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Petroleomics: advanced molecular probe for petroleum heavy ends

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To look into complex mixtures of petroleum heavy ends at the molecular level, ultra high-resolution mass spectrometry, i.e. resolving power >50 000, is needed to resolve overlapping components for accurate determination of molecular composition of individual components. Recent progress in Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) incorporated with soft ionization techniques adaptable to liquid chromatography enables analysis of petroleum high ends, i.e., heavy oils, residua and asphaltenes. FT-ICR MS at the Future Fuels Institute of Florida State University and the National High Magnetic Field Laboratory (NHMFL) routinely provides 1 000 000 resolving power at 400 Da, with root mean square (rms) mass measurement accuracy between 30 and 500 ppb for 5000–30 000 identified species in a single mass spectrum. Phase correction of the detected ion signal increases resolving power 40–100%, improving mass accuracy up to twofold. Overlapping ionic species that differ in mass by as little as one electron mass (548 μDa) can be resolved. A database of more than 100 000 components of different elemental composition has been generated at NHMFL.

Keywords: FT-ICR MS; Future Fuels Institute; elemental composition; accurate mass measurement; ultra high-resolution mass spectrometry; FTMS

INTRODUCTION

Petroleum, along with coals and shale oils, is the most complex mixture in nature, containing thousands to millions of different components. Bulk properties, such as API gravity, boiling points, flash point, metal content, etc., are measured by a battery of physical testing methods. More sophisticated analytical instruments, such as vibrational spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, have been used to determine the functionality and gross structure of the mixture. However, to determine the composition of petroleum and its fractions at the molecular level for correlation and prediction of the properties/performance of the products as well as the processability of the feeds, mass spectrometry (MS) has become an indispensable method of choice. The combination with chromatography further enhances complex mixture analysis, particularly for the distribution of isomers.[1–3]

MS was initially exclusively used by physicists for studying basic properties of substances and for the discovery of elements and isotopes.[4] It evolved as a powerful chemical identification and measurement device for organic analysis during World War II when it was first used in the petroleum industry for the analysis of light ends, such as petroleum gases and naphtha. One important application was for product quality control and process improvement of aviation gasoline for allied forces to gain advantage in aerial dogfights. The earliest and most common method of ionization was electron-impact ionization (EI), which yields structural information from the molecular and characteristic fragment ions. However, in a complex mixture of heavy petroleum fractions, the multitude of closely related components precludes the use of characteristic ions for compound identification. This problem was partially resolved by coupling gas chromatography (GC) with MS (GC–MS) for petroleum distillates up to the high ends of vacuum gas oils (VGO) boiling at ~500 °C.[1] GC coupled with tandem mass spectrometry (GC–MS/MS) further expanded the differentiation of isomers and epimers, particularly for overlapping sterane biomarkers of geochemical significance.[2] However, for heavy petroleum fractions, the distribution of molecular ions generated by soft ionization methods, such as field ionization (FI) and field desorption (FD), provides an interpretable molecular profile of the corresponding neutral species present in the mixture.[4,5] The current challenge is to determine the elemental composition of the ionic species, particularly for isobaric components that are difficult to resolve (several different ionic species may lie underneath a single unresolved mass spectral peak), leading to better chemical understanding of refining processes and providing assessment and prediction of properties and performance of the feedstock and products.

DISCUSSION

History

Early mass spectrometers were based on a permanent magnet (or electromagnet) as the mass analyzer, with heated batch inlet system, EI as an ionization source and Faraday cage or electron multiplier as the detector.[4] Over the last 60–70 years, numerous methods of sample introduction, ionization, mass analyzers and detector systems have been developed. Figure 1 lists the most commonly used techniques over time with various combinations.

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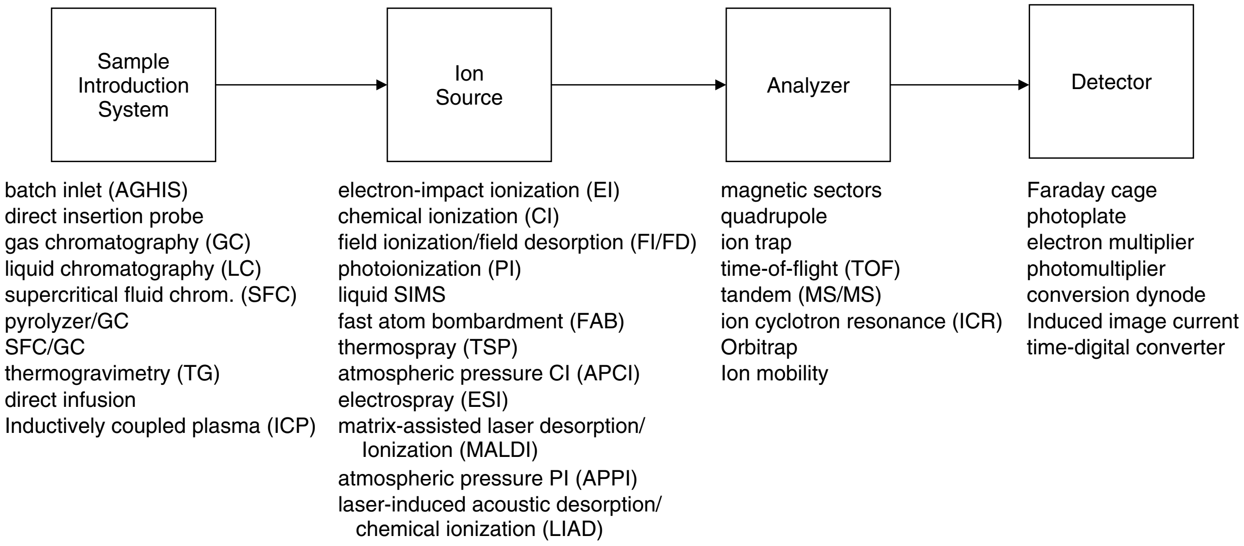


Figure 1. MS techniques developed for petroleum mass spectrometric analysis.

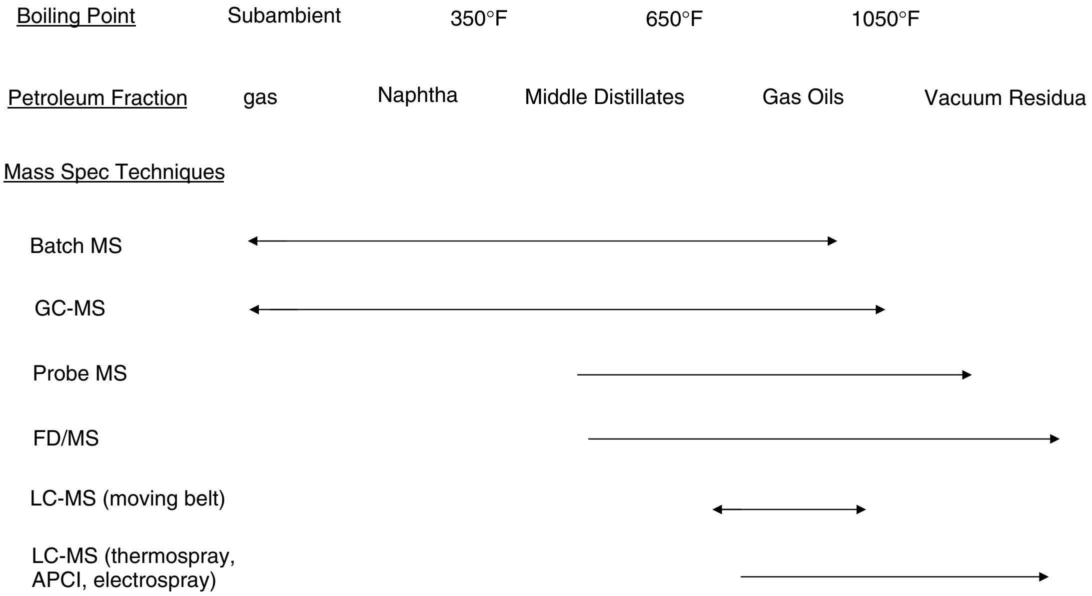
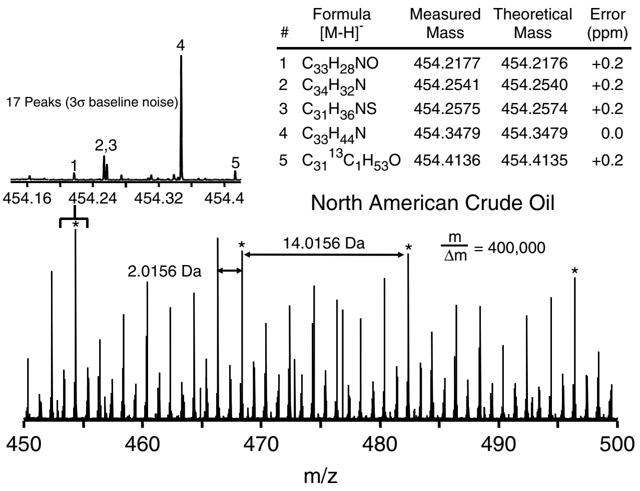


Figure 2. Types of sample introduction and ionization targeted for various petroleum fractions.

Front-end chromatographic separation reduces interference from isobaric components and provides differentiation of isomers.[1] Different ionization methods provide information on structure, molecular weight and functionality of the molecule. The type of mass analyzer used to separate ionic species determines resolving power, sensitivity and accuracy of the mass measurement. Finally, the detector type determines the final output of mass spectral recording. Modern mass spectrometers employ computerized data systems for instrument control and data acquisition. Different petroleum fractions require different combinations of mass spectrometric components for compositional analysis of the mixtures. Figure 2 shows different types of sample introduction and ionization used for the analysis of various petroleum fractions.

Due to the need to resolve isobaric components for quantitation and determination of elemental composition, double-focusing magnetic/electrostatic sector mass spectrometers were introduced.[6,7] However, after continuous improvement over many years, the double-focusing MS was limited to resolving power not much greater than 50 000 at low masses in static scans of narrow mass range. The resolving power drops significantly to <10 000 when the mass spectrometer is scanned from 50 to 500 Da, i.e. a decade, even at a very slow rate. Therefore, it was limited to resolution and accurate determination of component elemental compositions that differ by more than a few millidaltons (mDa or millimass units). Notably, the common and important 3.4 mDa split between $^{32}SH_4$ and $^{12}C_3$ could not be resolved in heavier components (i.e., boiling points greater than light distillates). High resolution could be achieved only at the expense of sensitivity. In addition, the resolution of isobaric peaks decreased rapidly with increasing mass.

The difficulty in resolving isobaric components of small mass difference is partially resolved by the use of a time-of-flight mass spectrometer (TOFMS) equipped with a reflectron.[5] A reflectron improves the accuracy of the mass measurement even though



#	Formula [M-H]⁻	Measured Mass	Theoretical Mass	Error (ppm)
1	$C_{33}H_{28}NO$	454.2177	454.2176	+0.2
2	$C_{34}H_{32}N$	454.2541	454.2540	+0.2
3	$C_{31}H_{36}NS$	454.2575	454.2574	+0.2
4	$C_{33}H_{44}N$	454.3479	454.3479	0.0
5	$C_{31}{}^{13}C_1H_{53}O$	454.4136	454.4135	+0.2

Figure 3. Elemental composition of a North American crude oil determined by the accurate mass measurement of FT-ICR MS operated at 400 000 resolving power.

the resolving power is only in thousands when no interfering ions are present. The resolving power required for overlapping mass peaks of different elemental compositions can be reduced by separating the interfering components responsible for the mass peak overlaps. The coupling of GC with reflectron-TOF-FIMS achieves the goal of measuring molecular ions with reasonable accuracy.[5] For higher boiling fractions, a direct insertion probe can be used to extend the ability of FIMS beyond the gas oil boiling range. Another method of analyzing high boiling fractions is field desorption (FD) in which the analyte is deposited onto a high field emitter without vaporization. However, uncertainty of mass assignment occurs frequently for TOFMS analysis of petroleum fractions beyond naphtha due to the limited resolving power of the mass spectrometer.

GC-TOFMS for accurate mass measurement works fairly well up to vacuum gas oil (VGO). Beyond VGO, the number of components with a given retention time (correlated with boiling point on a non-polar column) becomes very large. The highest boiling fractions (VGO and vacuum residua) tend to be more aromatic, more polar and heteroatom/metal-containing. Hence, selective ionization methods, electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI), may be able to ionize the majority of the components in these fractions.

A breakthrough in mass spectrometric resolving power came from the invention of Fourier-transform ion cyclotron resonance (FT-ICR) MS by Comisarow and Marshall.[8–10] FT-ICR MS for petroleum applications appeared in the early 1990s for ultra-high-resolution hydrocarbon analysis.[11,12] The inset table in Fig. 3 shows the elemental composition of five major ions in the inserted figure at upper left determined from the accurate masses measured by a 9.4 T FT-ICR MS operating at a resolving power of 400 000. The mass measurement errors in this example are 200 parts per billion (ppb) or better.

Much more reliable elemental composition determination is achieved by more accurate measurement of ionic masses. Continuous improvements in hardware and software made at the National High Magnetic Field Laboratory (NHMFL) allow routine acquisition of mass spectra with 1 000 000 resolving power at 400 Da and mass measurement accuracy between 30 and 500 ppb. An example will be given below.

Figure 4 shows the configurations of the 9.4 and 14.5 T FT-ICR mass spectrometers currently used at NHMFL.[13,14] Ions are guided by multipole ion optics into an external linear ion trap in which ions of a selected range of *m/z* pass through a set of transfer octopoles into the ICR cell. The number of trapped ions is carefully controlled to avoid the loss of resolving power due to shot-to-shot variation in ion–ion Coulombic interactions.

Detailed compositional differences

The advantages of accurate mass measurement at ultrahigh resolving power are demonstrated for a Chinese heavy crude oil and a South American heavy crude oil. Similar distributions appear in the broadband FT-ICR mass spectra of the two oils, as shown in Fig. 5.

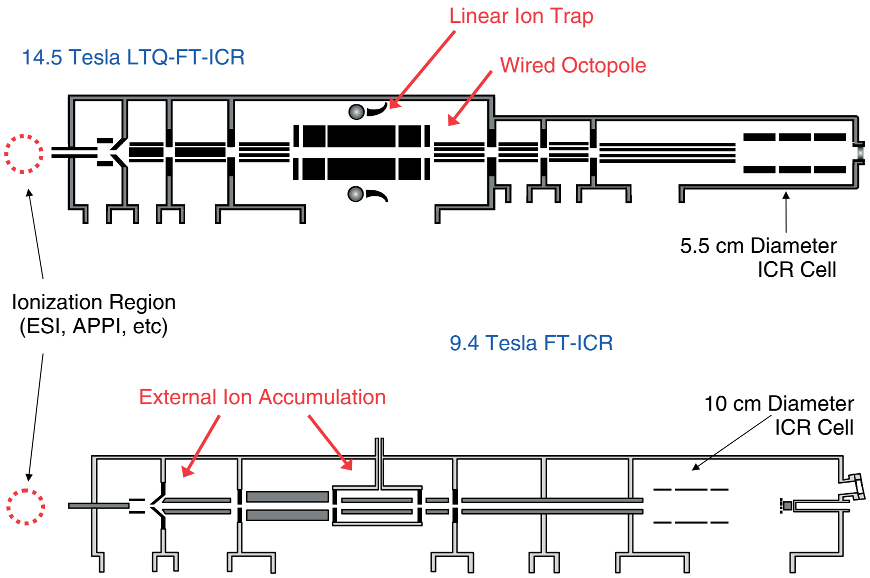


Figure 4. Configurations of NHMFL's 9.4 and 14.5 T FT-ICR mass spectrometers.

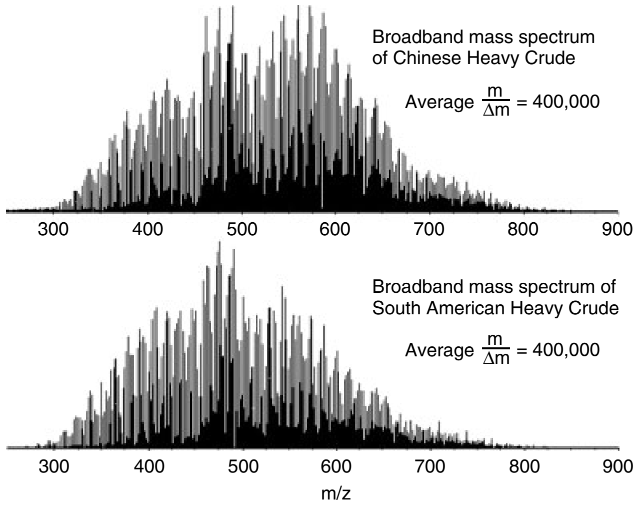


Figure 5. Similar broadband mass spectral patterns in FT-ICR mass spectra of Chinese (top) and South American (bottom) crude oils.

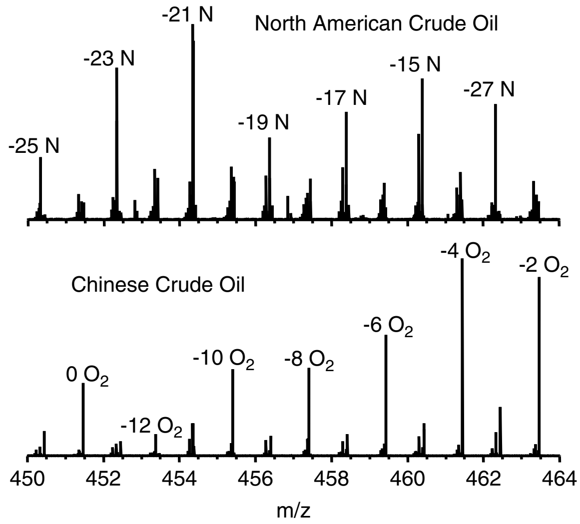


Figure 7. Zoom mass insets of negative ESI FT-ICR mass spectra of North American (top) and Chinese (bottom) crude oil in the mass range of 450–464 Da.

With ultrahigh resolving power shown in the zoom mass inset of Fig. 6, the differences in composition of these two crude oils are revealed. For example, a pair of nitrogen/oxygen-containing species (peaks 3 and 8) and a pair of nitrogen/sulfur-containing species (peaks 4 and 9) at 478 Da in South American crude oil are not present in Chinese crude oil.

More striking differences are found between negative ESI FT-ICR mass spectra of a North American crude oil and a Chinese crude oil, as shown in Fig. 7. These two crude oils yield similar broadband positive-ion ESI FT-ICR mass spectral patterns. In the same mass range of 450–464 Da as for negative ESI, however, North American crude oil contains mostly N_1 compounds whereas Chinese crude oil contains mostly O_2 species. Based on our previous studies of model compounds and other samples, the nitrogen species in North American crude oil are pyrrolic (five-ring nitrogen) compounds, whereas the O_2 species in Chinese crude oil are most likely naphthenic acids. Pyrrolic nitrogen compounds are of less concern than basic nitrogen compounds for the deactivation of hydroprocessing catalysts. However, the presence of the acidic species is of concern due to their corrosivity to the refining units.

Data visualization

The compound distribution based on elemental composition of a complex mixture is best represented by three-dimensional isoabundance plots. Figure 8 shows compound distributions for members of a single heteroatom class, S_1 (i.e. containing one sulfur in addition to carbons and hydrogens), for various distillation

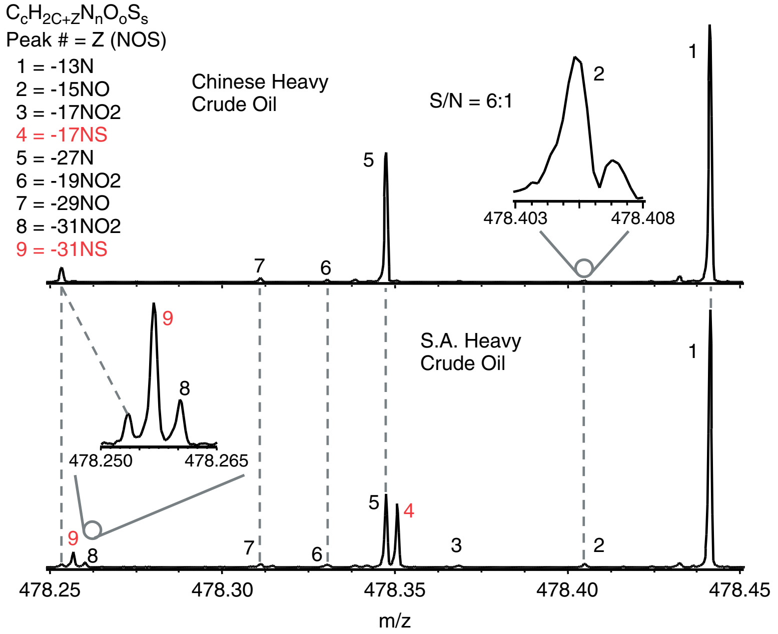


Figure 6. Zoom mass insets of ultra-high-resolution FT-ICR mass spectra of Chinese (top) and South American (bottom) crude oils at nominal mass 478 Da.

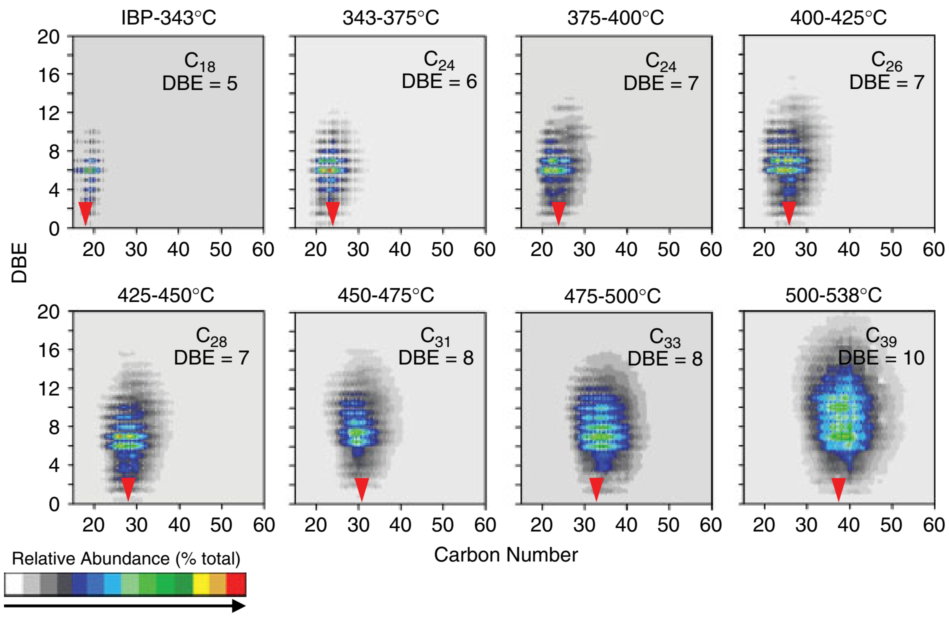


Figure 8. Double bond equivalents *versus* carbon number images for the S_1 class from various distillation cuts of an *Athabasca bitumen* heavy vacuum gas oil analyzed by FT-ICR MS by APPI doped with toluene (reproduction from Ref. [16]).

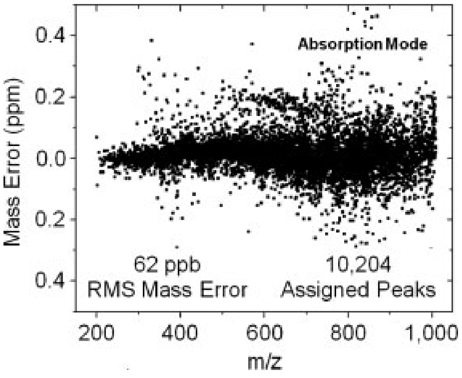


Figure 9. Mass error versus *m/z* for a North American light crude oil. Mass measurement errors are reduced by segmented calibration of narrow *m/z* sub-regions, incorporation of an abundance-dependent calibration term and absorption-mode data analysis (data provided by J. J. Savory).

cuts from an *Athabasca bitumen* heavy vacuum gas oil (HVGO) doped with toluene and analyzed by positive ion APPI FT-ICR MS.[15,16] In these isoabundance plots, double bond equivalents (DBE = number of rings plus double bonds to carbon) are plotted against carbon number, with color-coded relative abundance.[17] In general, DBE represents aromaticity and carbon number correlates with boiling point to some extent. The temperatures shown at the top of each plot are the boiling range for each individually analyzed distillate (relative abundance is scaled or normalized to the most abundant component for each distillate).

Accurate mass measurement with a walking mass calibration

The measured FT-ICR frequencies are typically converted to mass-to-charge ratio by the relation, $m/z = A/f + B/f^2$, in which f is the measured ICR frequency[18] and data are fitted across the entire mass spectrum by the use of a homologous series of peaks of known *m/z*. Recently, systematic mass errors were discovered by the analysis of residual mass error as a function of *m/z* and peak abundance.[19] Segmented calibration of narrow *m/z* sub-regions and incorporation of an additional calibration term to account for ion abundance-dependent frequency shift minimize the systematic error. The improved results are demonstrated in Fig. 9 for a North American light crude oil analyzed by positive-ion electrospray FT-ICR MS. For 10 204 assigned peaks, the root mean square (rms) error is 62 ppb, with 99% of the assigned masses within ±200 ppb of the 'true' masses calculated by summing the known elemental masses in the molecular formula.

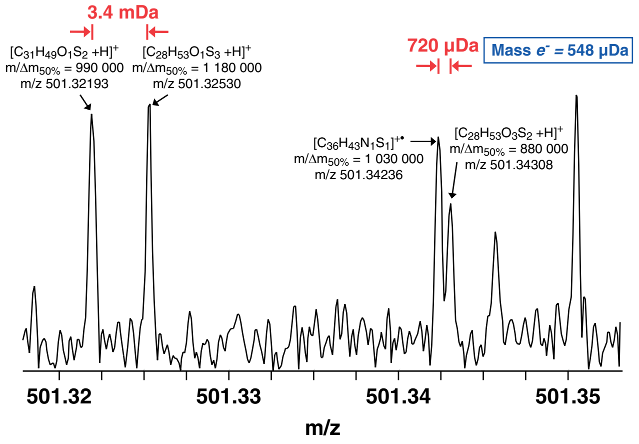


Figure 10. A doublet of a sulfur/nitrogen-containing compound and a sulfur/oxygen-containing compound at a resolving power sufficient to distinguish overlapping peaks corresponding to a mass difference close to that of an electron mass.

Absorption-mode data analysis

Phase correction of the measured FT-ICR signal allows data display in absorption mode, thereby increasing the resolving power by 40–100% (depending on peak shape) compared with conventional magnitude-mode display and improves mass

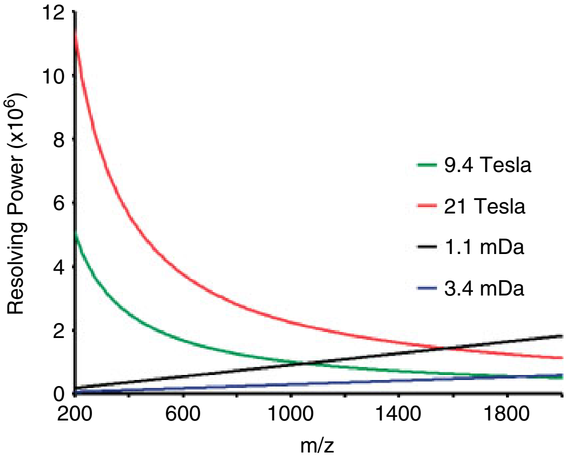


Figure 11. Attainable (required) FT-ICR mass resolving power as a function of mass-to-charge ratio (*m/z*) for a 6-s detection period and absorption-mode data processing at 9.4 T (green), a 6-s detection period and absorption-mode data processing at 21 T (red), for resolution of a 1.1-mDa split (C_4 *vs* $^{13}CSH_3$, black), or resolution of a 3.4-mDa split (C_3 *vs* SH_4, blue).

measurement accuracy up to twofold.[20] As a result of phase correction, two species with mass difference near the mass of a single electron, 548 μDa, can be resolved in a broadband mass spectrum containing thousands of components. Figure 10 shows an example of resolving two peaks, a sulfur/nitrogen-containing compound $C_{36}H_{43}N_1S_1$ at measured mass, 501.34236 Da, from a protonated peak of a sulfur/oxygen-containing compound, $C_{28}H_{53}O_3S_2$, at measured mass, 501.34308 Da. The difference in mass between the two components of the doublet is 720 μDa. Without adequate resolving power, the elemental composition of the unresolved peak would be easily mis-identified from the 'weight averaged' mass of the underlying species. Note that all of the major peaks shown have resolving power near or greater than 1 000 000.

21 T FT-ICR mass spectrometer

Recently, NHMFL received National Science Foundation (NSF) funding to build a 21-T FT-ICR mass spectrometer, with projected improvements in mass resolving power (2.2×), mass accuracy (5×) and dynamic range (5×) relative to current state-of-the-art performance at 9.4 T.[21] Fig. 11 shows achieved resolving power at 9.4 T (6-s detection period, absorption-mode data analysis)[20] with the projected improvement at 21 Tesla and also shows the resolving power required to differentiate two closely spaced mass doublets, $^{12}C_3$ *versus* SH_4 (3.4 mDa) and $^{12}C_4$ *versus* $^{13}CSH_3$ (1.1 mDa). Note that the projected resolving power at 21 T resolves the 1.1 mDa split at all masses up to 1600 Da, covering essentially all distillable petroleum species and much of the undistillable vacuum residua. The 21 T system is under development and is projected to be operational in 2013.

CONCLUSION

Recent developments in FT-ICR MS, including ICR cell ion population control, access to absorption mode display, ion abundance-adjusted calibration and incorporation with soft ionization techniques enable us to probe into petroleum high ends: heavy oils, residua, asphaltenes, etc., with high mass measurement accuracy for the determination of elemental composition of individual molecular species.[22–24] A huge data base has been generated at NHMFL. For example, as many as 244 components of the same single nominal mass have been resolved at a resolving power of more than 1 300 000.[25] More than 100 000 components of different elemental compositions have been identified and collected from the distillates of more than 50 crudes oils by ESI, APCI and APPI FT-ICR MS. The database contains mostly aromatic, acidic, basic and porphyrinic components of petroleum heavy ends, spanning a mass range of 200–1200 Da. It can be used for correlating or correcting the elemental composition determined by lower resolution MS. The next challenge will be in data mining, or informatics, to correlate the composition with properties and performance of the complex mixtures.

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