GEOCHEMICAL INVESTIGATIONS OF POLAR FRACTION OF CRUDE OILS FROM DIFFERENT SEDIMENTARY BASINS BY ORBITRAP MASS SPECTROMETRY.

Thamires S. Mello, Bruno Q. Araújo, Vinicius F.Sardela, Celeste Y. Siqueira, Henrique M G. Pereira, Francisco R. de Aquino. Neto.

Universidade Federal do Rio de Janeiro, Instituto de Química, LAGEQUIM/LADETEC, Rio de Janeiro, RJ, Brazil.

Problems in petroleum refineries, such as emulsion formation, contamination and corrosion, occur due to the presence of polar compounds, even though they are low concentration(c.a. 5%). These compounds have at least one heteroatom such as S, N, O or metal ions such as V and Ni, referred to as sulfur, nitrogenous, oxygenated and organometallic organic derivatives (PETERS et al., 2005). Recently, high resolution mass spectrometry (HRMS) has been employed in the chemical characterization of petroleum (VAZ et al. 2013). The present work reports the application of high resolution mass spectrometry for characterization of polar fractions of four oils from the Gulf of Mexico and four oils from different Brazilian basins. The polar fractions were acquired by liquid chromatography and the HRMS analyzes were performed on the Orbitrap Hybrid Q-Exactive^{TM} (Thermo Scientific) mass spectrometer by direct infusion with electrospray ionization in positive mode, ESI-(+).

In the eight oil samples were identified 10 classes with heteroatoms: O, O_2, O_3, N, NO, NO_2, NO_3, N_2, N_2O and N_2O_2 (Figure 1). Among them, the most abundant were the classes with oxygen (O and O_2) and nitrogen (N). The BRS4 sample presents a greater contribution of oxygenated compounds in relation to the other samples. This oxygenated oil is the most biodegraded that corroborates with the depleted *n*-alkanes profile, presence of UCM (unresolved complex mixture), and the presence of abundant 25-norhopaneDuring the early stages of biodegradation, there is an increase in the abundance of O_2 compounds and a decrease when more advanced levels are reached, so for biodegraded samples oxygenate classes are predominant (VAZ et al. 2013).

Typical fingerprint was classified based on class distribution and the DBE (double bond equivalent). The samples that present the most intense series with lower DBEs (5 - 11) can be characterized with low stage of thermal evolution, because it contains low aromatic and naphthenic compounds, whereas the most thermally evolved have more DBE values between 15-25. In Table 1 may be observed that in all classes the most abundant DBE is less than 10, which would indicate a low degree to equilibrium of thermal evolution of the oils. Vaz et al. (2013) relates the increase of the degree of thermal evolution with the increase of the intensity of nitrogenated compounds. The increase of the relative intensity of these compounds and the reduction of the oxygenated and sulphur compounds are due to the reactions that occur in the thermal evolution like decarboxylation, dehydration, desulfurization, demethylation and cleavage of the C-C bond. The chemical bonds between C-O and C-S are more labile, so in more advanced stages of thermal evolution, the oxygen and sulfur compounds will be in a lower proportion in more evolved oils. Corroborating with the maturation results of the oils.

The identification of steroid carboxylic acids can help in the identification of the depositional environment of petroleum (VAZ et al. 2013) and pentacyclic acids derived from the lipids of the bacteria "bacteriahopanetetrol"(OURISSON et al., 1979). For samples grouped in similar nitrogen class were observed a high RDBE equal to eight with abundance of molecules with

14 and 15 carbons. The group of oxygenated compounds showed the abundant RDBE 5 e 9 and molecules with 12, 13 and 14 carbons. In addition, the distribution of NO group can be observed that RDBE equal to five is predominant in molecules with 12 carbon chains (Figure 1). Thus, high resolution Orbitrap mass spectrometry are important tool for investigation of polycondensate molecules in petroleum and the evaluation of polar fraction can provide unexplored geochemical information.

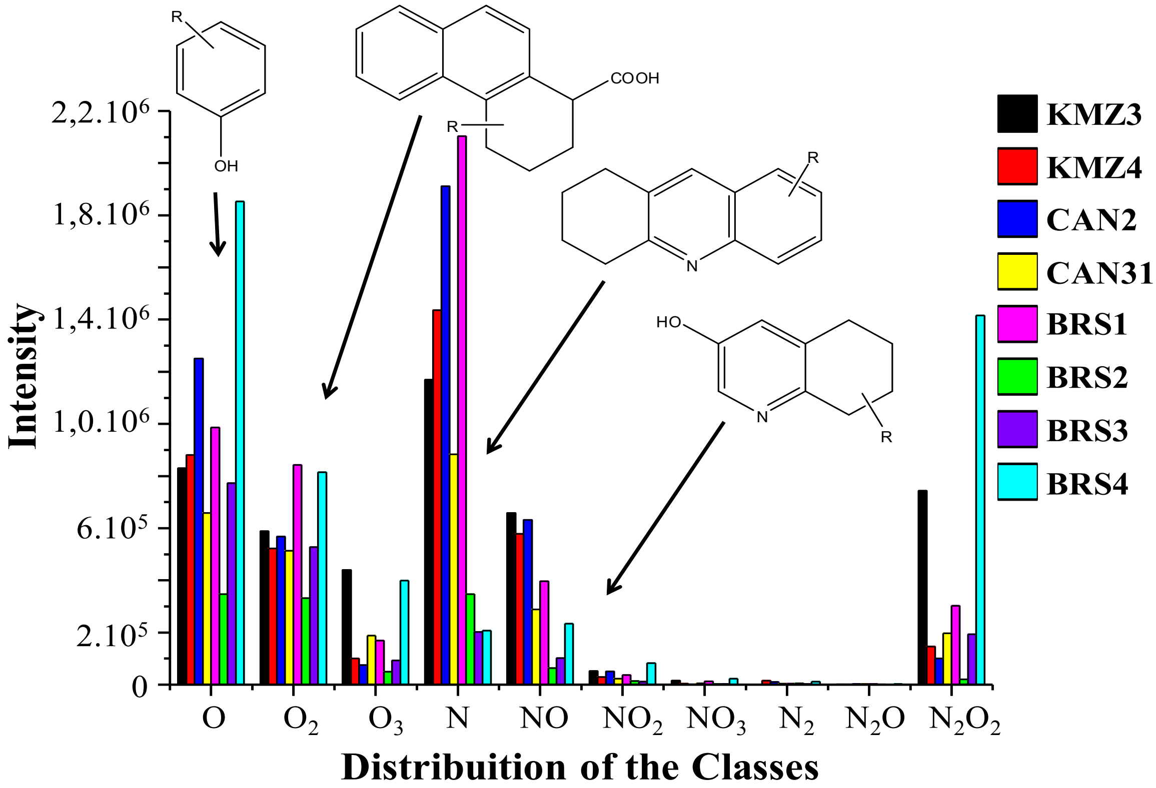

Figure 1 *Distribution of the classes in the samples by OrbitrapMS*

Table 1 *DBE values most abundant for each class.*

CLASS	O	O_2	O_3	N	NO	NO_2	NO_3	N_2	N_2O	N_2O_2
DBE	4-9	5, 6 and 9	4 and 5	6-9	5,6,7 and 9	5-7	2-5	7	1	2

PETERS, K. E.; WALTERS, C. C.; MOLDOWAN, J. M. 2005a. The Biomarker Guide: Biomarkers and Isotopes in the Petroleum Exploration and Earth History. 2th Ed. Cambridge University Press, 2, 1155.

OURISSON, G., ALBRECHT, P., ROHMER, M., 1979. .The hopanoides. Paleochemistry and biochemistry of a group of natural products., Pure Appl. Chem., v.51, 709-729.

VAZ, B. G.; SILVA, R. C.; KLITZKE, C.; SIMAS, R. C.; LOPES NASCIMENTO, H. D.; PEREIRA, R. C. L.; GARCIA, D. F.; EBERLIN, M. N.; AZEVEDO, D. A. 2013. Assessing biodegradation in the Llanos Orientales crude oils by electrospray ionization ultrahigh resolution and accuracy Fourier transform mass spectrometry and chemometric analysis. Energy & Fuels, v. 27, n. 3, 1277–1284.