APPLICATION OF MODERN ANALYTICAL TECHNIQUE GCxGC/TOFMS IN OIL SAMPLES OF THE GULF OF MEXICO.

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The complexity of the petroleum sample, with its numerous compounds, constitutes a big challenge for chemical composition investigation. The two-dimensional gas chromatography coupled to the time-of-flight mass spectrometer (GCxGC/TOFMS) is an analytical tool with a remarkable capability for resolving complex samples. This approach has been used to provide a more comprehensive geochemical characterization of the Gulf of Mexico oils. In addition, it was already used in the search and evaluation of unusual compounds, which are usually found at reduced concentrations in the samples, specifically in the fraction of saturated hydrocarbons. The geochemical evidence and distribution of the biomarkers provide criteria to distinguish rocks deposited in different environments, evaluating their origin and maturation. However, the possibility of collision is considered a problem, making the identification of some biomarkers a difficult task that is solved with the use of two-dimensional chromatography.

Analyses by GC × GC-TOFMS were performed on a Pegasus 4D system (Leco, St. Joseph, MI, USA), composed by an Agilent 6890 GC (Palo Alto, CA, USA) equipped with a secondary oven and a non-moving quad-jet dual-stage modulator and a Pegasus III (Leco, St. Joseph, MI, USA) time-of-flight mass spectrometer. A DB-5 column, 5%-phenyl-95%-methylsiloxane (30 m × 0.25 mm i.d., 0.25 mm df) was used as the first dimension column (1D). A BPX-50 column, 50%-phenyl-50%-methylsiloxane (1.5 m × 0.1 mm i.d., 0.1µm df) was used as the second dimension column (2D). Samples were evaluated by extracted ion chromatograms (EIC) using m/z 191 (hopanes, Ts and Tm), 217 and 218 (steranes), m/z 205 (methyl-hopanes), m/z 123 (seco-hopanes), based on Peters et al. (2005).

The ratio between triterpane (Trn), Tr24/Tr21, ranged from 1.59 to 0.69 and Tr26/Tr25 below 1 (0.44 to 0.78) suggesting contribution of marine organic material. Ratio C27 22,29,30-trisnorhopane/C27 22,29,30-trisnorhopane (Ts/Tm) less than 1, a deposition of organic matter in an anoxic environment in salt lakes, evaporites or marine carbonates. The correlation between the Hopanes (H29), H35/H34 versus H29/H30, of Guzmán-Vega and Mello, (1999) their geological ages are distributed between the lower Cretaceous and the Upper Jurassic. Peters et al. (2005) present values greater than 0.8 for the H35/H34 ratio and values greater than 0.6 for the H29/H30 ratio characterizing the origin of the rock oil as a carbonate marine. The values of the H35/H34 (0.83 - 1.08) and H29/H30 (1.23-1.60) ratios corroborating the carbonate marine environment.

The C33trisnorhopane/C33hopane ratio decreases with increasing maturation, with values between 0.06 to 0.09 lower than 0.15 indicating maturity rocks (MACKENZIE, et al., 1980). The ratio of steranes (Stn), S29β(β(S+R))/β(S + R)+αα(S+R), ranges from values close to zero to 0.7 and equilibrium range from 0.67 to 0.71. In the samples it ranged from 0.48 to 0.60, values below the equilibrium range. During the thermal evolution, the R-isomer is converted S-isomer, causing a mixture of R and S isomers (PETERS et al., 2005b), with increased thermal maturation. The samples obtained values between 0.39 and 0.65, above the equilibrium range, except the CAN31 that is outside the maturation range of the oil for parameter St29 20S/(20S + 20R).
In the fraction of saturated hydrocarbons the usual biomarkers, as well as the usual 2α-methyl-hopanes and 8,14-seco-hopanes, were identified (Figure 1a and 1b, respectively). Peters et al. (2005b) claim that seco-hopanes are resistant to biodegradation processes. For all the studied parameters, the samples present a profile of non-biodegradable samples, so the presence of seco-hopanes (SHn) is probably due to the early stages of diagenesis from bacteriohopanotetrol (WANG et al., 1990). Distribution of the methyl-hopanes (MHn) of the sample CAN18, predominant in marine depositional environments.

**Figure 1** Saturated hydrocarbon fraction from oil CAN18 and CAN19: (a) GCxGC-TOFMS EIC m/z 205 from oil CAN18, showing the hopanes and methyl-hopanes; (b) GCxGC-TOFMS EIC m/z 123 from oil CAN19, showing the 8,14-seco-hopanes.


