

USE OF ELECTRON PARAMAGNETIC RESONANCE (EPR) TECHNIQUE TO ESTIMATE PETROLEUM QUALITY AND BIODEGRADATION EXTENT

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Introduction: The composition of petroleum depends on its origin (organic matter, depositional environment and maturity) and secondary processes (after their accumulation in the reservoir), such as biodegradation. Biodegradation is an oxidation process, driven by microorganisms, leading to a decrease in hydrocarbon concentration and API gravity. Meanwhile, the proportion of resins and asphaltenes, sulfur and metals content, viscosity, density and total acidity number (TAN) of the oil increases, and therefore decreasing its quality (Head et al., 2010). Biodegradation and petroleum quality have been evaluated using diverse techniques, such as gas chromatography and Fourier-transform infrared spectroscopy (FTIR). However, the use of electron paramagnetic resonance (EPR) technique for this purpose has not yet been reported. The EPR technique has been used to determine the nature of oil's paramagnetic constituents which have atoms capable of sharing their electronic pairs. These paramagnetic constituents are composed of free radicals containing nitrogen, oxygen, sulfur and the vanadyl radical (VO^{2+}), mainly associated with asphaltenes and found in high concentrations in biodegraded oils (Tayeb, et al., 2015). The reservoir characterization of a biodegraded oil is very important for the industry because it determines its market value and its production methods. Therefore, it is necessary to develop a profiling tool capable of estimate the biodegradation extent of the oil in the reservoir. The present work applied the EPR technique in the identification of paramagnetic constituents present in three Brazilian oil samples with different quality (acidity and density) and level of biodegradation, which were confirmed initially by TAN, API gravity, gas chromatography and FTIR analyzes.

Results: Oil samples **1**, **2** and **3** had their levels of biodegradation, total acidity and density ($^{\circ}\text{API}$) determined. Figure 1A presents chromatographic profiles (GC-FID), TAN, $^{\circ}\text{API}$ values and the $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ ratios showing that oil **1** is light, with low acidity ($\text{TAN} < 0.5$) and very slight/non-biodegraded, while oils **2** and **3** are more biodegraded. Oil **2** has also low acidity and oil **3** has high acidity ($\text{TAN} > 0.5$) and is the most biodegraded, possibly with heavy biodegradation level. In order to evaluate the relationship between the FTIR and EPR responses and the biodegradation extent of the oils, the whole oil samples and their asphaltene fractions were analyzed by these techniques. In the FTIR analysis of the whole oil samples it was verified that the three oils had very similar spectra (data not shown), while in the analysis of the asphaltenes fractions it was possible to differentiate them (Fig. 1B). The difference between the spectra of the asphaltene fractions of light oil **1** and the more biodegraded oil **3** was demonstrated by the intensity of response in the region of $730\text{-}740\text{ cm}^{-1}$, indicating the presence of aromatic ring molecules. For the asphaltene fractions of oils **2** and **3** it was possible to identify, in the regions of $1250\text{ - }1300$ and $1350\text{ - }1400\text{ cm}^{-1}$, an intense response corresponding to the presence of nitrogenated and oxygenated groups, consistent with what is expected for more biodegraded oils. In the EPR analysis, the integrated signal intensity is proportional to the unpaired electron concentration of the compounds present in the analyzed sample. The results of the detection of free radicals in the asphaltene fractions showed that when the oils **1** (43° API) and **2** (25° API) were compared, significant differences were observed between the intensity values. However, the greatest differences between the intensity values for free radicals and VO^{2+} (vanadyl), associated with porphyrin, were observed in the comparison between asphaltenes from oils **2** (25° API) and **3**

(19° API), which is the most biodegraded oil with the highest total acidity (Fig. 1C). As a consequence of the biodegradation process, the high acidity of oil is usually the result of an increase in the concentration of oxygenated constituents related to the presence of the carboxyl and phenol groups. However, among these two groups, phenols are the ones that present a more intense RPE response because they have resonance between the oxygen's electron pair and the electrons from the electron cloud of the aromatic ring (Montanari, et al., 1998).

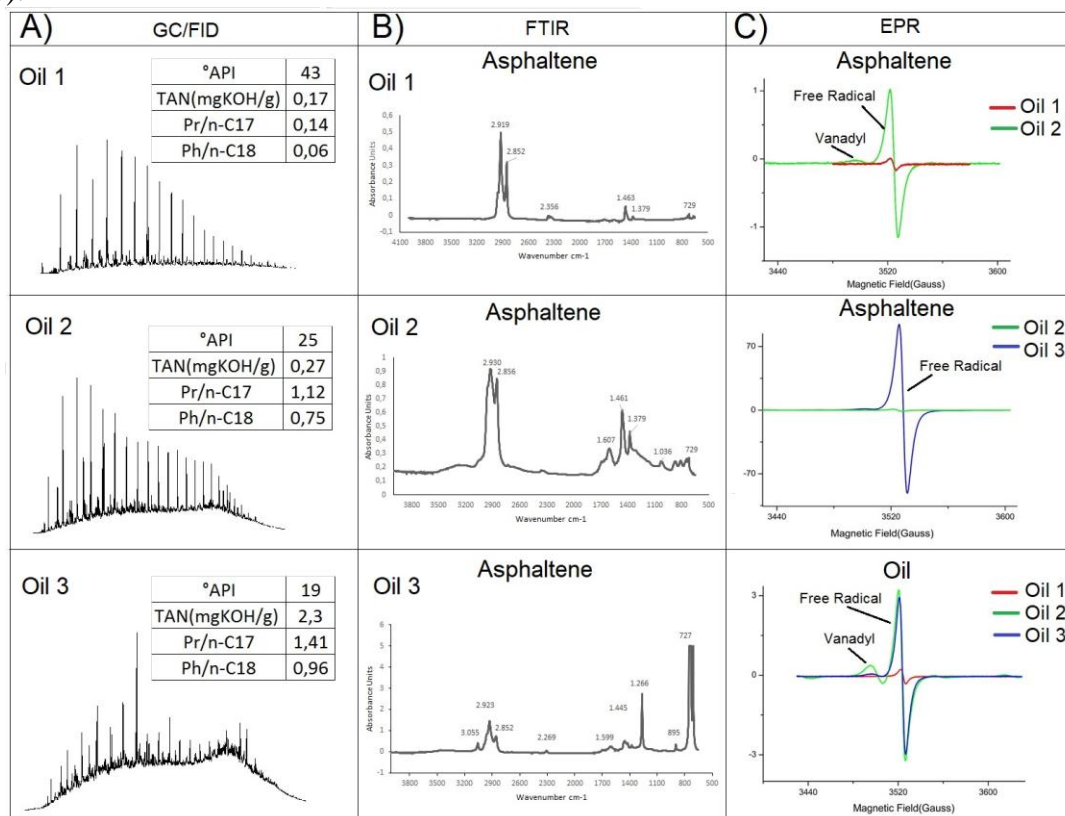


Figure 1: Comparison of the oil samples chromatographic profiles, API gravity, TAN values and the Pr/n-C₁₇ and Ph/n-C₁₈ ratios (A), FTIR spectra of oils' asphaltene fractions (B). Results of free radicals and VO²⁺ detection in the asphaltene fractions and in oil samples by EPR technique (C).

Conclusions: The combination of EPR and FTIR analysis of asphaltene fractions in the characterization of biodegraded oils showed that the electron paramagnetic resonance technique is able to differentiate oils with distinct quality, including different API gravity, acidity and biodegradation level. While comparing the total spectra of the three oils, it was observed that the EPR technique was sensitive to differentiate the biodegraded oils from the non-biodegraded one. It was also observed that the technique allowed the identification of vanadium through the vanadyl species in the oil samples, an important information for the oil refining step. These results, along with reservoir rock studies by EPR, may contribute to the development of a well logging tool.

References

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