EVALUATING ORBITRAP MASS SPECTROMETRY FOR GEOCHEMICAL CHARACTERIZATION OF CRUDE OILS

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Introduction

Traditionally, geochemical characterization of crude oil is based on bulk analyses, gas and liquid chromatography and mass spectrometry analysis of low polarity fractions (saturated and aromatic). Even in lower proportion compared with the hydrocarbon fractions of crude oil, the detailed characterization of NSO polar fraction can give to geochemists important insights about origin and alteration of petroleum. However, for a long time, the NSO fraction was poorly understood due to the analytical challenges that arise from its polarity. With the advances of the ultra-high-resolution mass spectrometry (UHR MS), now, a myriad of NSO polar compounds are routinely identified and assigned with unmatched mass resolution and accuracy from crude oil samples.

Typically in petroleomics, UHR MS is performed using Fourier Transform Ion Cyclotron Mass spectrometry (FT-ICR MS). Recently, a new type and less expensive of high-resolution mass spectrometer were introduced, the Orbitrap. Even showing inferior resolving power compared with modern FT-ICR, the Orbitrap is suitable for analysis of crude oil fractions.

A new procedure - known as Hetero-MPLC - allows the separation of the NSO fraction into six well-defined polar fractions (acidic, basic, low-polarity, medium-polarity, intermediary-polarity, and high-polarity NSO compounds fractions) by medium pressure liquid chromatography (MPLC) (Willsch et al., 1997). As H-MPLC reduce the inherent complexity of crude oil samples, here we fractionated seven crude oil and analyzed their high-polarity fractions by negative electrospray (ESI) coupled to Orbitrap and 7 T FT-ICR MS. Besides, we explore the question of whether the NSO profile obtained from Orbitrap and FT-ICR MS data combining with traditional geochemical biomarkers, can be used to classify crude oils according to its thermal maturity and origin in the same way.

Results and Discussion

Even exhibiting inferior resolving power, Orbitrap Q-Exactive was able to analyze the H-MPLC fractions in a similar way of FT-ICR MS. In general, the mass spectra show broadband profiles from m/z 200 - 1200 and illustrate typical crude oil profiles frequently obtained in UHR MS analyzes. It is important to note that each fraction has a very distinct profile, indicating that H-MPLC fractionation produces well-defined fractions.

The maturity trend of the seven-crude oil (A-G) is easily highlighted when a ternary diagram using the DBE (double bond equivalent) series 5, 7 and 14 of O2 class from high-polarity fractions is plotted. The variations between of three DBE series for O2 class stress a significant linear relationship with thermal maturity expressed by Ts/(Ts +Tm) ratio, as displayed in Fig. 1. These results are compared to the 7 T FT-ICR MS analysis of the same samples. Conclusions obtained from the Orbitrap Q-Exactive are essentially the same as those obtained from the FT-ICR measurements.
Fig 1. Ternary diagram for DBE 5, 7 and 14 of class O2 obtained from the ESI (-) analysis of the high-polarity fraction of seven crude oils performed by Orbitrap Q-Exactive (left) and FT-ICR MS (right).

To access the depositional environmental of crude oils we used an approach described recently by Rocha et al. (2018). This approach consists of plotting the relative amounts of Nx, Ox, and NyOx, in the ternary diagram. For both analyzers, Orbitrap Q-Exactive and FT-ICR MS, the samples are correctly classified following their depositional environmental (lacustrine or marine). The results suggest that the distribution of polar compounds could be related to their original content of organic matter that was deposited under different environmental conditions.

Conclusions

Ultra-high resolution mass spectrometry which measures thousands of compounds from petroleum is typically performed using FT-ICR, which by far has the highest resolving power available in mass spectrometry. However, FT-ICR MS is cost-prohibit for many laboratories. On other hands, Orbitrap mass spectrometry emerged with the promising potential to measure chemical compositional to relative complex mixtures. Here, we demonstrated that Orbitrap, even with lower resolving power, could be used for geochemical assessment of crude oil regarding thermal maturity and depositional environmental.

References


