

## APPLICATION OF GC×GC-TOFMS TO BIOMARKER CHARACTERIZATION IN OILS FROM DIFFERENTS BASINS.

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### Introduction

Oil geochemistry corresponds to a fundamental issue of any regional exploration for new frontiers and production program. It can be used to determine the number of sources in a basin and their respective stratigraphic and regional distribution, source, age, lithology, depositional environment (marine, non-marine, lacustrine) and thermal maturity (Peters et al, 2005).

The variety of chemical classes present in oils, as well as possible co-elutions in conventional chromatographic separations, makes the identification of biomarkers a difficult task (Aguar et al, 2010). Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry coupled to mass spectrometry (GC×GC-TOFMS) proved to be a powerful technique for the separation of complex matrices and is ideal for characterizing compounds with similar chemical structures. The main advantage of GC×GC is an enormous increase in the resolving power when compared to monodimensional GC. Additionally, different well-ordered groups that are characterized by distinct patterns can be distinguished in the bidimensional plane, providing important information about the chemical structures of the molecules of interest (Silva et al, 2014).

The aim of this work is to analyze different oils using GC×GC-TOFMS, to solve chromatographic coelution, processing the full mass spectra (TOFMS) and the analysis of unusual compounds that are typically encountered at trace levels in petroleum samples.

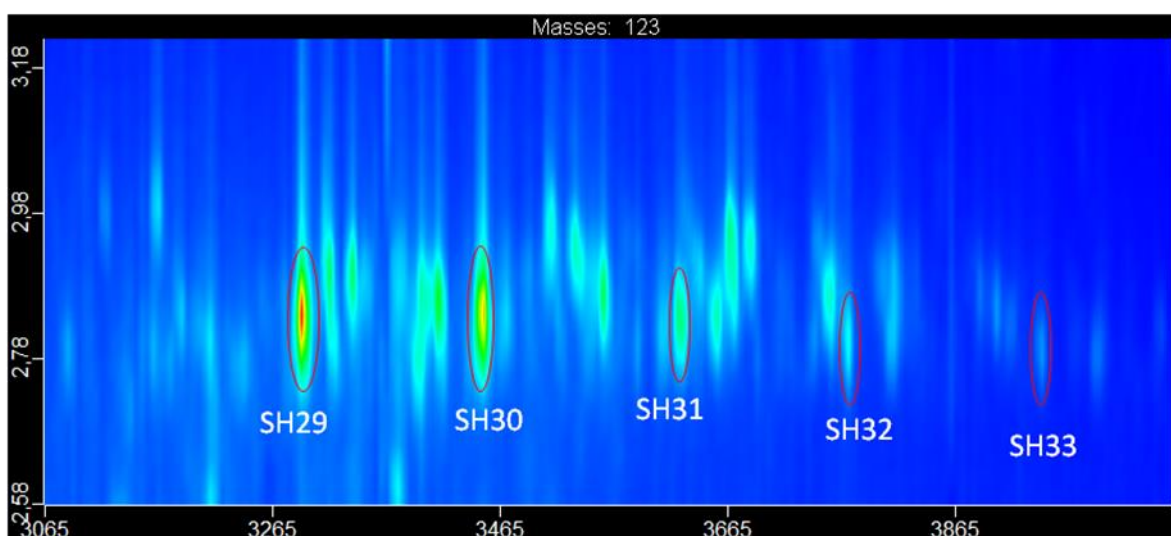
### Results

Seven crude oil samples (Table 1) from different basins from Mexico and Brazil were selected based on their different sources and biodegradation levels in order to study the molecular composition changes for different depositional paleoenvironments. Samples were evaluate from extracted ion chromatograms (EIC) using *m/z* 191 (tri-, tetra- and pentacyclic terpanes), *m/z* 205 (methylated hopanes), *m/z* 217 (steranes) and *m/z* 123 (secohopanes).

Table 1. Sample details, including sample code, basins, field and location for the oil samples investigated.

Samples	Basin	Field	Location
KUF-1 (83D)	Sonda de Campeche	Ku-Maloob-Zaap	Gulf of Mexico
KUC (1297)	Sonda de Campeche	Ku-Maloob-Zaap	Gulf of Mexico
Zaap D (10)	Sonda de Campeche	Ku-Maloob-Zaap	Gulf of Mexico
Sol-AM	Solimões	Urucu River	Amazon-Brazil
Jub-CAM	Campos Mar BC-60	Jubarte	Espírito Santo-Brazil
Cac-CAM	Campos Mar BC-61	Cachalote	Espírito Santo-Brazil
Pot-CE	Potiguar Mar	Carauna	Ceará – Brazil

The oil Cac-CAM is severely biodegraded, as shown by a lack of normal alkanes and an increased relative concentration of unresolved complex mixtures (UCM). The others oils has a good preservation from biodegradation. A C<sub>24</sub> tetracyclic terpane and a serie of tricyclic and pentacyclic terpane were detected. Gammacerane (Gam) was detected almost all samples analysed. Moreover, moretanes, secohopanes and steranes series were identifield. The secohopanes (Figure 1) are derived from the hopane or moretane series via the opening of the C-ring during the early stages of maturation and degradation of hydrocarbons (Peters and Moldowan, 1993). These compounds are highly resistant to biodegradation. There are six possible configurations because of the stereochemistry of carbons 8 and 14, but all six secohopane configurations were not observed. This was most likely due to coelution combined with the low concentrations of these compounds in the oils. In this study, it was possible to identify secohopanes C<sub>27</sub> to C<sub>33</sub>, with the highest concentrations observed in secohopanes C<sub>29</sub>, C<sub>30</sub> and C<sub>31</sub>. Unusual compounds such as hopenes were detected in samples from Mexico.



**Figure 1.** Secohopanes identifield in the samples.

## References

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