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Analysis of Hydrocarbon-bearing Fluid Inclusions (HCFI) using time-resolved fluorescence spectroscopy

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ABSTRACT

Hydrocarbon-bearing fluid inclusions (HCFI) are microscopic cavities within rocks that are filled with petroleum oil, the composition of which may not have changed since the trapping event. Thus, the composition of that entrapped oil can provide information about the formation and evolution of the oil reservoir. This type of information is important to the petroleum production and exploration industries. Crude oil fluorescence originates from the presence of cyclic aromatic compounds and the nature of the emission is governed by the chemical composition of the oil. Fluorescence based methods are widely used for analysis of crude oil because they offer robust, non-contact and non-destructive measurement options. The goal of our group is the development of a non-destructive analytical method for HCFI using time-resolved fluorescence methods.

In broad terms, crude oil fluorescence behavior is governed by the concentration of quenching species and the distribution of fluorophores. For the intensity averaged fluorescence lifetime ($\tau$), the best correlations have been found between polar or alkane concentrations, but these are not suitable for robust, quantitative analysis. We have recently started to investigate another approach for characterizing oils by looking at Time-resolved Emission Spectra (TRES). TRES are constructed from intensities sampled at discrete times during the fluorescence decay of the sample.

In this study, TRES, from a series of 10 crude oils from the Middle East, have been measured at discrete time gates (0.5 ns, 1 ns, 2 ns, 4 ns) over the 450-700 nm wavelength range. The spectral changes in TRES, such as time gate dependent Stokes’ shift and spectral broadening, are analyzed in the context of energy transfer rates. In this work, the efficacy of using TRES for fingerprinting individual oils and HCFI is also demonstrated.

Keywords: crude oil, petroleum, hydrocarbons, fluorescence, Time-resolved Emission Spectra (TRES), energy transfer, fluorescence lifetime, hydrocarbon-bearing fluid inclusions (HCFI).

1. INTRODUCTION

Hydrocarbon-bearing fluid inclusions (HCFI) occur in rock and vein forming minerals, e.g. quartz and calcite, and contain micron scale samples of trapped hydrocarbon oil. In addition to hydrocarbon fluids, at room temperature, HCFI can also contain traces of other fluids such as H$_2$O, gases such as CO$_2$ and CH$_4$, and solids that were either entrapped along with or precipitated from the liquid phase at later times. The accurate determination of the composition of the trapped oil in single fluid inclusions can yield (together with micro-thermometric studies) fundamental information about the history of oil formation and migration in sedimentary basins, which is important to both the petroleum production and exploration industries and to the geological community.

Destructive analysis of HCFI can be done either as bulk ensemble analysis or as a single inclusion analysis. The bulk fluid inclusion analysis is typically done by crushing rock samples and extracting the fluids trapped in inclusions for chromatographic analysis. The oil composition data obtained this way may suffer from variety of problems including mixing of fluids from multiple nonhomogenous HCFI populations and contamination from material within the rock sample itself or lab contamination. Analysis of single inclusions is, in principle, much better. It requires opening of HCFI (laser ablation or high energy beam ions), but the very low quantities of oil typically contained in HCFI ($\phi$ 10$\mu$m ~10$^{-9}$ g) restricts analysis with gas chromatography and/or mass spectroscopy to rather large inclusions or groups of inclusions.

Optical micro-spectroscopy, on the other hand, offers good diagnostic potential for non-destructive HCFI analysis. The most common spectroscopic methods are based on infrared absorption and Raman, and fluorescence spectroscopy.

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UV fluorescence is commonly used for identification of HCFI$^{1,3,14}$ and the high sensitivity of fluorescence and wide range of available techniques$^{15}$ makes it a potentially viable tool for HCFI analysis. Fluorescence of petroleum products, which originates from the presence of polycyclic aromatic fraction, is directly governed by chemical composition and physical properties of the oil.$^{16}$ In general, heavy oils (low API$^\dagger$ gravity) tend to have relatively broad, more shifted to the red and less intense fluorescence bands,$^{17}$ lower quantum yields,$^{18}$ and shorter fluorescence lifetimes$^{19}$ as compared to light oils (high API gravity). These effects are produced by higher concentrations of fluorophores and quenchers in heavy oil, which yields higher rates of energy transfer and quenching.$^{16,20-23}$ The use of fluorescence color is widely used as a qualitative guide for assessing the maturity of crude oil in bulk$^{24}$ and in HCFI,$^{3,5,13}$ but this technique is intrinsically prone to error.$^{25,26}$ In principle, all techniques based on measurement of fluorescence intensity and spectral distribution can be adversely affected by instrumental factors such as excitation source intensity variation, detector spectral sensitivity variation, and also by the physical properties of sample such as opacity, geometry, turbidity, scattering properties, and photobleaching.$^{27}$ Alternatively, time-resolved based fluorescence techniques are not only largely free of these artifacts, but also contain information that is lost in time-averaging processes inherent to steady-state methods.$^{15}$ These techniques have also been used to characterize various petroleum products down through the last 30 years.$^{19,23,28}$ The early studies were mainly driven by a need to develop a tool for monitoring the environmental pollution, with no attempts made to correlate experimental data with chemical composition.$^{28-30}$ In principle, all techniques based on measurement of fluorescence intensity and spectral distribution can be adversely affected by instrumental factors such as excitation source intensity variation, detector spectral sensitivity variation, and also by the physical properties of sample such as opacity, geometry, turbidity, scattering properties, and photobleaching.$^{27}$ Alternatively, time-resolved based fluorescence techniques are not only largely free of these artifacts, but also contain information that is lost in time-averaging processes inherent to steady-state methods.$^{15}$ These techniques have also been used to characterize various petroleum products down through the last 30 years.$^{19,23,28}$ The early studies were mainly driven by a need to develop a tool for monitoring the environmental pollution, with no attempts made to correlate experimental data with chemical composition.$^{28-30}$ In principle, all techniques based on measurement of fluorescence intensity and spectral distribution can be adversely affected by instrumental factors such as excitation source intensity variation, detector spectral sensitivity variation, and also by the physical properties of sample such as opacity, geometry, turbidity, scattering properties, and photobleaching.$^{27}$ Alternatively, time-resolved based fluorescence techniques are not only largely free of these artifacts, but also contain information that is lost in time-averaging processes inherent to steady-state methods.$^{15}$ These techniques have also been used to characterize various petroleum products down through the last 30 years.$^{19,23,28}$ The early studies were mainly driven by a need to develop a tool for monitoring the environmental pollution, with no attempts made to correlate experimental data with chemical composition.$^{28-30}$ In principle, all techniques based on measurement of fluorescence intensity and spectral distribution can be adversely affected by instrumental factors such as excitation source intensity variation, detector spectral sensitivity variation, and also by the physical properties of sample such as opacity, geometry, turbidity, scattering properties, and photobleaching.$^{27}$ Alternatively, time-resolved based fluorescence techniques are not only largely free of these artifacts, but also contain information that is lost in time-averaging processes inherent to steady-state methods.$^{15}$ These techniques have also been used to characterize various petroleum products down through the last 30 years.$^{19,23,28}$ The early studies were mainly driven by a need to develop a tool for monitoring the environmental pollution, with no attempts made to correlate experimental data with chemical composition.$^{28-30}$

In our laboratory, we have been investigating the fluorescence behavior of crude oils with the idea of developing a robust, quantitative method for oil characterization using mainly the intensity averaged fluorescence lifetime ($\tau$).$^{20-23,31}$ Recently, we have measured fluorescence lifetimes from a series of HCFI and correlated the data with those obtained from 23 crude oils.$^{32}$ The best correlations have been found between $\tau$ and polar or alkane concentrations. These results, although not suitable for highly accurate quantitative analysis, allow us to classify the entrapped oils according to polar and alkane concentrations. In this previous study the oils were sampled from diverse sources and locations, and their extensive geological range contributes to the scatter in calibration models for oil composition.

![Figure 1: Schematic diagram of Time-resolved Emission Spectra (TRES). TRES are obtained during the time windows denoted by $t_1$, $t_2$, $t_3$. For graphic simplicity only a single decay curve is shown.](image)

In this work, we investigate another approach for characterizing oils by conducting a detailed time-resolved fluorescence study on a set of 10 well-characterized crude petroleum oils from a single geographical locality (Middle East) using

$^\dagger$The API gravity is a measure of density and is related to the density by the formula:

$\text{API gravity} = \left(\frac{141.5}{\text{specific gravity at 15.6°C}}\right) - 131.5$ i.e. $\text{H}_2\text{O} = 10° \text{API}$.
Time-resolved Emission Spectra (TRES). Conceptually, TRES are fluorescence emission spectra constructed from intensities sampled at discrete times during the fluorescence decay of the sample (Figure 1). TRES have been previously demonstrated to have potential as a tool for discriminating different oils types. However, neither any fundamental studies into crude oil photophysics nor any correlations of spectral parameters with chemical composition were reported in these studies. Here, the correlations between spectral parameters such as time-gate dependent batochromic shift, spectral broadening and chemical composition are examined in the context of fluorescence energy transfer rates. In addition, we also demonstrate the potential for using TRES for the fingerprinting of the individual HCFL and matching the data with bulk oils.

2. MATERIALS AND METHODS

2.1. Apparatus and procedures
Fluorescence data from bulk oils and the inclusion samples were recorded using the Diode Laser Fluorescence Lifetime Microscope (DLFLM) developed in-house and described in detail elsewhere. In brief, this Time Correlated Single Photon Counting (TCSPC) system is built around an Olympus BX-60 microscope and a 405 nm laser diode. The instrument is capable of measuring fluorescence lifetimes (0.1 ns+), steady-state and Time-resolved Emission Spectra (TRES) over the wavelength range 450-800 nm.

All bulk oil studies were carried out on neat non-degassed crude oil, held in 1 mm path-length, quartz cuvettes at room temperature. The cuvettes were solvent and acid washed between the samples to prevent any cross contamination.

The fluorescence emission spectra were corrected using wavelength-dependent output of a tungsten filament calibrated relative to black body radiation.

Fluid inclusions measurements were carried out on non-epoxied wafer following the procedure described by Ryder and Przyjalgowski et al.

2.2. Materials
The crude oil samples were provided by the Petroleum Geochemistry Division of Fugro Robertson (FR), Llandudno, North Wales. The crude oil samples originate from various different locations across the Middle East and represent two different oil reservoir intervals. The crude oils were analyzed in FR laboratory by column chromatography after removal of the volatile hydrocarbon fraction by topping. The concentration of alkane, polar and aromatic fractions obtained from chromatographic fractionation do not sum to 100% because of the column losses. Therefore the compositional data were normalized to obtain corrected concentrations. The most salient data about the oils is given below in Table 1.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Reservoir interval</th>
<th>API [deg]</th>
<th>Asphaltene [%]</th>
<th>Corrected alkane [%]</th>
<th>Corrected aromatic [%]</th>
<th>Corrected polar [%]</th>
<th>Sulfur [%]</th>
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<tr>
<td>ME-1</td>
<td>Cretaceous</td>
<td>32.7</td>
<td>3.4</td>
<td>61.6</td>
<td>29.8</td>
<td>8.6</td>
<td>1.63</td>
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<tr>
<td>ME-2</td>
<td>Cretaceous</td>
<td>28.9</td>
<td>4.2</td>
<td>61.7</td>
<td>30.3</td>
<td>8.0</td>
<td>1.43</td>
</tr>
<tr>
<td>ME-3</td>
<td>Cretaceous</td>
<td>30.8</td>
<td>3.0</td>
<td>62.1</td>
<td>30.3</td>
<td>7.6</td>
<td>1.67</td>
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<tr>
<td>ME-4</td>
<td>Cretaceous</td>
<td>39.2</td>
<td>0.9</td>
<td>71.1</td>
<td>22.1</td>
<td>6.7</td>
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<td>ME-5</td>
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<td>44.1</td>
<td>0.1</td>
<td>80.4</td>
<td>15.9</td>
<td>3.7</td>
<td>0.60</td>
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<tr>
<td>ME-6</td>
<td>Jurassic</td>
<td>39.6</td>
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<td>76.3</td>
<td>19.7</td>
<td>4.0</td>
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<tr>
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<td>44.2</td>
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<td>77.0</td>
<td>21.2</td>
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<tr>
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<td>47.8</td>
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<td>ME-10</td>
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<td>24.7</td>
<td>8.9</td>
<td>51.2</td>
<td>41.4</td>
<td>7.4</td>
<td>2.67</td>
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The fluorite hosted hydrocarbon-bearing fluid inclusion sample F3a originated from Cave-in-Rock mining district, Illinois, USA.
3. RESULTS AND DISCUSSION

3.1. Bulk oils studies

Figure 2 shows Time-resolved Emission Spectra (TRES) of ten Middle Eastern (ME) crude oils measured for 0.5 ns, 1 ns, 2 ns and 4 ns time gates over 450–700 nm wavelength range.

Figure 2: (A-J) Time-resolved Emission Spectra (TRES) of ten Middle Eastern oils measured over 450–700 nm wavelength range with 405 nm excitation. The spectra were normalized at the wavelength of maximum fluorescence intensity (λ_max). For the ease of comparison the oils are listed in order of increasing API gravity.
Similarly to steady-state data the TRES show broad emission bands (Figure 2 A-J) devoid of any vibronic structure, which indicates that the fluorescence emission originates from complex mixtures of fluorophores with overlapping emission and absorption spectra.\textsuperscript{16,17} Two chief processes that govern the fluorescence dynamics of crude oils are energy transfer and fluorescence quenching.\textsuperscript{16,17,19-21,31,32} An important point of note is that steady-state fluorescence emission data is the average of the time-resolved emission spectra over the intensity decay of the sample and as a consequence some information is irreversibly lost in the time averaging process. Because TRES are constructed from fluorescence intensities sampled at discrete times during the decay of the sample, an obvious implication is that TRES provide more insight into fluorescence dynamics than steady-state based measurements and thus should provide more information about fluorescence quenching and energy transfer. In general, one would expect to find that the spectral changes in TRES follow similar trends to those observed in steady-state spectra. Briefly, the position of the wavelength of maximum fluorescence emission intensity ($\lambda_{\text{max}}$) and spectral width (FWHM)\textsuperscript{‡} are primarily influenced by the extent of collisional energy transfer process, whereas fluorescence intensity is strongly influenced by quenching rates. However, there was no attempt made to measure the absolute fluorescence intensities. Moreover, the normalization method used, i.e. the individual TRES spectra were normalized at wavelength of the maximum fluorescence intensity, obscures the relative difference between the fluorescence intensities for the different time gates.

![Figure 3](image-url)

**Figure 3:** Plot of API gravity for ten Middle Eastern oils versus: (A) the time gate dependent batochromic shift ($\lambda_{\text{max,4ns}}-\lambda_{\text{max,0.5ns}}$); (B) the time gate dependent spectral width difference (FWHM\textsubscript{4ns}-FWHM\textsubscript{0.5ns}). The dashed lines represent the linear fits ($r^2$ stands for the correlation coefficient).

### 3.1.1. Spectral correlations

The position of $\lambda_{\text{max}}$ is primarily governed by the extent of collisional energy transfer so it depends above all on the nature, concentration, and population distribution of chromophores and fluorophores in the oils. In brief, heavy oils (low

\textsuperscript{‡}The acronym FWHM refers to the full spectral width measured at half maximum of fluorescence intensity
API gravity) tend to have more red-shifted fluorescence bands then lighter, usually more mature, oils (higher API gravity). It stems from the fact that there are fewer fluorophores in light oils. Moreover, light oils contain relatively lower populations of large, small energy band gap, aromatics as compared to heavy oils. Overall this leads to a reduction in energy transfer rates and less red-shifted emission. The common feature of crude oils TRES is also a progressive shift to the longer emission wavelength with increasing time gates (Figure 2 A-J). This time gate dependent batochromic shift is symptomatic of higher contribution of the energy transfer produced emission at later time gates to the total emission and the difference between $\lambda_{\text{max}0.5\text{ns}}$ and $\lambda_{\text{max}4\text{ns}}$ varies from ~100 nm for the heavy oils to <20 nm for the light oils. The value of that batochromic shift depends on the concentration and on the specific distribution of fluorophores and is negatively correlated with API gravity (Figure 3 A).

Similar argument can be advanced for time gate dependent spectral width difference ($\text{FWHM}_{4\text{ns}}$-$\text{FWHM}_{0.5\text{ns}}$) and API gravity also shows negative correlation with $\text{FWHM}_{4\text{ns}}$-$\text{FWHM}_{0.5\text{ns}}$ (Figure 3 B).

It was already established that the alkane fraction at 405 nm excitation wavelength acts as an inert solvent in which fluorophores and quenchers are diluted. As such, the increase in alkane fraction causes a reduction in the collisional energy transfer rates. Therefore one would expect to find that alkane fraction correlates negatively with $\lambda_{\text{max}0.5\text{ns}}$-$\lambda_{\text{max}4\text{ns}}$ and $\text{FWHM}_{4\text{ns}}$-$\text{FWHM}_{0.5\text{ns}}$. This is indeed the case as can be seen from the Figure 4 A, B.

Because fluorescence of crude oils derives from the presence of polycyclic aromatics, a natural implication is that aromatic concentration should correlate with spectral parameters.

![Figure 4](image.png)
There is a general trend towards higher values of \(\lambda_{\text{max}}(4\text{ns}) - \lambda_{\text{max}}(0.5\text{ns})\) and FWHM(4\text{ns}) - FWHM(0.5\text{ns}) with increasing concentration of aromatic compounds, although there is a significant degree of scatter around the trend line (Figure 5 A, B). This general trend is due to increased rates of energy transfer.

However, the correlations between spectral parameters \(\lambda_{\text{max}}(4\text{ns}) - \lambda_{\text{max}}(0.5\text{ns})\) and FWHM(4\text{ns}) - FWHM(0.5\text{ns}) and compositional data, discussed above, while useful for general qualitative discussion, are rather not suitable for qualitative analysis.

### 3.1.2. Contour plots

An alternative way to visualize TRES is by means of contour plots that represent the three-dimensional time gate-emission wavelength-intensity data set as two-dimensional maps (time gate–emission wavelength) with isointensity contours. This approach allows a general comparison between different crude oils on the basis of concentration and chemical composition.

The compositional diversity of ME oils results in a range of TRES contour plots as seen in Figure 6 A-J. These contour plots were constructed using the TRES data as in Figure 2, i.e. the individual TRES spectra were normalized at the wavelength of maximum fluorescence intensity \(\lambda_{\text{max}}\). With this method of normalization, the wavelength distribution of fluorescence intensity reveals information about the extent of the energy transfer.
Figure 6: Continued on the next page.
The crude oil TRES contour plots show a general trend for shifting of the isointensity contours from long emission wavelength to short emission wavelength with increasing maturity (Figure 6 A-J). This trend represents the gradual decrease in energy transfer and quenching rates with increasing oil maturity.

The heaviest oil, ME-10 (Figure 6 A), which has relatively high concentration of polar and asphaltene compounds as compared to the other ME oils, shows prominently different contour plot topology. For ME-10, the contour lines representing intensity from 1.0 down to 0.9 stretch diagonally from ~450 nm to ~525 nm and from ~525 to ~625 nm window. This broad distribution of relatively red-shifted fluorescence intensity, as related to the other ME oils, is symptomatic of the large contribution of energy transfer excited fluorescence. The contour plot for oil ME-2 looks fairly similar (Figure 6 B), however the 0.9 intensity lines span diagonally from ~450 nm to ~480 nm and from ~480 nm to ~575 nm, which indicates a small drop in energy transfer compared to ME-10. Oil ME-10 represents lower alkane and higher aromatic concentrations resulting in elevated rates of energy transfer as compared to ME-2.

The bottom row (Figure 6 I, J) shows TRES contour plots for the two lightest, the most mature oils ME-8 and ME-9, which have a relatively large concentration of alkane constituents (~80%) combined with a rather low aromatic concentration (~20%). In each case, the contour lines representing the intensity down to 0.9 fall into ~450-465 nm window. This drift of contour lines towards shorter emission wavelengths is a result of a drop in energy transfer in the light oils.
Moving from the top of Figure 6 to the bottom one observes a progressive reorientation of isointensity contours from longer to shorter emission wavelength. This change in contour plot topology is due to a gradual decrease of the energy transfer rates with increasing oil maturity.

3.2. Fluid inclusion case study

Figure 7: TRES contour plot of HCFI F3a.

Figure 7 show TRES contour map for fluid inclusion F3a. The contour lines representing the 0.9 intensity lines fall into ~450-460 nm and ~475-510 nm window and overall the plot looks fairly similar to that of the oil ME-5 (compare Figure 7 and Figure 6 H). Our previous studies based on the intensity average fluorescence lifetime have identified inclusion F3a as containing high alkane and low polar concentrations hydrocarbon fluid. Also the recovered values and wavelength dependence of $\tau$ for F3a and ME-5 (~3-9 ns) are fairly similar. The above indicates that the oil entrapped in the inclusion F3a comprises similar types and distributions of fluorophores as the oil ME-5.

4. CONCLUSIONS

The gross composition metrics obtained from standard analysis correlate with spectral changes in TRES for a geographically related set of crude petroleum oils. This suggests scope for developing accurate quantitative methods for oils characterization using TRES. All the crude oil TRES contour plots show a general trend for isointensity lines to move from long emission wavelength to short emission wavelength with increasing maturity. This trend represents the gradual decrease in energy transfer rates with increasing oil maturity.

We have presented the first TRES collected from individual HCFI. TRES contour plots allow us to fingerprint the single HCFI and to peg the data to bulk oil contour maps.

In summary, the normalization method used allows for qualitative analysis of a dominant process in crude oil fluorescence, the energy transfer. However, it masks the relative differences in fluorescence intensities measured at different time gates for the individual oils. Moreover, as with any form of normalization it obscures huge variations in intensities observed for different crude oil samples. Currently we are investigating a different method of TRES normalization by looking at the spectra with respect to their relative intensity i.e. 0.5 ns spectrum is normalized at $\lambda_{\text{max}}$ and the traces at later time gates (1-4 ns) are scaled to it. This approach, which retains the relative intensities, should provide the information about the extent of fluorescence quenching.
ACKNOWLEDGEMENTS

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