PETROLEOMICS BY ESI(-) FT-ICR MS AS A TOOL TO ASSESS SOURCE AND THERMAL MATURITY OF BRAZILIAN CRUDE OILS

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Introduction

Geochemical assessments of crude oil samples are typically carried out to identify their origins (depositional environments), thermal evolution level of their source rocks and to evaluate possible post-accumulation alterations such as biodegradation. Crude oils consist predominantly of hydrocarbon compounds, comprising paraffin, cycloalkanes, and aromatics (~85%), followed by polar compounds (~15%), such as nitrogen-, sulfur-, oxygen-containing compounds (NSO compounds). Even though NSO compounds are present in smaller concentrations, they can be used to assess the mechanisms of generation, migration, and alteration of crude oils.

The ultrahigh mass resolution and accuracy of FT-ICR MS are ideal for the analysis of complex heteroatomic compounds, allowing for the assignment of detected masses to chemical formulas (Marshall et al., 2007). When coupled with the electrospray ionization technique (ESI) the detailed composition of selective polar species can be resolved from the pseudo-molecular ions produced (Qian et al., 2001). Ultrahigh resolution mass spectrometry has characterized thousands of hydrocarbon and polar species in petroleum and related products.

In this study, we show the application of ESI(-) FT-ICR MS results in association with traditional geochemical parameters to evaluate thermal maturity, source input and depositional environments from oil samples.

Results and Discussion

Using ESI FT-ICR MS in the negative mode, we track the changes on polar compounds controlled by thermal maturity. This technique allowed us to visualize and assess compositional variability for a sub-group of heteroatomic compounds. Sulfur-containing compounds are destroyed with ongoing maturity, and oxygen-containing compounds progressively decrease due to decarboxylation and dehydration reactions. In contrast, nitrogen-containing compounds increase at high maturity levels. DBE (double bound equivalent) values increase, expressing the aromaticity and condensation of their constituents. The carbon number distribution shifts progressively toward the lower carbon number region, which indicates an enrichment of lighter compounds in the expelled oils and the occurrence of substantially dealkylated species in the polar fraction as maturity increases. The carbon number distribution of DBE’s 5 and 6 for the O2 class (related to steranoic and hopanoic acids respectively) decrease with ongoing maturity. The maturity-related changes of the acidic O2 compounds for the expelled oil samples enable us to create six regressions to be used as new maturity parameters covering the full range of oil generation (Rocha et al., 2018a).

Lacustrine-derived oils seems to be enriched in Nx compounds, while the dominance of Ox compounds is observed in marine-derived oils. The most abundant class detected in crude oils
studied was N1, followed by O1, O2, and N1O2 with remarkable differences between marine and lacustrine oils distribution. Kerogen type plays an important role in the heteroatomic profile of the crude oils analyzed. Organic matter from kerogen Type I has high H/C atomic ratio and low oxygen content, while organic matter from Type II kerogen contains higher O/C atomic ratio and high abundance of carboxylic acid groups and ester groups (Vandenbroucke and Largeau, 2007). Such differences result in a clear separation based on polar species found in marine and lacustrine oils generated from Type I and Type II kerogens. Oil-oil correlations show significant differences between the oils, basically on DBE distributions of selected heteroatomic classes of crude oils evaluated, allowing a quick geochemical assessment of their origin (Rocha et al., 2018b).

Conclusions

The use of negative ESI FT-ICRMS technique is a reliable and valuable tool for performing geochemical assessments from NSO compounds pattern. In association with geochemical traditional tools, it is possible to achieve a full comprehension of crude oil composition, besides obtaining information about origin and maturity parameters.

References


