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Time-resolved fluorescence microspectroscopy for characterizing crude oils in bulk and hydrocarbon-bearing fluid inclusions.

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Abstract:

Time-resolved fluorescence data was collected from a series of 23 bulk crude petroleum oils and 6 microscopic Hydrocarbon-bearing Fluid Inclusions (HCFI). The data was collected using a Diode Laser Fluorescence Lifetime Microscope (DLFLM) over the 460-700 nm spectral range using a 405 nm excitation source. The correlation between intensity averaged lifetimes (τ) and chemical and physical parameters was examined with a view to developing a quantitative model for predicting the gross chemical composition of hydrocarbon liquids trapped in HCFI. It was found that τ is nonlinearly correlated with the measured polar and corrected alkane concentrations, and that oils can be classified on this basis. However, these correlations all show a large degree of scatter, preventing accurate quantitative prediction of gross chemical composition of the oils. Other parameters such as API gravity and, asphaltene, aromatic, and sulphur concentrations do not correlate well with τ measurements. Individual HCFI were analysed using the DLFLM and time resolved fluorescence measurements were compared with τ data from the bulk oils. This enabled the fluid within the inclusions to be classified as either low alkane/high polar or high alkane/low polar. Within the high alkane/low polar group, it was possible to clearly discriminate HCFI from different locales and to see differences in the trapped hydrocarbon fluids from a single geological source. This methodology offers an alternative method for classifying the hydrocarbon content of HCFI, and observing small variations in the trapped fluid composition, that is less sensitive to fluctuations in the measurement method than fluorescence intensity based methods.

INDEX HEADINGS: Crude oil, fluorescence, petroleum, hydrocarbon, fluid inclusion, lifetime, time-resolved, microscopy.

Introduction:

Hydrocarbon-bearing Fluid Inclusions (HCFI) are small micro-cavities, generally < 10 µm in diameter, filled with fluid trapped during crystallization or healing of the fractures in minerals such as quartz, fluorite, or calcite. HCFI can consist of monophase hydrocarbon fluids or multiphase mixtures with gases, liquids, aqueous solutions, and/or solids being present. The accurate determination of the chemical composition of the hydrocarbon fluids can provide (together with micro-thermometric studies) information about the crystal growth, temperature, and timing of fluid trapping and migration. This information is of significant importance to the petroleum exploration industry, particularly in regard to the study of petroleum reservoirs, where it may be necessary to chart small changes in fluid composition. HCFI analysis can be done either by crushing bulk rock samples and extracting the trapped fluid for analysis or by the analysis of single fluid inclusions. The oil composition data obtained from bulk fluid inclusion analysis (by crushing) suffers from a variety of problems including: sample destruction, mixing of fluids from multiple fluid inclusion populations, and contamination from materials within the rock sample itself.
mixing of fluids is especially disadvantageous because the most volumetrically abundant type of inclusion will bias the results, and the constituents of aqueous fluid inclusions could also contaminate the extracted fluid. Analysis of single HCFI is potentially much better, but there are few quantitative techniques. The most informative methods require the extraction of the liquid from individual inclusions by drilling (mechanically, laser assisted, or ion etched) and subsequent analysis by Gas Chromatography and/or Mass Spectroscopy. Unfortunately, this results in sample destruction, and it is time-consuming. The most common non-destructive spectroscopic methods for the analysis of HCFI are FT-IR, Raman, and fluorescence spectroscopies. Raman spectroscopy is unusable (apart for the simplest hydrocarbon gases) with visible or near-IR excitation because of fluorescence interferences. FT-IR can be adversely affected by the presence of water in trapped fluids, interference from the host mineral, and other problems. Fluorescence based methods are widely used for studying HCFI and the most common identification method is by observing their fluorescence under UV illumination. The high sensitivity, wide variety of different techniques, and non-destructive nature of fluorescence makes it a potentially useful tool for HCFI analysis.

The use of visually determined fluorescence colour, for example, is widely used as a qualitative guide for assessing the maturity of oil trapped in fluid inclusions. However, the use of fluorescence colour is intrinsically prone to error, and does not yield quantitative results. However, it has been used, when calibrated with oils from the same basin/reservoir, to show variation in HCFI composition (changes in API gravity) in a single fluid inclusion assemblage. The fluorescence of crude oils is strongly influenced by chemical composition and physical properties of the oil. In general, heavy oils (low API gravity) tend to have relatively broad, more shifted to the red, less intense fluorescence bands and shorter fluorescence lifetimes in comparison to light oils (high API gravity). Those changes are produced by higher concentration of fluorophores and quenchers in heavy oils, which lead to higher energy transfer and quenching rates.

The excitation wavelength is also a factor that influences fluorescence behaviour of crude oils. Increasing the excitation wavelength results in narrowing of the fluorescence emission bands, and a reduction in Stokes’ shifts, fluorescence lifetime, and quantum yields. This is due to the excitation of different populations of fluorophores, which changes the fluorescence emission, the collisional quenching, and the energy transfer rates. The red-green quotient \( Q = \frac{I_{650nm}}{I_{500nm}} \), and the wavelength of maximum fluorescence emission intensity \( \lambda_{max} \), were found to correlate with API gravity and gross chemical composition (%w saturates, aromatics, polars and asphaltenes) for a set of HCFI synthesized using a sample set of Canadian crude oils. Both \( Q \) and \( \lambda_{max} \) were also shown to correlate well with gross chemical composition of Athabasca bitumen sub-fractions. Synchronous fluorescence excitation-emission spectroscopy was successfully applied as a possible tool for fingerprinting of oils trapped in HCFI sourced from the same oil field. More recently, Total Synchronous Fluorescence Scan Spectroscopy (TSFS) has been used to discriminate different refined and crude petroleum liquids, although, the technique does not yet offer a quantitative analytical method.

\[
API \text{ gravity} = ((141.5/\text{specific gravity at 15.6°C}) - 131.5)
\]
However, steady-state based fluorescence measurements suffer from several drawbacks. In general, all techniques based on the measurement of the absolute fluorescence intensity can be adversely affected by excitation source intensity variation, non-linear detector sensitivity, and photobleaching.\textsuperscript{27} The apparent fluorescence intensity and spectral distribution can be also be influenced by the physical properties of the sample such as geometry, opacity, sample turbidity, and the scattering properties of both the actual inclusion and host mineral. The last factor is particularly important in the context of HCFI studies where there is a large variation in sample type. Photobleaching of synthetic and natural HCFI has been shown to cause changes in the fluorescence emission intensity.\textsuperscript{28}

Time resolved fluorescence techniques,\textsuperscript{29} which have also been employed for characterization of petroleum products, are not only largely free of these artefacts,\textsuperscript{21,30} but in addition contain information that is lost in the time-averaging process inherent in steady-state methods. In the case of crude oils, which are complex mixtures of fluorophores, time-resolved fluorescence measurements offer the best approach for fully revealing the influence of quenching and energy transfer processes on fluorescence behaviour. As early as 1974, the fluorescence lifetimes of several petroleum products, including crude oils, were measured.\textsuperscript{31} A positive correlation between API gravity (for 4 crude oils) and fluorescence lifetime (measured at $\lambda_{\text{max}}$) was observed, and it was noted that fluorescence lifetime was dependent on the emission wavelength. Several later studies proposed the use of fluorescence lifetimes as a tool for monitoring oil pollution at sea.\textsuperscript{32,33,34} In 1987, McLimans mentioned the potential of using time resolved spectroscopy for analysis of HCFI.\textsuperscript{13} Mullins and Wang\textsuperscript{20} outlined the importance of energy transfer and quenching as the main factors influencing fluorescence lifetime behaviour of crude oils. In our laboratory, the use of fluorescence lifetime measurements for the characterization of crude petroleum oils is being investigated, with the objective of developing quantitative analytical methods for the prediction of both physical (API gravity) and compositional data such as aromatics, polars, alkane, and sulphur concentration.\textsuperscript{21,30,35,36}

In this work, we have conducted a detailed time-resolved fluorescence study on a set of 23 well-characterised, crude petroleum oils, from different geological sources, and on 6 hydrocarbon bearing fluid inclusions. The correlation between the compositional/physical data and the intensity-averaged fluorescence lifetime ($\bar{\tau}$) of the bulk crude oils was examined with the goal of developing a quantitative analytical method for characterising the composition of the oils trapped within HCFI.

**Materials and methods:**

The crude oil samples originated from thirteen different locations worldwide and were derived from seven different source rocks. The physical details and gross chemical composition, and the geographical and source rock information of the oils analysed in this study have been published in detail elsewhere.\textsuperscript{35,36} Table 1 outlines the most salient information and Fig. 1 shows a ternary plot of the gross chemical composition of the crude
The topped oils (198, 199, 201, 202)* were excluded from the gross chemical composition calibration models and used only in API gravity model as explained in a previous study.36 The inclusions ranged in size from ~30 μm to ~100 μm and the sample set consisted of inclusions with one (solid), two (liquid + vapour), and three-phase (liquid + vapour + solid) hosted by fluorite and quartz. Fig. 2 shows the different phases quite clearly. The inclusions originated from three different locations: inclusions F3a, F6b/d, and F8a were obtained from the Annabel Lee Mine, Hardin Co., Cave-In-Rock mining district, Illinois, USA, inclusion JP1 was from Baltic Quarry, South Wales, and JP2 from La Riqueza, Argentina. A suite of different fluorite rock samples was cut in-house to produce a number of wafers for analysis. Inclusions F6b and F6d were found on different wafers from the same rock sample (fluorite with barite coatings), while F3a and F8a were from two different rock samples. For the Baltic Quarry and La Riqueza samples, measurements were carried out on the whole quartz crystal.

Fluorescence lifetimes from bulk crude oil and inclusion samples were recorded using the Diode Laser Fluorescence Lifetime Microscope (DLFLM) developed in-house (Fig. 3). The system, which was described previously,37 has been modified to improve the accuracy of the lifetime measurement. In the earlier version of the DLFLM, a standard trinocular attachment (U-TR30, Olympus) was used in which the video port was used as the entry/exit for the laser excitation and fluorescence emission system. The field lens within the video port tube caused severe back reflections, making fitting of the fluorescence decay curves difficult. Furthermore, this arrangement prevented fitting a camera for sample observation to the microscope.37 The DLFLM was modified by connecting a double port tube accessory (U-DPT, Olympus) directly onto the microscope body, and then fitting a standard trinocular port (U-TR30) to one of the ports. That operation required fabrication of two one-piece flanges because of different sizes of dovetail mounts in U-TR30 and U-DTP ports. The U-DPT port is fitted with a three-way slider in which the light coming from the microscope objective can be either: directed to the U-TR30 port for visual observation of the sample, pass straight through to the monochromator and PMT detector for fluorescence measurements, or the light can be split 50:50 between the two ports for simultaneous observation and fluorescence measurements. In the standard U-DTP, in the “straight through” position, there is an optical flat (~20 mm thick), which causes excessive back reflections when the 405 nm laser is used. We removed this optical flat, eliminating the back reflection problem. This results in a small vertical disparity between the laser focus and the image plane, which does not adversely affect lifetime measurements. This U-DTP and U-TR30 combination mounted in reverse fashion also enabled a web camera (ToUcam, Phillips) to be fitted using a camera adapter (C-2000Z-ADP, Olympus).

All bulk oil studies were carried out on neat, non-degassed crude oil, held in 1 mm pathlength quartz cuvettes at room temperature. For the fluid inclusion measurements, it is critical that samples are free of any auto-fluorescing agents such as epoxy fixatives. Therefore, all fluid inclusion measurements were made on non-epoxied wafers or on the whole crystal sample. The fluorescence colour of the HCFI, under 405 nm excitation, was

* Topped oils are oils in which the light hydrocarbon fraction has been removed by gentle heating. In this case, the oils were heated at 60ºC for one hour.
visually observed via the microscope eyepiece, using a 435 nm longpass filter to block the scattered laser light. The instrument response function (IRF) was measured using a $10^5$ M DASPI methanol solution (in a sealed 10 mm pathlength quartz cuvette), at the same wavelength as the matching decay curve to discriminate against any monochromator timing effects.\textsuperscript{27} Fluorescence decay data was collected over the 460 - 700 nm wavelength range with a 20 nm step size, and the intensity-averaged fluorescence lifetimes ($\tau$) were calculated using the same criteria and methods as detailed in previous studies.\textsuperscript{21, 30, 35, 36}

Results and Discussion:

Bulk oil studies:

The plots of emission wavelength versus intensity-averaged fluorescence lifetime ($\tau$) for the crude petroleum oils show similar wavelength dependence pattern (Fig. 4) as observed previously.\textsuperscript{21, 30, 35, 36} The shortest $\tau$, in all cases, was found at the shortest emission wavelength sampled (460 nm), before reaching its maximum at around 560 – 700 nm, depending on the individual oil. This is because each emission wavelength represents a different population of emitting fluorophores with different rates of energy transfer and quenching. The increase at shorter wavelengths is due to collisional energy transfer, whereas the decrease at longer wavelengths is attributed to increase in collisional quenching and higher rate of internal conversion process.\textsuperscript{20, 30} The use of 405 nm laser diode excitation, as opposed to the 380 nm LED used in previous studies, also results in significant differences in measured $\tau$ values.\textsuperscript{35, 36} In general, $\tau$ decreases with increasing excitation wavelength, and in the case of the light oils the decrease is quite significant. The light oil (Fig. 4A, #7098) shows a decrease in $\tau$ of ~10 ns (19 down to 9 ns) at an emission wavelength of 550 nm, going from 380 to 405 nm excitation.\textsuperscript{35, 36} For the heavy oils, such as 7032 (Fig. 4D), there is a smaller difference, as the $\tau$ values are all around 1.0 ± 0.5 ns. The changes in $\tau$ are due to the excitation of different fluorophore populations, indicating the importance of specifying the exact excitation parameters for petroleum fluorescence studies. A further factor is that the LED has a broad excitation band with a spectral width of ~10 nm, which results in the direct excitation of a wider range of fluorophores compared to the narrow spectral width laser diode.\textsuperscript{21}

As with our previous studies using 380 nm LED excitation,\textsuperscript{36} no useful correlation was found between either the corrected/uncorrected aromatic concentration, or the asphaltene concentration, and $\tau$ at any of the emission wavelengths in the 460-700 nm range.\textsuperscript{38} In each case, the scatter about the linear fit lines was too great for quantitative measurements. Similarly, for API gravity, the relationship between $\tau$ and API gravity showed a considerable degree of scatter (Fig. 5). For the 4 emission wavelengths displayed, there is a general tendency to longer lifetimes as the API gravity increases (Fig. 5). The variation in $\tau$ values as a function of emission wavelength (above ~600 nm) is different for the heavy oils (increasing lifetime with increasing emission wavelength) and the light/medium oils (decreasing lifetime). Similar trends were found for other emission wavelengths sampled and in previous studies from this laboratory.\textsuperscript{21, 30, 35, 36}
The increase in lifetime with API gravity stems from the fact that there are fewer fluorophores and quenching species in the light oils as opposed to heavy oils. This leads to light oils having lower energy transfer and quenching rates, yielding relatively longer fluorescence lifetimes. Even though there is a positive correlation for each emission wavelength, the degree of scatter around the fit line is very large and there are a number of outliers. In particular, oil 7098 and oil 7633 have unusually long lifetime in comparison to other oils with similar API. They both have relatively low polar, low sulphur and high alkane concentration that substantially reduces quenching rates yielding long fluorescence lifetimes. On the other hand, oil 7062 displays atypically short lifetimes for its API gravity of 36. This oil combines comparatively high polar and sulphur contents, which leads to increased quenching and in turn provides for those short lifetimes. These results clearly show that API gravity cannot be estimated with any accuracy from the $\tau$ data collected using 405 nm excitation.

We have already established that quenching and the concentration of polars have the greatest influence on $\tau$. The same is found with 405 nm excitation (Fig. 6), but the data is best fitted using a logarithmic model, rather than a reciprocal model used for the 380 nm excitation data. There is a slightly better correlation when using the measured concentration (Fig. 6A) as opposed to the corrected polar concentration (Fig. 6B). There was no improvement at any of the other emission wavelengths sampled. The considerable scatter for both plots around the fit line occurs predominantly for the mid range oils with polar concentrations of 5-15%. This scatter is probably due to variation in the concentration of other oil constituents, in particular the alkane fraction.

There is a generally negative correlation between the average fluorescence lifetimes and sulphur concentration, indicating that many of the sulphur containing constituents act as quenchers. Similarly, in this work we find that $\tau$ decreases with sulphur concentration (Fig. 7). However, there is a substantial amount of variation, especially for oils with sulphur concentration around 0.1-1% (shaded area), which prevents the quantitative estimation of sulphur concentration. This could be due to variations in the polar constituents, although using a combined polar and sulphur concentration (Fig. 8) does not yield any improvement in the correlations with $\tau$ when compared to Fig. 6A. This would suggest that for the mid-range oils, not all of the sulphur-containing species act as quenchers.

The alkane fraction, which is largely non-fluorescent at this excitation wavelength, tends to act as a solvent, diluting the fluorophores and quenchers, leading to a reduction in the rates of collisional quenching and energy transfer. There is a general trend towards longer lifetimes as the alkane concentration increases but the degree of scatter is very large, which makes any accurate fitting impractical (data not shown for 405 nm excitation). As in the previous study, where the corrected alkane concentration was used, a clear exponential growth dependence can be seen (Fig. 9A). Similar dependence can be seen if a combined concentration of alkane and losses is used (Fig. 9B) and, given that there is no significant difference whether a corrected or measured polar concentration is used (Fig. 6) one can assume that the column losses represent mainly light alkane fractions. The plots in Fig. 9 can be used to discriminate light from heavy oils, but caution still needs to be exercised. All that can be inferred is that long lifetimes of 8 ns (or more) are obtained from oils with corrected alkane concentrations of 80-85% or greater.
In summary, the direct correlation of $\tau$ and individual gross chemical composition measurements is not suitable for quantitative use. In each case, there is significant scatter for the mid-range oils, which is due to the influence of the other constituents. It therefore makes sense to try to correlate $\tau$ with a composite parameter that takes into account the variation of the other significant constituents. If we plot $\tau$ (measured at 540 nm) versus the ratio between combined polar and sulphur concentration, and the combined alkane and losses concentration (PS/AL), the degree of scatter is slightly reduced (Fig. 10). The PS/AL ratio can be taken as an approximation of the quencher concentration, with low PS/AL values representing the light oils. The $\tau$ data is best fitted to a simple exponential curve, with the least scatter being observed for $\tau$ values of ~1.0 ns. This represents the heavy oils (API gravities < 22), all of which have PS/AL ratios of > 0.3. The only anomaly is the oil 7062, which has a relatively high API gravity (36º) but has very short lifetimes; however, the high PS/AL ratio indicates a large quencher concentration (polar conc. =17.2%, asphaltene conc.=10.8%). Unfortunately at PS/AL ratios of < 0.2, the data becomes scattered again as the oils get lighter. This is a consequence of the quencher concentration being diluted by increased alkane content, which leads to a greater sensitivity of fluorescence lifetime to small changes in quencher concentration. There could also be a greater influence exerted by the nature and type of fluorophores in the lighter oils. A logarithmic fit was also done on the data but the degree of scatter is still excessive at PS/AL values of ~0.1. However, Fig. 10 and the PS/AL value can be used to discriminate oils with high quencher concentrations, irrespective of the API gravity.

**Fluid inclusions studies:**

Samples F3a, F6b, F6d, F8a, and JP1 displayed a relatively strong fluorescence (405 nm excitation) that appeared green in colour as visually observed via the microscope binocular eyepiece. No fluorescence colour was visible via the binocular eyepiece for sample JP2, and the approximate fluorescence intensity was nearly an order of magnitude lower than that measured for a bulk sample of the heavy crude oils.† In Fig. 11 the $\tau$ - wavelength dependence for 5 HCFI (Fig. 11A) are plotted, along with data from several light oils for comparison (Fig. 11B). As in the case for bulk oils, the shortest $\tau$ (excepting JP2), was found at 460 nm (the shortest emission wavelength sampled), before reaching a maximum between 540 - 680 nm.

JP1 differs from the F series inclusions with a maximum $\tau$ at 540 nm, which then decreases substantially at longer wavelengths. This indicates a considerably different chemical composition of the entrapped oil, which arises because it originated from a different geographical location. The JP1 lifetime-wavelength plot resembles that of the light oil 7098 (44.6 API), a mature oil with a very low polar (0.7%) and high alkane content. However, JP1 has longer lifetimes than 7098 and the wavelength of maximum lifetime is blue shifted (10-15 nm) which indicates a lower quencher concentration and a reduced distribution of fluorophores in the inclusion.

† We did not attempt to make accurate quantitative measurements of the fluorescence intensities from the HCFI.
Inclusion F3a has a maximum $\tau$ of $\sim8$ ns at about 650 nm, similar in magnitude to that of 7098 and 7633, although the wavelength dependence pattern is different. The plot shape is similar to that for the oils 7058, 7703, 199, and 201, with slightly longer lifetimes in the red part of the spectrum. This would indicate that the trapped oil has a high alkane concentration and relatively low polar concentration, which indicates a more mature oil. The red shift for the wavelength of maximum lifetime would also indicate that the oil is less mature than sample JP1.

The recovered $\tau$ values for samples F6b, F6d, and F8a are longer than for any of the bulk crude oils studied indicating that the trapped oils have lower polar and/or higher alkane concentrations than the bulk oils. The red shifted wavelength of the lifetime maximum indicates a fairly broad distribution of fluorophores. F6b and F6d show the same lifetime-wavelength curve indicating that they contain identical samples of oil. From Fig. 6 and 9, the oil entrapped in F6b and F6d has an estimated composition of $<10\%$ polar and $>90\%$ corrected alkane concentrations. Sample F8a has shorter lifetimes indicating a greater degree of quenching, which is probably due to a slightly higher polar concentration. The lifetime-wavelength plots for all 4 Cave-In-rock samples have the same shape indicating that the oils have similar populations of fluorophores. However, the large differences in lifetime between the HCFI indicate that the oils have different quencher concentrations in solution. It could be that in F6b and F6d the polar quenchers have precipitated out of solution forming the solid phases which are visible in Fig. 2B and 2C. The reduced polar concentration in the liquid phase leads to an increase in the measured fluorescence lifetime. For F3a and F8a, there are no clearly visible solid phases, which could indicate that the polar constituents are still in solution, resulting in higher quenching rates/shorter lifetimes.

The final HCFI sample, JP2, was found to have very short $\tau$ values ($\sim$0.7-0.1 ns), indicating the presence of a heavy oil and/or bitumen. The lifetime data from JP2 is plotted in Fig. 12, for comparison with two heavy oils (7033 and 7188). The very short $\tau$ indicates extensive fluorescence quenching, which is probably due to a high polar concentration ($>20\%$, from Fig. 6A). However, the solid nature of the material and the unusual wavelength dependence of $\tau$ prevent any further correlations. From the shape of the plot, it seems to indicate that the longer wavelength fluorescence is quenched at a much greater rate than that emitting below $\sim$500 nm. This longer wavelength emission has been shown to originate from energy transfer processes, and another study has shown that at these elevated polar concentrations, quenching occurs mainly via a static mechanism (quenching sphere of action or the formation of ground state complexes). The higher quenching rate at longer wavelengths could arise from both the donor and acceptor molecules being quenched. Conversely, at shorter wavelengths where emission is more likely to originate from direct emission, quenching only occurs at a single fluorophore. This effectively doubles the quencher concentration leading to a drop in lifetime. We are currently investigating this unusual behaviour using time-resolved fluorescence emission spectroscopy.
Conclusions:
In our quest to develop a quantitative method for the analysis of crude petroleum oils from different locations using fluorescence lifetime methods, we have used the intensity averaged fluorescence lifetime (τ) parameter. Using 405 nm excitation, τ data was collected from 23 crude petroleum oils and 6 HCFI. As in previous studies with 380 nm excitation sources, the best correlations are found with either the corrected alkane or the measured polar concentration, while API gravity does not correlate well. However, there is little scope for developing accurate quantitative prediction models based on these non-linear correlations because there is extensive scatter. This scatter is due to the extensive geological range from which the samples originated and because the simple τ model cannot account for the complex distributions of fluorophores from the different oil types. It seems plausible, however, that a more restricted set of oils, perhaps sampled from a single basin, would yield better results, and this is currently being investigated. In this case, the oils are derived from the same organic source material, which should lead to a smaller variation in chemical compositions. However, the data obtained on the bulk oils can enable the classification of oils trapped in HCFI into alkane rich (85% +) or polar rich oils (20% +) based on the correlations found with the bulk oils. The best discrimination is based on the (polars+sulphur)/(alkane+loss) ratio where oils can be separated into two groups: high and low-medium quencher concentrations.

Using a modification of an earlier experimental setup, τ data were easily obtained from the HCFI samples. Comparing the HCFI and crude oil data shows that the τ-wavelength dependence follows similar trends, except for the solid JP2 sample. For the samples F3a, F6b, F6d, F8a, and JP1 we can estimate that the trapped oils have low polar / high alkane concentrations, indicating late maturity oils. In addition, the lifetime-wavelength plots show that F6b and F6d have identical hydrocarbon content, while F3a and F8a have similar oils but with a higher quencher concentration. The differences are probably due to more polar species remaining in solution in F3a/F8a when compared to the F6 samples where they could have precipitated out into the solid phase. In case of JP2 (probable bitumen inclusion) we get a clear indication that the inclusion content is low alkane / high polar material. However, the measured lifetimes for 4 of the 6 HCFI are considerably larger than the calibration oils, indicating that the trapped fluids are much lighter or have lower polar concentrations than the calibration oils. This highlights a problem in using dead oils where the very light hydrocarbon fractions have been removed or lost in the extraction/sampling phases. In HCFI, one would expect that these fractions are still present, thus raising the API gravity, and more importantly the alkane concentration, resulting in longer lifetimes. We hope to improve the classification method for HCFI by extending the fluorescence lifetime range covered by the calibration model, by using alternative methods for calculating fluorescence lifetime, and by developing a more complete photophysical model for petroleum fluorescence.

‡ Dead oils are oils in which the dissolved gas component has been lost. This component is largely of methane or other light alkanes.
Acknowledgements:

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</tr>
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<td>39.5</td>
<td>40.16</td>
<td>3.87</td>
<td>7.65</td>
<td>48.32</td>
<td>0.59</td>
</tr>
<tr>
<td>7090</td>
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<td>53.14</td>
<td>4.74</td>
<td>10.50</td>
<td>31.62</td>
<td>0.26</td>
</tr>
</tbody>
</table>

* These topped oils were only used for the API models.

Table 1: Fractionation data for the crude petroleum oils used in this fluorescence study.
<table>
<thead>
<tr>
<th>Oil #</th>
<th>API gravity</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Polars</th>
<th>Column Loss</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>7093</td>
<td>30.9</td>
<td>33.86</td>
<td>19.35</td>
<td>11.47</td>
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<tr>
<td>7098</td>
<td>44.6</td>
<td>42.18</td>
<td>4.61</td>
<td>0.70</td>
<td>52.51</td>
<td>0.043</td>
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<tr>
<td>7130</td>
<td>15.6</td>
<td>43.57</td>
<td>17.47</td>
<td>24.56</td>
<td>14.40</td>
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<td>7169</td>
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<td>44.71</td>
<td>18.83</td>
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<td>16.44</td>
<td>0.50</td>
</tr>
<tr>
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<td>46.39</td>
<td>12.32</td>
<td>2.61</td>
<td>38.68</td>
<td>0.09</td>
</tr>
<tr>
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<td>52.20</td>
<td>23.9</td>
<td>4.39</td>
<td>19.51</td>
<td>0.10</td>
</tr>
<tr>
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<td>19.33</td>
<td>40.17</td>
<td>8.1</td>
<td>0.44</td>
</tr>
<tr>
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<td>50.73</td>
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<tr>
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<td>3.73</td>
<td>26.34</td>
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Table 1: Continued.
<table>
<thead>
<tr>
<th>Sample</th>
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<th>Host</th>
<th>Colour*</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
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<td>F3a</td>
<td>Cave-In-Rock, Illinois, USA</td>
<td>Fluorite</td>
<td>Yellow-brown</td>
<td>liquid + vapour</td>
</tr>
<tr>
<td>F6b</td>
<td>Cave-In-Rock, Illinois, USA</td>
<td>Fluorite</td>
<td>Yellow</td>
<td>liquid + vapour + solid</td>
</tr>
<tr>
<td>F6d</td>
<td>Cave-In-Rock, Illinois, USA</td>
<td>Fluorite</td>
<td>Yellow</td>
<td>liquid + vapour + solid</td>
</tr>
<tr>
<td>F8a</td>
<td>Cave-In-Rock, Illinois, USA</td>
<td>Fluorite</td>
<td>Yellow</td>
<td>liquid + vapour</td>
</tr>
<tr>
<td>JP1</td>
<td>Baltic quarry, South Wales</td>
<td>Quartz</td>
<td>Pale yellow</td>
<td>liquid + vapour</td>
</tr>
<tr>
<td>JP2</td>
<td>La Riqueza, Argentina</td>
<td>Quartz</td>
<td>Black</td>
<td>solid</td>
</tr>
</tbody>
</table>

* as visually observed using transmitted white light illumination.

**Table 2:** Source, host mineral, and appearance details for the fluid inclusions analysed.
Figure 1: Ternary plot of the gross chemical composition of crude petroleum oils used in this study. The topped oils (198, 199, 201, 207) are marked with a hollow circle. The concentrations are corrected for column losses.

Figure 2: Photomicrographs of the fluid inclusion used in this study viewed under transmitted white light. A). F8a, B). F6d, C). F6b, D). F3a, E). JP1, F). JP2. Sample images are not all on the same scale.
Figure 3: DLFLM set-up: LDH 400 – 405 nm violet pulsed laser diode, BF – 405 nm excitation filter, ND - neutral density filter, M – mirror, DM - dichroic beamsplitter, LP – 435 nm longpass filter, L – lens, PMT- photomultiplier tube, SPC 730- integrated TCSPC PC card, DC- Philips ToUcam digital web camera, U-DPT – Olympus double port accessory, U-TR30 - standard Olympus trinocular attachment.

Figure 4: Plot of average fluorescence lifetime ($\bar{\tau}$) versus emission wavelength for a set of crude oils studied: A) Light oils, API gravity = 50.6 - 36˚; B), C) Medium oils, API gravity = 36.8˚ - 24.8˚, D) Heavy oils, API gravity = 21.6˚ - 12.8˚.
Figure 5: Plot of average fluorescence lifetime ($\tau$) versus API gravity [$^\circ$] at the emission wavelengths of: A) 460 nm; B) 500 nm; C) 540 nm; D) 700 nm. The best linear fit and the value of correlation coefficient $r$ for each emission wavelength are also plotted.
Figure 6: Plot of average fluorescence lifetime ($\bar{\tau}$) versus: A) measured polar concentration; B) corrected polar concentration; at the emission wavelength of 540 nm. The best logarithmic fit and the value of correlation coefficient $r$ for each concentration are also plotted.

Figure 7: Plot of $\bar{\tau}$ measured at 540 nm versus sulphur concentration (log scale).
Figure 8: Plot of combined polar (as measured) and sulphur concentration versus $\tau$ measured at 540 nm. The best logarithmic fit and the value of correlation coefficient are also plotted.

Figure 9: Plot of $\tau$ versus: A) corrected alkane concentration; B) sum of alkane concentration and column losses at the emission wavelength of 540 nm. The best exponential growth fit and the value of correlation coefficient $r$ for each concentration are also plotted.
Figure 10: Plot of the ratio of the sum of measured polar and sulphur concentration divided by the sum of alkane and column losses concentration versus $\tau$ measured at 540 nm. The best logarithmic fits and the value of correlation coefficients $r$ are given.

Figure 11: Plot of $\tau$ versus emission wavelength for: A) HCFI samples, B) several light crude oils, API gravity = 50.6° - 40.1°.
Figure 12: Plot of $\tau$ versus the emission wavelength for a bitumen sample JP2 along the two heaviest oils studied.
References


38  M. A. Przyjalgowski, A. G. Ryder, unpublished results.