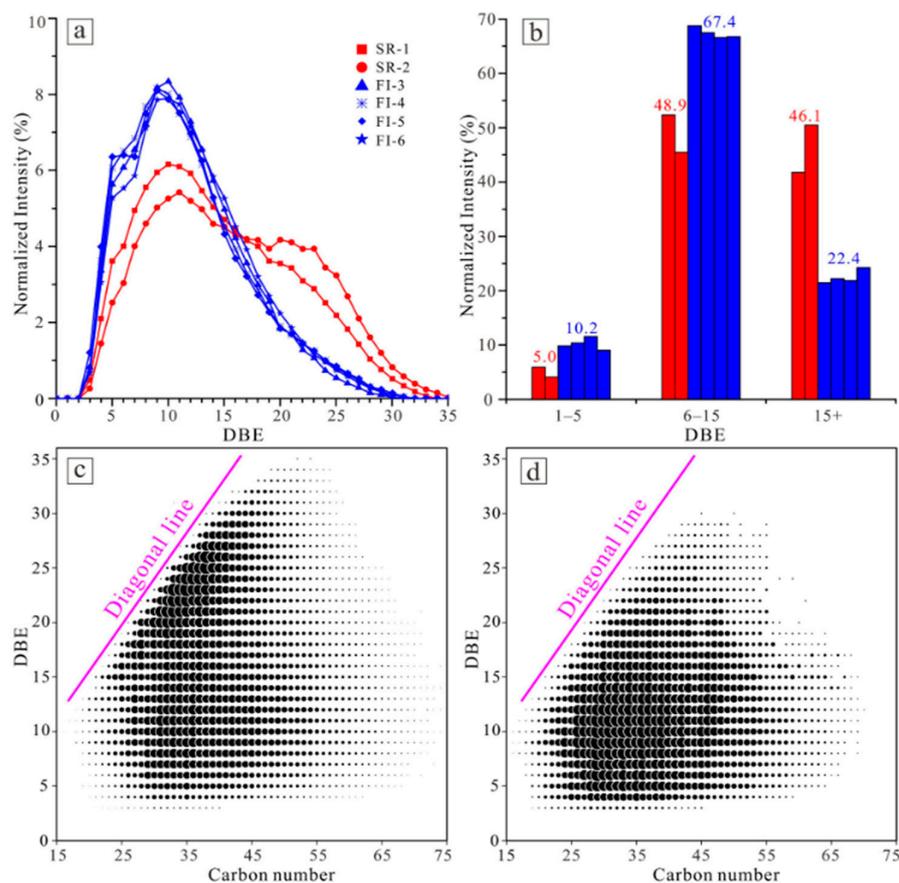


Figure 8. (a) Double bond equivalent (DBE) distributions of hydrocarbon (HC) in the two source rock (SR-1 and SR-2) extracts (red) and four fluid inclusion (FI-3 to FI6) oils (blue). (b) Normalized intensity of the low (DBE_{1–5}), medium (DBE_{6–15}), and high (DBE₁₅₊) DBE groups of HCs in the SR extracts (red) and FI oils (blue) with numbers indicating average values. (c) DBE versus carbon number plot of HCs in a representative SR extract (SR-2). (d) DBE versus carbon number plot of HCs in a representative FI oil (FI-6). The normalized intensity (%) is expressed relative to the total monoisotopic ion abundance of the HC class. The magenta-colored diagonal line delineates the minimum carbon number of a non-alkylated planar polycyclic aromatic core molecule within every DBE class. Reprinted with permission from Ref. [92]; Copyright 2022, Elsevier.

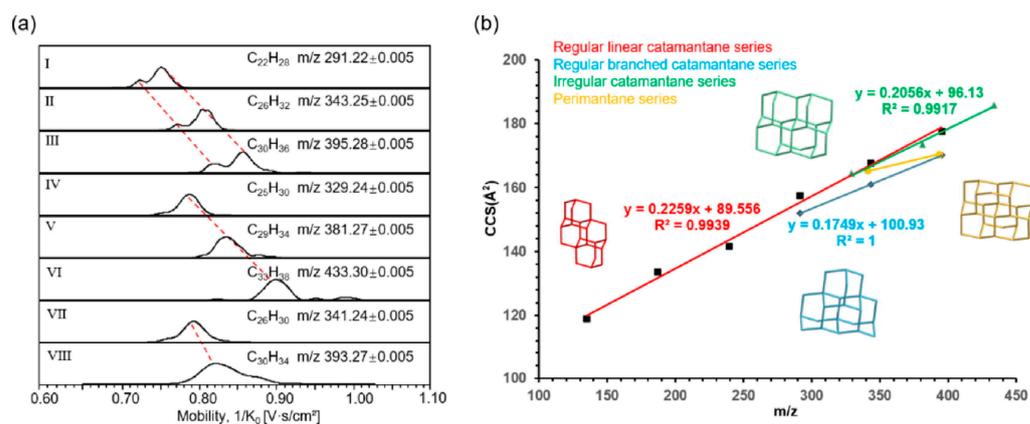


Figure 9. Analysis of the diamondoids present in the ZS1C crude oil using TIMS-MS as the illustration of the third dimensional MS characterization method: (a) Extracted ion mobiligrams recorded for unsubstituted diamondoids belonging to different series. (b) Linearity between the collision cross-section (CCS) values and m/z values of the unsubstituted diamondoids with varying molecular weights, structures, and conformations. Reprinted with permission from Ref. [80]; Copyright 2023, Elsevier.

5. Conclusions and Prospective

Petroleum hydrocarbons play important roles in both petrochemistry and geochemistry. This review focuses on the significant progress of hydrocarbon analysis in petroleomics in recent years. The development of soft ionization methods to ionize hydrocarbons is a key prerequisite for UHRMS analysis of petroleum hydrocarbons. Currently, the mainstream soft ionization techniques are based on chemical derivatization or chemical ionization. Among them, the chemical ionization-based APCI method has a greater advantage due to its simplicity of operation, no pretreatment, and wide universality. Another crucial issue is how to process huge and complex UHRMS data to present molecular compositions and structure information. Unfortunately, few data evaluation methods have been developed to interpret UHRMS data of hydrocarbon compounds in petroleum. Therefore, it is believed that the development of soft ionization and data processing techniques will remain hot research topics in this field in the foreseeable future.

It is undoubtedly the case that UHRMS analysis of hydrocarbons is a great breakthrough in petroleomics studies; it has filled the gap of hydrocarbons' characterization in heavy distillation oils. Many studies related to the characterization of hydrocarbons in various petroleum samples using UHRMS have been reported and achieved significant results. With the maturity of the technology, UHRMS analysis of petroleum hydrocarbons will definitely bring richer molecular structure information to petrochemists and geochemists, and also provide more data support to the field of molecular refining and biomarker discovery. It is worth mentioning that characterization of target molecules by solving ionization and data processing problems is a scientific and systematic MS analytical method; the method can also guide the identification of compounds in other complex mixtures.

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