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Influence of chemical composition on the fluorescence lifetimes of crude petroleum oils.

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ABSTRACT

Fluorescence based methods are increasingly being used for the analysis of crude oils because they offer high speed, low cost, non-contact, and non-destructive testing options. The fluorescence of crude oils is due to the presence of a wide range of cyclic aromatic compounds, with the intensity and temporal behaviour of this fluorescence being directly related to chemical composition. In particular, we have found that the Fluorescence Lifetime (FL) measured at a range of different emission wavelengths is correlated with the concentrations of the aromatic and polar fractions of petroleum oils, and the density (API gravity).

We have analysed 22 different crude oils from around the world with API gravities of between 10 to 50. The fluorescence steady-state emission spectra and fluorescence lifetimes at a range of emission wavelengths were measured for 380 nm excitation. It was found that the correlations between the chemical and physical characteristics of the crude oils and the measured fluorescence parameters are highly non-linear. Furthermore, there is a wide degree of scatter in the observed data for medium oils, which have similar physical properties but widely varying chemical compositions. We discuss these findings in the context of developing quantitative methods of analysis for crude petroleum oils based on fluorescence lifetime measurements.

Keywords: Fluorescence, lifetime, petroleum, API gravity, asphaltene, sulphur, aromatic.

1. INTRODUCTION:

The non-contact, non-destructive, and rapid analysis of crude petroleum oils is desirable for environmental protection, process control, or oil exploration purposes. Most petroleum oils are fluorescent because of the presence of cyclic aromatic hydrocarbons and therefore, fluorescence techniques can be used to fulfil this analysis function.¹

The fluorescence behaviour of petroleum oils is based not only on the chemical and physical composition but also on the excitation wavelength employed. In general, light oils (high API gravities) will have narrow, intense emission bands with small Stokes shifts while heavy oils (low API gravities) tend to have broad, less intense bands with greater Stokes shifts. This is due to the high concentration of fluorophores present in heavy oils, which in turn leads to a high rate of collisional energy transfer, yielding a red shift in the emission spectrum. Heavy oils also tend to contain appreciable amounts of materials, which quench fluorescence non-radiatively, resulting in low fluorescence intensities. Conversely, light oils (high API gravity), with more dilute fluorophore concentrations, have reduced rates of energy transfer, and so a narrower emission

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band.^{2, 3} The lower concentration of quenching species in light oils also results in a higher fluorescence emission intensity. These effects also impact on the fluorescence lifetime of petroleum oils, with heavy oils having shorter lifetimes on average, than lighter oils.^{4, 5}

The excitation wavelength affects the steady state fluorescence spectra and lifetime of crude oils, by reducing the Stokes shift, and by narrowing the emission band as the excitation wavelength increases. This is due to a reduction in energy transfer rates because the longer wavelength excitation is preferentially exciting larger PAH molecules with lower bandgaps and therefore lowers energy transfer rates. Longer wavelength excitation also results in a shortening of the observed fluorescence lifetimes.^{6, 7, 8}

The use of fluorescence based methods for the characterisation of petroleum products has been widely demonstrated. Steady state fluorescence emission spectroscopy has been used to characterize bulk petroleum materials from liquid oils, both crude and refined,⁹ to solid asphaltenes,¹⁰ bitumens,¹¹ and kerogens.^{12, 13} However, steady state fluorescence measurements can be very sensitive to intensity fluctuations due to sample turbidity or source / detector instability, and inner-filter effects. Fluorescence lifetime based sensing methods can overcome these problems and provide a method that is easier to calibrate. Furthermore, the instrumentation can be made very compact and robust using the latest generation of semiconductor excitation sources and detectors.¹⁴

Fluorescence lifetime analysis of crude and refined petroleum oils have shown that there was a clear increase in lifetime with increasing API gravity and that there was also an increase in lifetime with longer emission wavelength up to ~600 nm when using a pulsed nitrogen laser (337 nm excitation).¹⁵ Other excitation sources which have been used to obtain oil lifetimes have included: a synchrotron source (316 nm),⁴ a frequency tripled Nd:Yag laser (355 nm),¹⁶ visible (460 and 510 nm)⁵ and UV Light Emitting Diodes (380 nm).⁶ In all cases the same general trends are observed but since the full oil composition is rarely provided it can be difficult to determine which constituents of petroleum oils have the largest influence on the lifetimes. Furthermore, the use of different excitation wavelengths and calculation methods for fluorescence lifetimes, can make it difficult to compare the findings of the various studies.

We have been investigating the fluorescence lifetime behaviour of petroleum crude oils with a view to developing a robust quantitative method for oil composition suitable for both bulk and microscopic analysis.^{5, 6} In this previous work, there was only a very limited chemical information available on the composition of the oils (API gravity, aromatic concentration, and sulphur content) In this work we describe the effect of a wide range of chemical parameters on the fluorescence lifetime behaviour of a series of petroleum oils and how this impacts on the development of quantitative methods based on fluorescence lifetimes.

2. EXPERIMENTAL:

2.1 Apparatus and Procedure.

All optical measurements were made with the neat, non-degassed oil or tar, held in 1 mm pathlength, Teflon stoppered, quartz cuvettes at room temperature. Steady-state fluorescence measurements were made using a Perkin-Elmer LS-50B fluorescence spectrometer using an excitation wavelength of 380 nm, operating with a 10 nm bandpass, and fitted with a front surface sampling accessory. Fluorescence lifetimes were measured using a Time Correlated Single Photon Counting (TCSPC) system with a 380 nm LED excitation source, which had been assembled in-house.⁵ The Instrument Response Function (IRF) was obtained from a non-fluorescing suspension of alumina in a 1 mm pathlength quartz cell and was assumed to be wavelength independent. Lifetimes were obtained by deconvolution of the decay curves using the FluoFit software program (PicoQuant GmbH, Germany) and were fitted to bi- and tri-exponential models. All lifetimes quoted were fit to a χ^2 value of less than 1.2 and with a residuals trace that was fully symmetrical about the zero axis. The average lifetimes quoted throughout are the intensity averaged lifetime, defined as $\bar{\tau} = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i$.

2.2 Materials:

The crude petroleum oil samples (Table 1) originated from a variety of different locations worldwide and were kindly provided by Robertson Research International (RRI). The chemical analysis for each oil was carried out by RRI; the most salient data is reproduced below.

Oil #	API ^a	Asphaltenes (%)	Aromatics (%)	Alkanes (%)	Polars (%)	S (%)	Wax (%)
1	12.8	16.2	25.55	19.35	26.32	5.51	1.7
2	13.3	1.1	19.33	32.40	40.17	0.44	17.6
3	15.6	0.05	17.47	43.57	24.56	0.35	2.1
4	19.1	17.5	26.52	30.58	22.17	5.38	3.9
5	21.6	1.4	18.53	44.72	20.31	0.50	4.3
6	24.8	0.7	2.93	67.00	3.73	0.05	13.0
7	29.4	0.8	23.9	52.20	4.39	0.10	8.3
8	29.8	0.06	29.1	55.20	10.5	--	--
9	30.4	0.03	28.5	54.60	10.5	--	--
10	30.9	3.5	19.3	33.86	11.47	0.36	1.89
11	31.5	0.1	28.8	58.00	11.20	--	--
12	32.3	1.0	13.95	42.87	6.57	0.32	0.6
13	32.7	1.5	2.70	43.78	12.2	0.11	5.1
14	34.3	0.1	12.32	46.39	2.61	0.09	1.3
15	36.0	10.8	23.33	32.28	17.2	1.74	4.06
16	36.0	1.7	12.37	50.73	4.89	0.17	1.6
17	38.0	0.3	23.70	63.1	10.20	--	--
18	39.5	0.5	3.87	40.16	7.65	0.59	0.9
19	40.1	0.04	18.15	34.08	3.45	0.96	3.57
20	44.6	7.5	4.61	42.18	0.70	0.04	0.95
21	45.1	0.4	6.59	38.84	1.93	0.10	4.6
22	50.6	0.0	1.79	12.83	1.58	0.49	1.3

^a The API gravity of an oil is related to the density by the formula:

$$\text{API gravity} = ((141.5/\text{specific gravity at } 15.6^\circ\text{C}) - 131.5).$$

Table 1: Chemical composition and API gravities of the oils utilised in this study. All data supplied courtesy of Robertson Research International.

The samples varied in colour from pale straw coloured to black. The viscosities also showed a large degree of variation from free flowing liquid to immobile tars.

3. RESULTS & DISCUSSION:

The average fluorescence lifetime of crude petroleum oils is very dependant on the emission wavelength at which it is measured (Fig. 1). This is because each emission wavelength represents a different population of emitting species produced by either direct excitation by the LED or by energy transfer processes.⁶

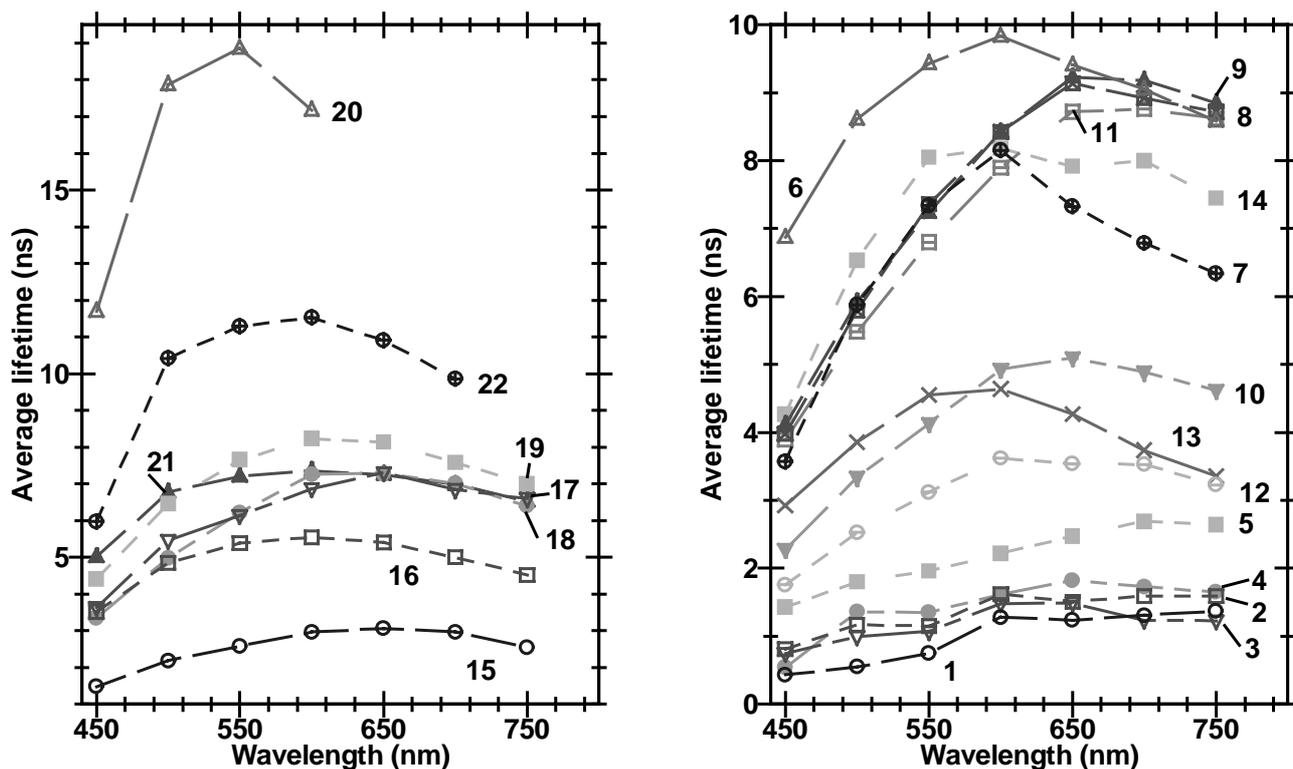


Figure 1: Plots of average fluorescence lifetime versus emission wavelength for: (A) Light oils (API > 35); and (B) Medium to heavy oils (API < 35). 380 nm LED excitation.

In general, the increase in fluorescence lifetime is due to collisional energy transfer processes, while the decrease at longer wavelength is due to increased quenching rates of the red emitting species. Another important facet of these plots is the fact that there is a large lifetime spread (~20 ns) and that there is considerable overlap between the light and medium/heavy oils. For example, oil #6 with an API of 24.8 has very similar lifetimes at all emission wavelengths to that of the light oil #22 (API = 50.6). This highlights the difficulty in using lifetimes to predict or correlate the API gravity of crude petroleum oils.

Plotting the average fluorescence lifetime (at 450 nm) versus API gravity (Fig. 2A) shows that there is a general trend to longer lifetimes with higher API gravities, as has been noted previously.^{5, 6} This is expected since the lighter oils contain lower concentrations of emitting fluorophores and quenching species, which results in less collisional quenching and energy transfer processes, and yielding relatively longer lifetimes. However, the plot shows a number of outliers and a considerable

degree of scatter about the trend line. This is not due to measurement error but rather due to the compositional complexity of the oils. In the case of the two outliers (6 & 20) with very long lifetimes, the large deviation from the trend line is because they both have very low aromatic, polar, *and* sulphur concentrations in comparison to the other oils. Since these three components of petroleum provide the majority of the potential quenching and energy transfer molecules, the low combined concentration results in long fluorescence lifetimes. We have also examined the fluorescence lifetime dependence on API gravity at emission wavelengths between 500 and 785 nm, and found there is no substantial reduction in the degree of scatter.†, 17 These results highlight the difficulty in using a purely physical parameter (API gravity) for characterising oil types, based on a measurement method that derives directly from the source chemical composition (fluorescence).

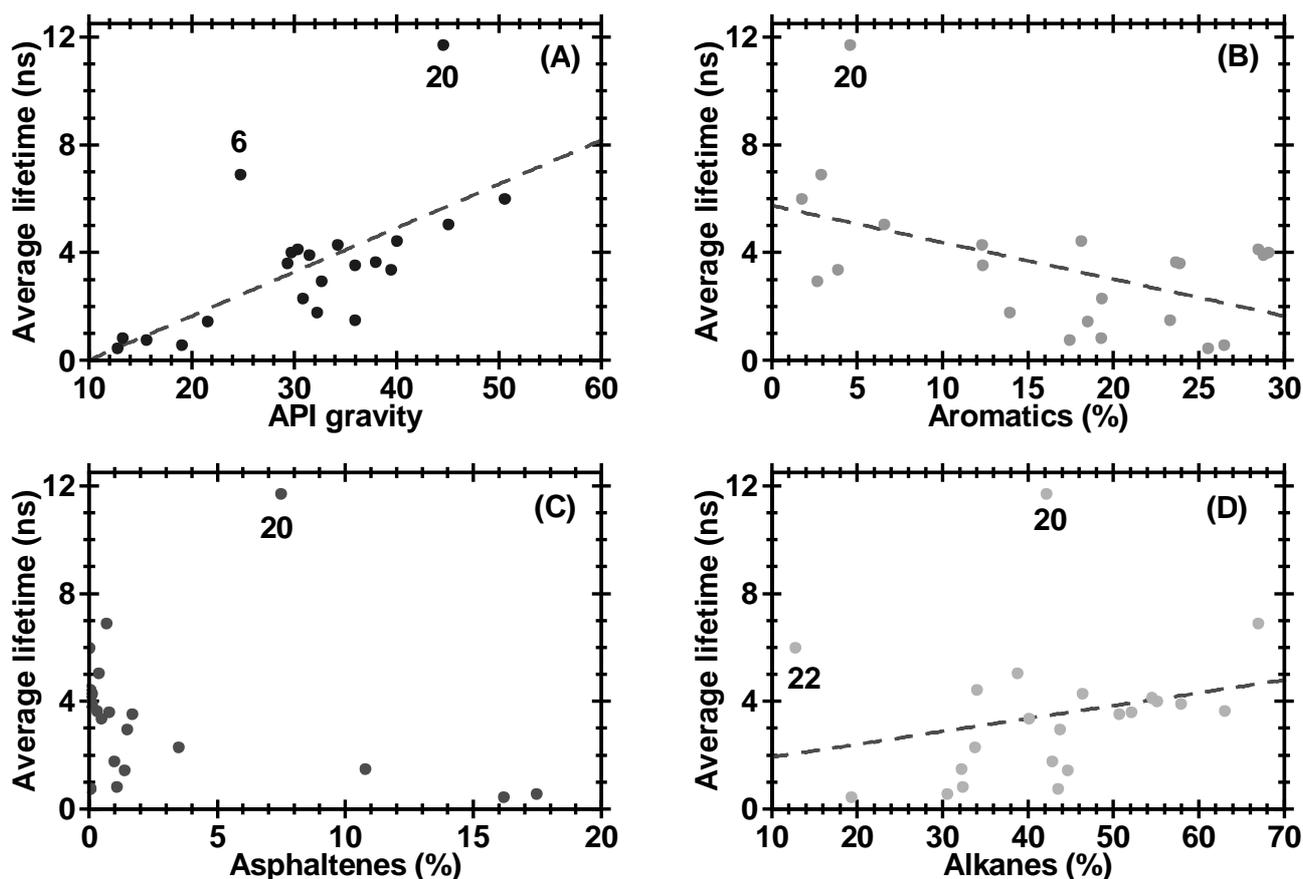


Figure 2: Plots of average fluorescence lifetime versus: (A) API gravity; (B) Aromatic concentration (% by weight); (C) Asphaltene concentration (% by weight); (D) Alkane concentration (% by weight). All data acquired at an emission wavelength of 450 nm using 380 nm excitation.

In the case of aromatic concentration, (Fig. 2B), there is a slight decrease in the average lifetime with increasing aromatic concentration but again the degree of scatter is very large, reflecting the influence of different chemical components. The slight negative correlation is due to the fact that, as the petroleum oil gets denser, the concentration of large Polycyclicaromatic Hydrocarbons (PAH) increases. These molecules have small bandgaps, and higher collisional quenching

† Similar results were found for all the other chemical parameters provided for the oils.

rates, than those in light oils and therefore there is a decrease in the fluorescence lifetime. However, this trend is small and is overshadowed by the large degree of scatter caused by other components of the oils, primarily via collisional quenching.

The asphaltene[§] fraction, which is composed of high molecular materials, would be expected to contain a large proportion of materials that should quench fluorescence. For most oils, this is the case (Fig. 2C) with oils of high asphaltene concentrations having short lifetimes except for oil 20, which has a very long lifetime and an asphaltene concentration of 7.5%. This would seem to indicate that asphaltenes might not be a good source of quenchers, particularly in light oils. This could be due to the very low solubility of the asphaltene fraction, in which case the asphaltenic materials in light oils will be suspended as a colloid or emulsion in the hydrocarbon fluid and are not available to quench the fluorophores which are dissolved in the mainly alkane liquid phase.

The plot of alkane concentration versus average lifetime (Fig. 2D) again shows a high degree of scatter and a weak positive correlation. The alkane fraction, which is non-fluorescent (at this excitation wavelength), acts as a non-quenching solvent in which the fluorophores and quenchers are dissolved. As such, a greater alkane concentration results in a lower fluorophore concentration, a reduced rate of energy transfer, and therefore a longer fluorescence lifetime. However, these dilute fluorophore populations are much more sensitive to quenching and this is why there is such a degree of scatter in the plot.

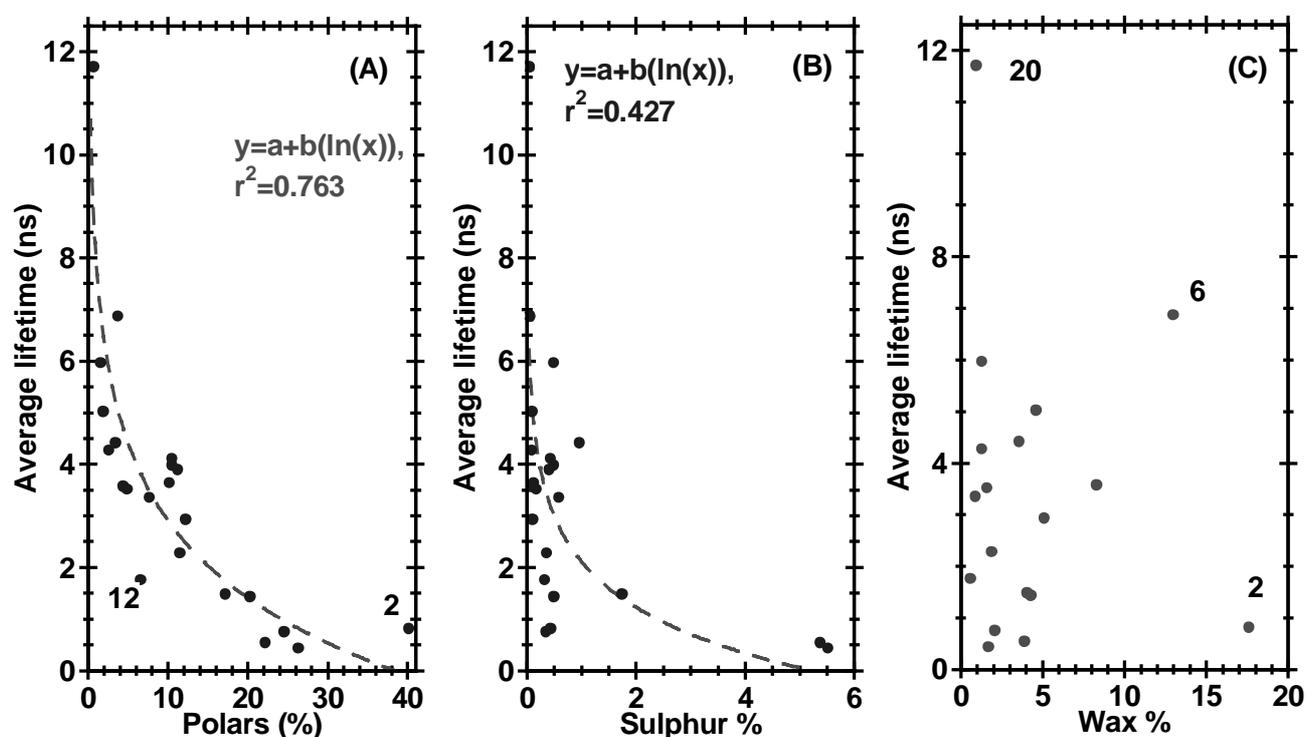


Figure 3: Plots of average fluorescence lifetime versus: (A) Polar concentration (% by weight); (B) Sulphur concentration (% by weight); (C) Wax concentration (% by weight); All data acquired at an emission wavelength of 450 nm with 380 nm excitation.

[§] The insoluble residue remaining after hexane or pentane extraction of crude oils.

The most significant factor influencing the fluorescence lifetime of crude oils is the polar concentration (Fig. 3A) which displays a near logarithm dependence ($y=a+b(\ln(x))$). This is because the vast majority of fluorescence quenchers would tend to be polar molecules, and as such, oils with high polar concentrations will have short lifetimes. However, there is a considerable degree of scatter, which indicates that other factors need to be considered. This scatter could be due to the different populations of polar quenchers having different quenching rates, and because the oils all originate from different sources, the populations may be considerably different resulting in different quenching rates and lifetimes. The other case is that the polar populations for each oil are substantially the same except for concentration and that the variation is introduced by variations in the concentrations of other oil constituents. The presence of sulphur containing compounds also cause a large decrease in the average fluorescence lifetime (Fig. 3B) but again there is a large degree of variation particularly for oils with sulphur concentrations in the 0.1 to 1% range. This makes it difficult to estimate the sulphur concentration on the basis of fluorescence lifetime measurements alone.

The concentration of waxes in the oils does not correlate well with fluorescence lifetime and there is a considerable degree of scatter (Fig. 3C). This is to be expected since waxes (long chain saturated hydrocarbons) do not absorb light at this excitation wavelength and will not quench fluorescence either. In effect they are a hydrocarbon solvent and their only effect on lifetime would be due to an increase in viscosity, the effect of which is negligible in petroleum oils where quenching and energy transfer dominate.

4. CONCLUSIONS:

The descriptive parameters obtained from standard chemical analysis of crude petroleum oils (API gravity, aromatic / asphaltene / polar /alkane / sulphur concentrations) do not correlate very well with the average fluorescence lifetimes measured using 380 nm excitation. In each case, the influence of other oil components results in large differences in the fluorescence lifetime behaviour of oils with similar composition. The most significant factor influencing the fluorescence lifetime is the concentration of quenching species, which are primarily the sulphur, polar, and asphaltene fractions.

Since no single factor can account for the fluorescence lifetime variation we are investigating a new series of descriptors for crude petroleum oils that will better describe the variation in fluorescence lifetimes. These new descriptors will be based on the most significant factors from traditional chemical analyses and it is hoped that these may be more suitable for use in qualitative and quantitative analysis.

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