i.d., 0.1 μm df) was used as the second-dimension column (2D). The selected samples were pre-fractionated to saturated hydrocarbon and aromatic fractions. Due to the high content of n-alkanes, some of the saturated fractions were treated with urea to achieve the branched and cyclic hydrocarbon fraction (B/C). The saturated hydrocarbon, B/C and aromatic fractions were dissolved in dichloromethane before chromatographic analysis.

Results and Discussion

The use of a powerful analytical technique such as GC×GC-TOFMS accesses new opportunities for geochemical data analysis, which may be considered as a step towards a High Resolution Molecular Organic Geochemistry. Recent results from our group have shown how non-conventional compounds are important to differentiate paleoenvironment depositional conditions. In fact, in a group of 20 oils from the same basin, minor differences in the GC×GC-TOFMS data analysis have been observed (Casilli et al., 2014). In another example, Kiepper et al. (2014) differentiated samples with 3β- and 2α-methyl-hopane series (as suggested by Farrimond et al., 2004) and onocerane isomers, present at trace level, as proxies of the different depositional paleoenvironment.

In this work, GC×GC-TOFMS has been used as an important tool in biomarker investigation, paving the path for a true HRMOG approach. The oils investigated allowed the characterization of different depositional paleoenvironment and their mixtures. The biomarker ratios for H30/Stααααα (S+R), Tr26/Tr and % 3βMH31/H30 are, respectively: Oil A: 9, 1.74, 2; Oil B:12, 1.48, 2; Oil C: 8.99, 1.42, 1.93; Oil D: 7.53, 1.33, 1.87; Oil E: 9.3, 1.97, 1.73; Oil F: 3.59, 1.3, 1.47; Oil G: 2.36, 1.21, 1.72; Oil H: 1.89, 0.9, 0.18; Oil I: 0.79, 0.82, 0.66; Oil J: 1.01, 1.03, 0; Oil K: 1.57, 1.25, 0; Oil L: 1.68, 1.41, 0.55. Plotting these values, the classification in three depositional paleoenvironments was not clearly obtained by conventional parameters (H30/Stααααα (S+R) vs Tr26/Tr) (Figure 1a). On the other hand, the oils have been easily differentiated by combining a non-conventional parameter (%3β-MH31/H30) and a conventional one (H30/Stααααα (S+R)) (Figure 1b).

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Another HRMOG example is related to the separation of C30 24-n-propylenes - derived from 24-n-propylcholesterols, which are biosynthesized by sea water Cryrophyte algae (Peters et al., 2005) -, from interferents like the C30 4-methyl-24-ethylcholestanes.

The presence of these compounds in crude oil is an important tool to identify marine organic material input in the source rock. Positive identification of the 24-n-propylcholestanes by GC-MS/MS in MRM mode (414>217) can be difficult due to low concentrations and coelutions with C30 4-methyl steranes. On the contrary, as reported in Figure 2, the GC×GC-TOFMS permitted its separation and reliable identification.

**Figure 2.** EIC m/z 414 showing the separation of 24-alkylcholestanes and mass spectra of 4α-methyl-24-ethylcholestone (a) and 24-n-propylenes (b).

**Conclusions**
GC×GC-TOFMS allowed the separation and identification of non-conventional biomarkers, besides the usual ones. It is evident the outstanding contribution of non-conventional compound for the classification of Brazilian oils from different depositional paleoenvironment.

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**References**

