Petroleum Analysis by Orbitrap Elite Mass Spectrometer with Multiple Ionization Methods

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Overview

Purpose: A brief comparison of three different ionization methods was carried out on the ultra-high resolution mass spectrometer (Thermo Scientific[™] Orbitrap Elite[™] Hybrid Ion Trap-Orbitrap MS) for petroleum analysis. A comparative analysis was made on ionization efficiency, ion distributions, and ionization competition. The three ionization method are electrospray (ESI), atmosphere pressure chemical ionization (APCI) and atmosphere pressure photo ionization (APPI).

Methods: The extracted petroleum samples were directly injected by syringe pump into the mass spectrometer. Three different ionization sources (ESI, APCI, APPI) were used and the data were collected and analyzed by Thermo Scientific[™] Xcalibur software.

Results: APPI is the most promising ionization method for petroleum analysis because nonpolar compounds can be ionized more efficiently than by APCI and ESI. The absence of radical ions in the APPI method enables efficient data processing and formula prediction.

Introduction

The mass spectrometer has proven itself in the petroleum industry as an essential analytical and process control instrument. The instrument is touted as a means to analyze and separate crude oil and petroleum samples that contain complicated hydrocarbons which have very similar masses. Because the organic composition of the polar components of petroleum is so complex, its characterization was until recently limited to bulk properties (such as color, viscosity and density) until the emergence of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) which offers the highest available, mass resolving power, and mass accuracy. The need to volatilize the sample limited the obtainable molecular weight range (especially for heteroatom containing species). Since electron impact ionization produced extensive fragmentation (especially of alkyl chains), electrospray ionization (ESI) is a soft ionization technique and more useful to characterize polar compounds. But ESI has the limited reach for petroleum analysis since petroleum crude oils typically contain 90% hydrocarbons, nonpolar compounds.

An ion trap based hybrid mass spectrometer (Orbitrap Elite MS) , with sufficiently high mass resolving power (m/ Δ m 240,000 @ m/z 400) and a m/z range up to 2000 Da was utilized to analyze petroleum samples extracted from crude oil which were injected directly by syringe. Three ionization methods, electrospray ionization (ESI), atmosphere pressure chemical ionization (APCI) and atmosphere pressure photo ionization (APPI) were used and ion distribution and polarity of compounds were studied. Various MS scan modes and ion transfer optical potentials were investigated to determine the approaches that provided high quality information with a wide m/z range.

Methods

Sample Preparation

Samples: The extracted samples from refinery pipelines supplied by Taxon Bioscience

Samples were dissolved into 1 mg/mL by Toluene, then diluted to 250μ g/mL by different solvent based on the ionization method prior to direct injection.

Dilution solvent

- For APPI and APCI: Toluene
- For ESI: 1% Formic Acid and 5% DCM in 50:50 Toluene:Methanol

Mass Spectrometry

Ionization Source:

Electrospray (HESI II)

Atmosphere Pressure Chemical Ionization (APCI)

Atmosphere Pressure Photo ionization (APPI)

Ion Trap and Orbitrap Elite (Mass Resolution = 240,000)

Positive scan

AGC: 5E4 - 5E6

Mass Spectrum (average of 100-200 scans)

Data Collection and Analysis

Xcalibur software

Results

Ionization Methods

Three different ionization techniques, ESI, APCI and APPI, are available in the lon Max ion source platform. The complementary nature of the application of each ionization method is summarized in Figure 1, which shows the APPI has more broader application than APCI, typically for the non-polar compounds. The advantage of using APPI on non-polar compounds has recently been accepted for petroleum analysis.

FIGURE 1. The targeted compounds of three different ionization techniques with regard to the polarity and molecular weight of analytes. (Ref.1)



The ionization mechanism of ESI, APCI and APPI was illustrated in Figure 2. APPI ion source uses a Krypton lamp, which emits photons at 10.0 eV and 10.6 eV. Photon energy from Krypton lamp is sufficient to ionize most analytes, and is lower than the ionization potentials of common reversed-phase solvents such as water, methanol, and acetonitrile.

FIGURE 2. The ionization mechanism of (a) ESI source (HESI II), (b) APCI, and (c) APPI. Positive charge (protonation) is added by potential through (a) ESI probe, (b) corona discharge needle, (c) Krypton lamp. (Ref. 2)



Optimization of Orbitrap Elite MS

Thermo Scientific Orbitrap Elite MS is a high performance hybrid mass spectrometer combining the use of an Orbitrap analyzer with a linear ion trap. The DC potential of the optic lens in the first vacuum stage can be optimized to the ion distribution of petroleum compounds which typically cover the mass range 200 – 1000 m/z. By optimizing the DC potential, the kinetic energy of ions was controlled, which means the ions could be accelerated or slowed down as appropriate.

In this study, the setting of 00-offset in Figure 3 was observed to have a significant impact on the intensity of ions from petroleum. Ions have the same velocity from the vacuum drop in the first vacuum stage after the ion beam passes through the transfer tube. The increasing of the 00-offset potential slows down the ions, allowing the low m/z ions to be prevented from entering the linear trap mass analyzer and Orbitrap mass analyzer.

FIGURE 3. Schematic of the Orbitrap Elite Hybrid MS. The 00-offset lens is located between S-Lens and square quadrupole. (Ref. 3)



FIGURE 4. The impact of 00-offset potential on the ion distribution of petroleum sample. APCI was used to ionize sample and linear ion trap was the mass analyzer.



As shown in Figure 4, the adjustment of the 00-offset potential from 0 to 6 V led to an intensity decrease for low m/z ions and the accumulation of high m/z ions. The access of the 00-offset is important for petroleum analysis because it can control the low m/z ions entering the mass analyzer, thereby allowing the capacity of analyzer (ion trap and/or Orbitrap analyzer) to be fully used by the targeted high m/z ions. As shown in Figure 4, 00-offset was optimized at 6 and used for data collection in experiments.

In order to obtain optimal performance in the trapping device, the ion population needs to be kept within a certain range. Therefore, a procedure is needed to predict the appropriate accumulation time. Automatic control of the number of ions in the Orbitrap analyzer is achieved by measuring the total ion charge from a pre-scan and by calculating the ion injection time. Automatic Gain Control (AGC[™]) ensures that the ion trap is always filled with the optimum number of ions for any scan type.

As shown in Figure 5, the AGC optimization was studied along with ion distribution. The AGC setting was found to have a significant impact on ion distribution. Although the higher AGC setting allowed more ions to enter the Orbitrap mass analyzer, 2.9E6 (AGC: 5E6) vs 1.52E6 (AGC: 5E5) vs 1.80E5 (AGC: 5E4), the ion distribution of the petroleum sample was poor because more low m/z ions entered the Orbitrap mass analyzer. To maximize a broad m/z range distribution the low AGC setting of 5E4 is preferred. The package of ions is collected in the ion trap and the number of ions was controlled by AGC. The ion package is send to C-Trap and cooled down, focused and sent to the Orbitrap analyzer for analysis. C-trap, like all RF devices, has an m/z dependent potential well to trap ions. So if a mix of ions is sent into C-trap, the lower m/z ions are trapped by a deeper well and the high m/z ions are trapped by a shallower well. If a mix of ions fills up C-trap such that space charge starts to be of the same order as the well depth, then the high m/z ions will be spilled out firstly. By reducing the number of ions via setting a low AGC value, more high m/z ions could be obtained on spectrum.

FIGURE 5. The impact of Orbitrap MS AGC setting on the ion distribution of petroleum sample. APCI was used to ionize sample and Orbitrap was the mass analyzer. 00-offset was set at 6.



Comparison of ESI, APCI and APPI

With the same mass spec settings (00-offset: 6 and AGC: 5E4), three different ionization techniques were studied and compared.

As shown in Figure 6 and 7, the ion distributions were observed from the three ionization techniques. Briefly, ESI is much more efficient for polar molecules and typically ionized many highly polar compound, heteroatom-containing components (NnOoSs) of the petroleum sample. APCI shows the capability of ionizing the petroleum components, both polar and non-polar compounds, but mainly focusing on nonpolar compounds. APPI gives access to many of the remaining 90% of petroleum components – hydrocarbon compounds including benzo- and dibenzothiophenes, furans, cycloalkanes, and polycyclic aromatic hydrocarbons (PAHs) not observed by ESI.

FIGURE 6. The ion distribution of petroleum sample ionized by ESI, APCI and APPI separately. Orbitrap was the mass analyzer with the AGC setting of 5E4 and the 00-offset of 6.



FIGURE 7. The mass spectrum of petroleum sample over 549.0 – 552.0 m/z ionized by ESI, APCI and APPI.



FIGURE 8. The mass spectrum of petroleum sample over 600 – 650 m/z ionized by APCI and APPI. The ionized ions from APCI and APPI are identical.



As shown in Figure 8, APCI and APPI produced identical ions from 600 – 650 m/z which indicated all ions generated by APPI are protonated ions like those from APCI and that radical ions were not generated by APPI. The absence of radical ions significantly reduced the workload of predicting the formula of each ions.

Conclusion

The performance of ultrahigh mass-resolution Orbitrap Elite mass spectrometer and three ionization techniques on the petroleum analysis were investigated in this study.

- The adjustment on 00-offset lens and AGC is needed to get the correct ion distribution from petroleum samples.
- The compounds ionized by ESI are the polar compounds having a relatively low molecular mass.
- The nonpolar compounds in petroleum samples can be ionized by APCI and APPI, and APPI shows an advantage over APCI in ionizing the large nonpolar compounds.
- Only protonated ions are generated from APPI and radical ions were not observed, which simplified the data processing and formula prediction.

References

- 1. Product specification of APPI/APCI combination ion source, http://www.thermoscientific.fr/com/cda/product/detail/0,1055,19246,00.html
- 2. Application note 347: Mechanism of [M+H]+ Formation in Atmospheric Pressure Photoionization Mass Spectrometry, Thermo Fisher Scientific Inc.

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