OVERVIEW OF THE CHEILANTHANE STEREOISOMER SERIES FROM BRAZILIAN PRE-SALT AND POST-SALT CRUDE OILS BY GC/QqQ-MS AND GC×GC-TOFMS

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Introduction

The Brazilian marginal basins are the result of complex geological events associated with the opening of the South Atlantic Ocean. Because of that, there is a great variability in oil composition among them, making the crude oil characterization for exploration purposes difficult. A deep understanding of crude oil potential demands a detailed characterization of its constituents and this challenging task involves different analytical techniques. A couple of oils from the pre-salt and post-salt section from Campos Basin, and a single crude oil from the pre-salt layer of Santos Basin, both SE Brazil, were characterized by comprehensive two-dimensional gas chromatography (GC×GC)-time of flight mass spectrometry (TOFMS) and gas chromatography coupled to triple quadrupole mass spectrometry (GC/QqQ-MS) focusing on the cheilanthane series. The cheilanthane tricyclic terpanes abundance and distribution pattern can provide valuable information to assess organic matter input, the extent of thermal maturity, correlation of crude oils and source-rock extracts and biodegradation evaluation (Peters et al., 2005). At the present, there is no established specific origin and unequivocal depositional condition enhancing the abundance of tricyclic terpanes in petroleum. Recent studies (Dutta et al., 2006) showed that Tasmanites are not the only source of tricyclic terpanes and its origin is still controversial. Another issue is the mixtures of stereoisomers, which have similar structures, generating coelutions and similar mass spectral fragmentations. The objective was applying advanced chromatographic techniques trying to elucidate the extended cheilanthane isomers to corroborate with the thermal maturity parameters and for further geochemical application. It is important to highlight that there are only few studies regarding geochemical aspects on Brazilian pre-salt oils.

Results

Tricyclic terpanes were detected from C_{19} to C_{40} by GC×GC-TOFMS and from C_{20} to C_{46} by GC/QqQ-MS on single reaction monitoring (Figure 1). The extended tricyclic terpanes diastereoisomers could be detected on the GC/QqQ-MS in contrast with the GC×GC due to chromatographic method differences. For the compounds from C_{20} to C_{24}, 4 isomers can occur with isomerization (Chicarelli et al., 1988). Notably, some isomers were detected easily on the GC×GC when compared to GC/QqQ-MS. The C_{25}–C_{29} tricyclic terpanes are known to occur as diastereomeric doublet peaks on m/z 191 mass chromatograms, which arise by epimerization at C-22 in the side chain (Peters et al., 2005). New epimerizations can occur with increasing carbon side chain, therefore increasing the number of asymmetric centers. The GC/QqQ-MS chromatograms for the ion transitions [M^{+*}→191] corresponding the tricyclic terpanes C_{22}, C_{27}, C_{32}, C_{37} and C_{42}, known for its poor chromatographic resolution, showed higher intensity for the following tricyclic terpanes [M-15]^+ than for themselves. An interesting data was the detection of 6 peaks on the C27 transition [374→191] for all samples. Previous data from these samples (Barra et al., 2019) indicated the tricyclic terpanes are reflecting the maturity degree and the sample from post-salt is the least thermally evolved. All samples were pointed as lacustrine source of organic matter and the tricyclic terpanes did not reflect the different facies.
Conclusions

GC×GC could easily identify the tricyclic terpanes homologous from C20 to C24 than GC/QqQ-MS. In contrast, the GC/QqQ-MS was able to detect 6 peaks for the tricyclic terpane C27 transition compared to GC×GC.

References


