

Characterization of Brazilian oils by FTIR and SUVF spectroscopy. A comparison with GC/MS results

Caracterización por espectroscopía IRTF y FUVS de petróleos de Brasil. Comparación con los resultados obtenidos por CG/EM

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RESUMEN

La aplicación de IRTF y FUVS en varios petróleos de Brasil ha contribuido al establecimiento de parámetros complementarios que permiten evidenciar diferencias entre ellos. Estas diferencias están ligadas al ambiente de deposición de la roca madre (lacustre de agua dulce a salobre) como revelan los parámetros moleculares de CG/EM. También se han destacado las diferencias relacionadas con la biodegradación.

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

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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 (Permanyer *et al.*, 2000b; 2005) seem to indicate that FTIR and SUVF could also provide a 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

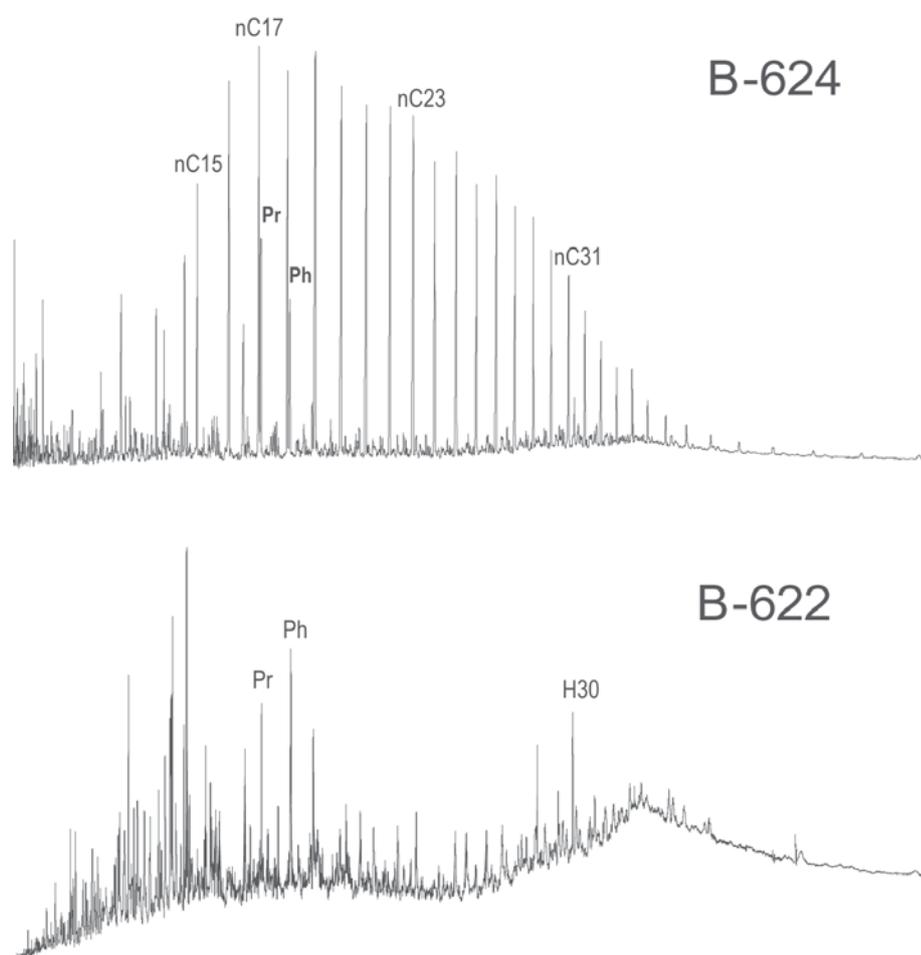


Fig. 1.- Whole oil CG/FID chromatograms of two oil samples from the same field in a Brazilian Basin, showing distinct biodegradation degrees. Sample B-622 is the most biodegraded.

Fig. 1.- Cromatogramas de gases de dos muestras del mismo campo de una cuenca de Brasil mostrando distintos grados de biodegradación. La muestra B-622 es la más biodegradada.

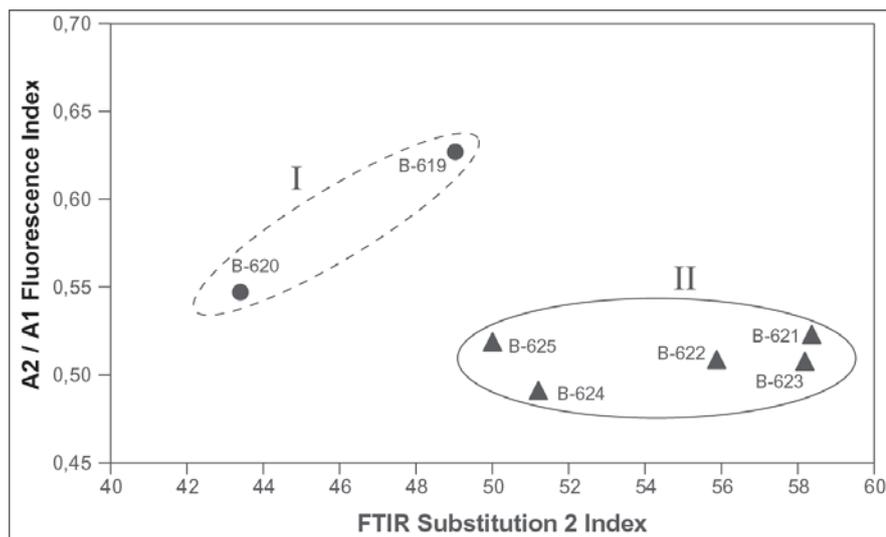


Fig. 2.- Fluorescence A2/A1 vs. FTIR Substitution 2 indexes clearly evidence two groups of oils.

Fig. 2.- Relación entre el índice A2/A1 de fluorescencia y el índice infrarrojo Substitución 2 evidenciando claramente dos grupos de petróleos.

fields (Table I) were analyzed. Previous studies (Gonçalves *et al.*, 2000) 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 the break-up of South America and Africa.

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

The oils share a number of common features, such as: low sulphur concentration (<0.1%), high wax content (saturates >60%), $\delta^{13}\text{C}$ 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 C₃₀ steranes.

Despite the similarities in bulk geochemical and molecular features, GC analyses revealed the existence of significant differences among the selected oils. B619 and B620 oils are characterized by a dominance of high weight molecular *n*-alkanes, pristane much higher than phytane, and odd/even *n*-alkane preference. Conversely, B621,

B622, B623 and B625 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 B624 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.

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 (B621 to B625) (Fig. 2).

Results provided by GC/MS reveal that samples B619 and B620 may correspond to oils generated in more fresh water environment, whereas the other oils may correspond to a more brackish environment. Cluster analysis using biomarkers ratios (Pr/Ph, Pr/nC17, Ph/nC18, CPI, C21/C23, C24/C26 and C25/C26 Tricyclics, C21Tricyclic/C30Hopane, Ts/Tm, Gammacerane/C30Hopane, C29/C30 and C35/C34 Hopanes, C29aaa (S/S+R), C29aaa (abb+aaa), %C27, %C28 and %C29 steranes, C30Hopane/Steranes) also differentiates the same two groups of oils as those deduced from FTIR and SUVF (Fig. 3).

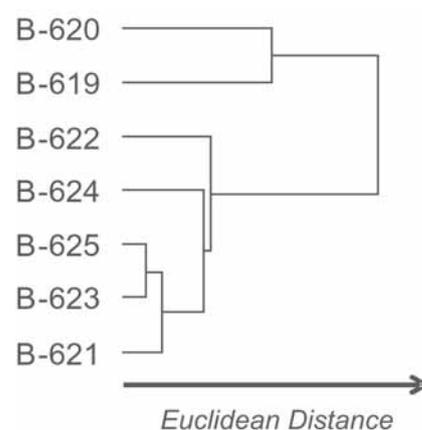


Fig. 3.- Cluster analysis using biomarkers ratios evidences two groups of oils.

Fig. 3.- Análisis de cluster a partir de relaciones de biomarcadores. Dos grupos de petróleos quedan diferenciados.

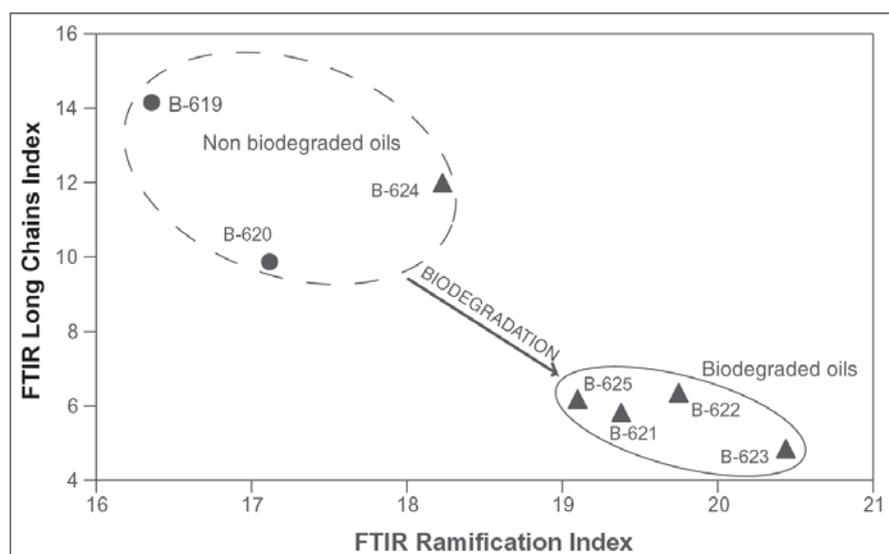


Fig. 4.- The non biodegraded sample B624 shows a more elevated value of Long Chains than other oils from the same group (B621 to B625) in Figure 3. Note that samples B619 and B620 are also non biodegraded.

Fig. 4.- La muestra no biodegradada B-624 presenta un mayor valor del índice de Cadenas Largas en comparación con otros petróleos del mismo grupo (B-621 a B-625) en la Figura 3. Nótese que las muestra B-619 y B-620 tampoco están biodegradadas.

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, the sample B624 falls closer to the first group (non biodegraded oils) than to the biodegraded oils from the second group (Fig. 4). 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.

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Sample	Well	Field
B-619	1	A
B-620	2	B
B-621	3	C
B-622	4	C
B-623	5	C
B-624	6	C
B-625	7	C

Table I.- Studied samples and correlation with the wells and oil fields. Oil fields and wells are from an offshore Brazil Basin.

Tabla I.- Correlación de las muestras estudiadas con sondeos y campos de petróleo de una cuenca en la plataforma de Brasil.

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