Abstract

FTIR and SUVF contributed to define complementary parameters to evidence differences between oils from Brazil. These differences are linked to source rock environment (lacustrine fresh or brackish) revealed by GC/MS molecular parameters. Also differences related to biodegradation were highlighted.

Key words: Fourier Transform Infra Red Spectroscopy, Synchronous Ultra violet Fluorescence, Gas Chromatography, Mass Spectrometry, Oil, Brazil.

Introduction

Previous studies have demonstrated that the application of spectroscopic techniques such as Fourier Transformed Infra Red (FTIR) and Synchronous Ultra Violet Fluorescence (SUVF) integrated gas chromatography analysis can provide basis for a better assessment of reservoir compartmentalization. (Permanyer et al., 2002a; 2002b).

Recent studies seem indicate that FTIR and SUVF could also provide good discrimination between oils from unlike origins. All studies up to now were carried out on oils from marine origin and not biodegraded.

This study shows the results of the application of such techniques in the geochemical assessment of oils from a Brazilian marginal basin. Seven oil samples from different wells and three fields (Table 1) were analyzed. Previous studies have showed that these oils were generated by a Neocomian source rock deposited under fresh to brackish water conditions within the rift lakes formed during the extensional event that culminated with break-up of South America and Africa.

The oils share a number of common features, such as: low sulphur concentration (<0.1%), high wax content (saturates >60%), $\delta^{13}C$ values ranging from -28 to -30‰, high hopane/sterane ratios (>15), Ts higher than Tm, low/medium relative abundance of gammacerane, and absence of dinosterane and C$_{30}$ steranes.

Despite the similarities in bulk geochemical and molecular features, GC analyses revealed the existence of significant differences among the selected oils. B-619 and B-620 oils are characterized by a dominance of high molecular n-alkanes, pristane much higher than phytane, and odd/even n-alkane preference. Conversely, B-621, B-622, B-623 and B-625 samples are marked by the depletion of n-paraffins and a pronounced unresolved complex mixture (“hump”) that rises above GC baseline, indicating that these oils were biodegraded (Fig. 1). The B-624 oil, although being from the same field, is entrapped in a distinct reservoir sequence and not affected by biodegradation processes. As a result, it displays a dominance of high molecular n-alkanes, pristane much higher than phytane, and odd/even n-alkane preference.
Methodology

Selected samples were submitted to liquid chromatography using a silica gel column. Saturated and aromatic hydrocarbons and NSO compounds fractions were eluted using \( n\)-hexane, \( n\)-hexane:dichloromethane and dichloromethane:methanol, respectively. Saturate hydrocarbon fractions were analyzed by Gas Chromatography and Gas Chromatography/Mass Spectrometry using a Hewlett-Packard 5890 series II gas chromatograph coupled to a Hewlett-Packard 5972 mass selective detector. The whole oil analyses were also undertaken by Gas Chromatography.

The samples were also analysed by FTIR and SUVF. The FTIR preparation and data acquisition were performed five times for each sample. Assignments of the main IR bands and indexes are determined according to previous studies (Guiliano et al., 1990; Pieri et al., 1996). The indexes were used to determine and compare the chemical composition of each sample. A deconvolution technique was applied to increase spectral resolution of overlapping infrared bands (Doumenq et al., 1991).

Fluorescence intensity is related to the quantity of aromatic compounds present in the sample. The analysis of UV fluorescence spectra of standard polycyclic aromatic hydrocarbons, which are present in crude oils, allows defining three main regions A1, A2 and A3. Each of these spectral regions is characterized by the number of condensed aromatic rings, yielding qualitative information on the nature of the aromatic species present in oils (spectral region from 280 to 580 nm) (Kister et al., 1996). The fluorescence index \((A2/A1\) ratio) represents the ratio of the aromatic compounds with 3 or 4 rings with respect to the compounds with 2 rings. The A3 represents aromatic condensation with 5 or more aromatic rings.

Results and Discussion

Various FTIR and SUVF parameters can be used to sample characterization. In this study we use Aliphaticity, Ramification, Substitution 2 and Long Chains FTIR parameters as well as A2 and A1 SUVF parameters. Particularly A2/A1 Fluorescence Index vs. Substitution 2 FTIR Index, show two main groups of samples. The first group (I) is formed by samples B-619 and B-620 and the second one (II) is formed by the others oils (B-621 to B-625) (Fig.2).

Results provided by GC/MS reveal that samples B-619 and B-620 may correspond to oils generated in more fresh water environment, whereas the other oils may correspond to more brackish environment. Cluster analysis using biomarkers ratios also differentiate the same two groups of oils as those deduced from FTIR and SUVF (Fig.3).

On the other hand the relation Ramification vs. Long Chains FTIR Index shows a differentiation in the oils from the second group related to biodegradation (Fig.4). The Long Chains Index decreases in biodegraded oils and consequently in the graph, the sample B-624 falls closer to the first group (non biodegraded oils) than to the biodegraded oils from the second group. This differentiation is also emphasized by Aliphaticity FTIR Index.

Conclusions

The integration of geochemical molecular parameters with those from spectroscopic techniques revealed the existence of two groups of oils, sourced from lacustrine fresh and brackish environments, with distinct biodegradation levels.

This work demonstrates that FTIR and SUVF techniques, primarily developed for reservoir geochemistry can also be helpful for differentiating oils from various origins or biodegradation stages.

Acknowledgements

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References


Table and Figure Captions

Figure 1.- Whole oil CG/FID chromatograms of two oil samples from the same field in a Brazilian Basin, showing distinct biodegradation degrees.

Figure 2.- Fluorescence A2/A1 vs. FTIR Substitution 2 indexes clearly evidence two groups of oils.

Figure 3.- Cluster analysis using biomarkers ratios evidences two groups of oils.

Figure 4.- The non biodegraded sample B-624 shows a more elevate value of Long Chains that other oils from the same group (B-621 to B-625). Note that samples B-619 and B-620 are also non biodegraded.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Well</th>
<th>Field</th>
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<tbody>
<tr>
<td>B-619</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>B-620</td>
<td>2</td>
<td>B</td>
</tr>
<tr>
<td>B-621</td>
<td>3</td>
<td>C</td>
</tr>
<tr>
<td>B-622</td>
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</tr>
<tr>
<td>B-625</td>
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Table 1