

Frequency Domain Fluorescence Lifetime Study of Crude Petroleum Oils

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Abstract Frequency domain (FD) fluorescence lifetime data was collected for a series of 20 crude petroleum oils using a 405 nm excitation source and over a spectral range of ~426 to ~650 nm. Average fluorescence lifetimes were calculated using three different models: discrete multi-exponential, Gaussian distribution, and Lorentzian distribution. Fitting the data to extract accurate average lifetimes using the various models proved easier and less time consuming for the FD data than with Time Correlated Single Photon Counting (TCSPC) methods however the analysis of confidence intervals to the computed average lifetimes proved cumbersome for both methods. The uncertainty in the average lifetime was generally larger for the discrete lifetime multi-exponential model when compared to the distribution-based models. For the lifetime distributions, the data from the light crude oils with long lifetimes generally fit to a single decay term. Heavier oils with shorter lifetimes required multiple decay terms. The actual value for the average lifetime is more dependant on the specific fitting model employed than the data acquisition method used. Correlations between average fluorescence lifetimes and physical and chemical parameters of the crude oils were made with a view to developing a quantitative model for predicting the gross chemical composition of crude oils. It was found that there was no sig-

nificant benefit gained by using FD over TCSPC other than more rapid data analysis in the FD case. For the FD data the Gaussian distribution model for fluorescence lifetime gave the best correlations with chemical composition allowing a qualitative correlation to some bulk oil parameters.

Keywords Fluorescence · Petroleum · Crude oil · Fluorescence lifetime · Frequency domain · Phase modulation

Introduction

Petroleum oils are complex mixtures of aliphatic, aromatic, and high molecular weight organic compounds and due to this heterogeneity, chemical analysis is complex and time consuming. Petroleum oils are typically characterised using liquid chromatography, separating into four major component classes based on differences in solubility and polarity: saturates, aromatics, resins, and asphaltenes (SARA). Details on ASTM standard methods and improvements on the determination of SARA components can be found in the literature [1, 2]. Each of the major SARA components can be further characterised by the use of Gas Chromatography–Mass Spectrometry (GC–MS) which provides unambiguous identification of individual components. These chromatographic techniques are however, time consuming, expensive, and destructive.

Molecular spectroscopy techniques such as Mid Infra-Red (MIR), Near Infra-Red (NIR) absorption, and Fluorescence emission have been used for many years as a fast and non-destructive tool in the analysis of crude oils [3–6]. For crude oils, the fluorescence emission is due to the presence of a multitude of aromatic hydrocarbons in varying concentrations. Factors such as the specific chemical composition (concentration of fluorophores and quenching

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species) and physical (viscosity and optical density) influence emission properties such as intensity, wavelength of emission, and lifetimes. For heavy oils, fluorescence emission is generally broad, very weak, and has short lifetimes, whereas lighter oils have narrower more intense emission bands, and longer lifetimes (Fig. 1) [7, 8]. The nature of the emission is governed by the complex interplay between energy transfer and quenching caused by the high concentrations of fluorophores and quenchers in petroleum oils. The complexity of crude oils usually prevents the resolution of any specific chemical component in terms of emission parameters.

Fluorescence lifetimes are potentially more useful for characterising crude oils than steady-state fluorescence data as the measurements are relatively insensitive to excitation intensity fluctuations, sample optical density and turbidity. Previous studies in our laboratory using Time Correlated Single Photon Counting (TCSPC) methods have shown that one can correlate various aspects of oil composition with lifetime changes [9–14]. Unfortunately, these studies also showed that accurate quantitative measurements were not possible using intensity averaged lifetimes calculated from TCSPC data. Another complicating factor with the TCSPC method was the time consuming nature of data analysis when fitting multi exponential decays to complex decay curves. This arises from a tendency in the fitting algorithms to return an abnormally high long lifetime component when using multi-exponential fit models on complex petroleum decay curves. This in turn, can generate a longer average lifetime which can skew results. Since there are an unknown number of emitting fluorophores represented by each decay measurement (at any emission wavelength) one cannot use techniques like global analysis to rectify the

situation. In practice, the solution required the refitting of the data multiple times and undertaking a support plane analysis to find the true minimum average lifetime.

The major alternative to the TCSPC method for lifetime determination is the widely used Frequency Domain (FD) methodology [15–17]. This method is potentially more useful for complex fluid analysis, since the data analysis can be more straightforward and rapid than for TCSPC. Using multiple modulation frequencies, the FD method can resolve fluorescence lifetimes in simple heterogeneous systems [18–20]. For complex systems comparable to petroleum oils, there are fewer examples in the literature, the most relevant being the Total Lifetime distribution analysis [21] which was used to characterise coal derived liquids. Here we report an initial FD lifetime based study of crude petroleum oils to evaluate the method for the qualitative and quantitative analysis of crude petroleum oils. We compare the FD and TCSPC methods in terms of analysis time, rapidity, and correlations to physical and chemical parameters. An evaluation of the FD data fitting models is also made in terms of correlating the resultant average lifetimes with the physical and chemical parameters of the crude oils.

Materials and methods

The phase and modulation data were obtained using an Alba Fluorescence Lifetime Imaging (FLIM) system (ISS Inc, Champaign, Ill., USA) based on an upright Olympus BX51 microscope fitted with a modulated (10 to 200 MHz) 405 nm laser diode excitation source. The fluorescence emission was wavelength separated into two wavelength ranges using pairs of bandpass filters in each of four different filter cubes (Table 1). The experimental setup enabled the simultaneous recording of phase and modulation data at two narrow wavelength ranges defined by the particular emission filters. The instrument was calibrated by the determination of the phase and modulation responses over a range of frequencies for a number of different standards of known fluorescence lifetime (reference stand-

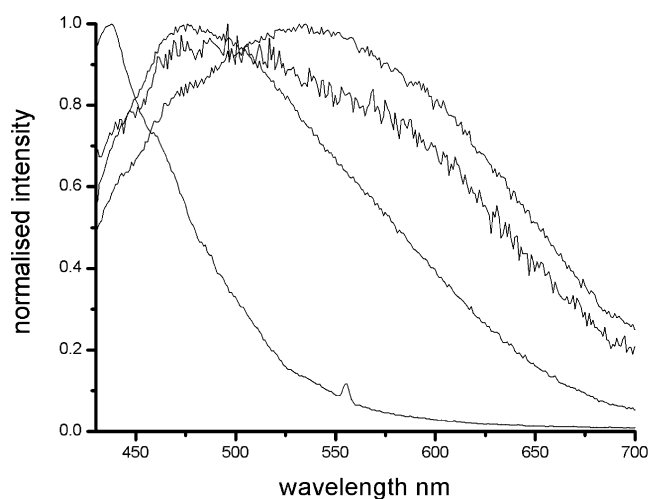


Fig. 1 Normalised steady state fluorescence emission spectra of a selection of crude petroleum oils excited at 405 nm. Light oils display a narrow yet strong fluorescence emission as opposed to medium to heavy oils which emit weakly over a broad emission range

Table 1 Dichroic cube and filter characteristics

Cube	Dichroic mirror	Filter1 (nm)	Filter2 (nm)	Reference standard
1	495 m	542–582	426–477	Coumarin 30
2	505 m	573–613	465–500	HPTS
3	562 m	480–520	600–650	LuciferYellow CH
4	570 m	510–560	575–650	Lucifer Yellow CH

ards, Table 2). Acetonitrile (spectrophotometric grade), Coumarin30, and Lucifer Yellow CH were obtained from Sigma Aldrich. HPTS (8-hydroxypyrene-1,3,6 trisulfonic acid trisodium salt) was obtained from Invitrogen. All materials were used without further purification. The choice of standard was predicted on the ability for excitation at 405 nm, a broad emission spectra which overlapped the bandpass filters of the lifetime system, a mono-exponential fluorescence lifetime in the range of the crude oil samples (1–10 ns), good solubility and photostability, and a reasonably large Stokes shift. Single exponential non-linear least squares fitting for each standard was performed using the instrument software and the quality of fit as judged by the proximity of the calculated lifetime (± 0.1 ns) and the goodness of fit (χ_R^2) value. Fluorescence lifetimes for the three standards were also verified by TCSPC measurements using a Fluotime 200 lifetime spectrometer (PicoQuant, Germany) and compared favourably to the literature values [22–24], and with previous studies in this laboratory [25]. All measurements were made at room temperature and the standard solutions were not degassed or deoxygenated. Lifetimes were calculated from phase and modulation responses relative to the phase and modulation responses from the chosen standard fluorophore.

The 20 crude oils tested had a wide chemical variance and were sourced from diverse geographical locations and rock types [12]. For the bulk crude oils, the FLIM system was operated in non-confocal mode (for higher throughput) and the neat, non-degassed crude oils were placed directly into a 1 mm path length quartz cuvette and then placed normal to the excitation source on the sample stage. All measurements were made in triplicate at room temperature (20–22 °C). The physical and chemical properties of these oils have previously been published in detail [12, 14].

Due to the large number of different emitting fluorophores at every emission wavelength the calculation of a fluorescence lifetime value is not a trivial task. Here the data were fit to discrete exponential, Gaussian and Lorentzian distribution models using a non-linear least squares fitting method as implemented by the instrument software (Vista, ISS, ver. 3.6). A single decay time was attempted for the distribution models; however, in most

cases 2 or 3 individual decay times were required for all model types to achieve a satisfactory fit. For all cases the intensity based average lifetime ($\bar{\tau}$) was reported [26].

The goodness of fit in each case was described by χ_R^2 which is defined as:

$$\chi_R^2 = \frac{1}{\nu} \sum_{\omega} \left[\frac{\phi_{\omega} - \phi_{c\omega}}{\delta\phi} \right]^2 + \frac{1}{\nu} \sum_{\omega} \left[\frac{m_{\omega} - m_{c\omega}}{\delta m} \right]^2 \quad (1)$$

where ν is the number of degrees of freedom (twice the number of sampled frequencies minus the number of variable parameters). The subscript c indicates calculated values of phase and modulation based on the chosen values of α_i (fractional contribution of the i th component) and τ_i (lifetime of the i th component). α_i and τ_i are varied in order to give a minimum value of χ_R^2 . $\delta\phi$ and δm are the uncertainties in the phase and modulation values respectively. The goodness of the model is judged on the minimisation of the value of χ_R^2 and also on the number of decay terms used [19, 26].

In order to determine the confidence limits on the average lifetimes reported, it is necessary to prepare a χ_R^2 surface plot, or Support Plane Analysis [26, 27]. This plots the value of (χ_R^2/χ_{Rmin}^2) versus the average lifetime obtained and the F_{χ} statistic (appropriate for ρ and ν degrees of freedom of the measurement method) is then used to determine the confidence interval.

$$F_{\chi} = \frac{\chi_R^2(\text{par})}{\chi_R^2(\text{min})} = 1 + \frac{\rho}{\nu} F(\rho, \nu, P) \quad (2)$$

where, $\chi_R^2(\text{par})$ is the value of χ_R^2 with a fixed parameter value, $\chi_R^2(\text{min})$ is the minimum value of χ_R^2 , ρ is the number of parameters, and $F(\rho, \nu, P)$ is the F statistic with ρ parameters and ν degrees of freedom with a probability of P . The F statistic values needed to calculate F_{χ} are described in Lakowicz [26]. A value of $P=0.32$ was used, representing one standard deviation. When dealing with complex decays and average lifetime values, the most facile means of generating a plot of (χ_R^2/χ_{Rmin}^2) versus the average lifetime is to systematically change the longest lifetime value only. This procedure is carried out in triplicate for each oil and the mean values of average lifetime are reported. We have observed that in practice [9–14], when studying complex systems, small changes in this long lifetime have the greatest impact on the average lifetime and χ_R^2 values. The situation is exacerbated as more lifetime terms are included in the fit model. An increase in the number of parameters increases the uncertainty significantly and thus there is a larger confidence interval range as shown in Table 3. An example of the support plane plots used to generate this data is shown in Fig. 2. The response of the χ_R^2 surface to change in the average lifetime is generally much broader for the discrete model than for the

Table 2 Reference standards used for lifetime calibration

Standard	Solvent	Concentration	$\lambda_{em}(\text{max})$	τ (ns)
Coumarin30	CH ₃ CN	10 ⁻⁵ M	488 nm	2.6
HPTS	0.2 M (phosphate buffer)	10 ⁻⁶ M	510 nm	5.4
Lucifer yellow CH	Water	10 ⁻⁵ M	533 nm	5.1

Table 3 Average lifetime and single decay distribution lifetimes calculated for the 542–582 nm emission band (empty cells indicate unable to fit)

Model		Gaussian (single)	Gaussian (multiple)	Lorentzian (single)	Lorentzian (multiple)	Discrete (multiple)
Oil	API	Average lifetime (ns)				
7703	50.6	6.47±0.07	6.72±0.30 (2)	5.67±0.06	6.14±0.21 (2)	7.42±0.86 (3)
7197	45.1	6.37±0.10	6.24±0.39 (3)	5.44±0.10	6.18±0.42 (3)	6.21±0.44 (3)
7098	44.6	7.89±0.17	7.89±0.17 (1)	7.25±0.16	7.14±0.28 (2)	10.80±1.64 (3)
7058	40.1	5.67±0.05	6.58±0.26 (3)	4.90±0.05	6.58±0.16 (3)	6.40±0.23 (3)
7086	39.5	4.98±0.06	5.77±0.38 (3)	4.32±0.05	5.74±0.38 (3)	5.66±0.32 (3)
7090	36.8	3.44±0.07	5.72±0.23 (3)	3.33±0.05	5.94±0.39 (3)	5.68±0.25 (3)
7193	36.0	3.11±0.04	5.16±0.24 (3)	3.00±0.04	5.04±0.94 (3)	5.18±0.26 (3)
7062	36	–	2.80±0.39 (3)	–	2.11±0.09 (2)	2.70±0.15 (3)
7186	34.3	6.53±0.07	7.57±0.50 (3)	5.71±0.07	8.19±0.74 (3)	6.78±0.33 (3)
7632	32.7	–	3.21±0.09 (2)	–	3.17±0.07 (2)	3.60±0.14 (3)
7324	32.3	–	2.85±0.06 (2)	–	2.72±0.06 (2)	3.16±0.15 (3)
7093	30.9	–	3.23±0.15 (2)	–	3.28±0.15 (3)	4.13±0.22 (3)
7187	29.4	5.75±0.06	6.04±0.23 (3)	4.97±0.08	5.38±0.11 (2)	6.09±0.22 (3)
7633	24.8	7.92±0.13	8.40±0.72 (3)	6.88±0.09	8.50±0.53 (3)	8.30±0.56 (3)
7169	21.6	–	1.90±0.10 (3)	–	1.96±0.10 (3)	1.91±0.13 (3)
7032	19.1	–	0.98±0.11 (2)	–	0.98±0.06 (2)	0.98±0.10 (2)
7130	15.6	–	1.04±0.07 (2)	–	1.03±0.08 (2)	1.36±0.21 (3)
7321	14.1	–	1.10±0.06 (2)	–	1.08±0.05 (2)	1.08±0.05 (2)
7188	13.3	–	1.27±0.08 (3)	–	1.29±0.09 (3)	1.28±0.10 (3)
7033	12.8	–	0.52±0.10 (2)	–	0.38±0.10 (2)	0.51±0.05 (2)

The number in brackets indicates the number of individual decay times used to achieve an accurate fit. The lifetimes reported here are the averages of fitting results from three separate fits

Gaussian or Lorentzian distribution models. Three decay parameters give the greatest uncertainty on the average lifetime reducing to a minimum when using a single decay. Although the quickest to fit, the discrete model gives the greatest temporal uncertainty range for long and middle average lifetimes while for short average lifetimes, all models show similarly small temporal confidence intervals.

If the uncertainty is expressed as a percentage of the average lifetime then the relative error is larger for the short lifetime oils. The intervals reported in Table 3 are comparable with those obtained for the TCSPC results and in each case the production of surface analysis plots for average lifetimes is a laborious manual process.

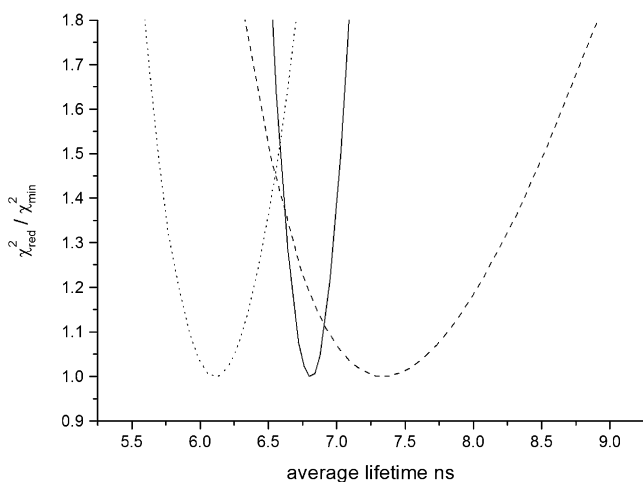


Fig. 2 Sample surface plot (Oil 7703 542–582 nm emission data) used to calculate the confidence interval in the average lifetime for the three fitting models: Discrete (*dashed line*), Lorentzian (*dotted line*), and Gaussian (*line*). The broader curve of the discrete model case indicates a much less precise determination of lifetime than for the narrower intervals determined for the single decay time distribution models

Results and discussion

In order to judge the average lifetimes obtained from the two methods, the TD lifetimes measured at a centre wavelength of 480 nm (approximately 13 nm bandpass) were compared to the FD lifetimes obtained using the 465–500 nm emission filter (Fig. 3). The TCSPC measurements covered ~473–487 nm, while the filter on the FLIM system sampled 465 to ~500 nm. This suggests that the TCSPC lifetimes originate from a sampled fluorophore population with a slightly greater fraction of bluer emitting, longer lived fluorophores than the population sampled by the FD instrumentation. For oils with a relatively long lifetime the FD data generated slightly longer lifetime values than the TCSPC data. However, there does not seem to be any consistent pattern, and one should therefore exercise caution when comparing lifetimes of complex fluids collected on different instrumentation.

In practical terms, data collection times for each method are comparable, although the shorter acquisition times for single

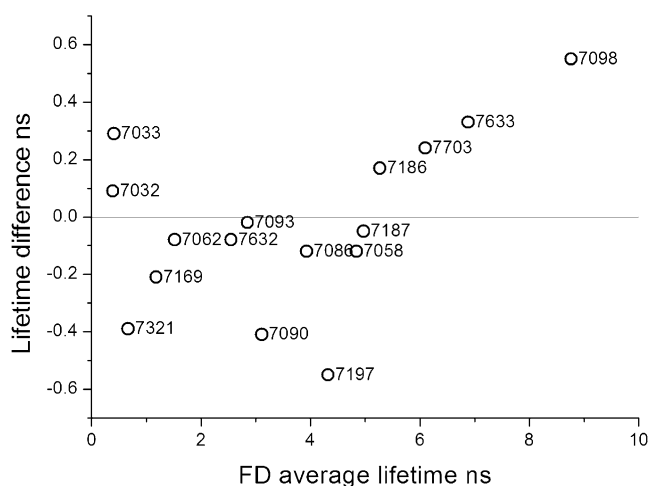


Fig. 3 Plot of the average lifetimes determined by Frequency Domain (FD) method and the difference with the TD average lifetimes determined using TCSPC. Both lifetimes calculated using discrete average lifetime model. Data recorded at a centre wavelength of 480 nm using 405 nm excitation. Positive lifetime differences indicate the oils whose FD average lifetimes are longer than the TCSPC measured average lifetimes

frequency phase and modulation measurements is a distinct advantage for rapid imaging or sensing applications. The greater sensitivity of TCSPC is an advantage with weakly emitting heavy crude oils however; the majority of oils are strongly fluorescent and are therefore better suited to FD analysis. The most significant difference between the two methods was fitting of the data to extract average lifetimes which were found to be faster for FD than for TCSPC although the evaluation of the parameter uncertainty was similar in both cases.

The phase modulation responses for a selection of the crude oils at different emission wavelengths are shown in Fig. 4. All show an increase in the modulation frequency at which a phase shift of 45 degrees occurs as the oils get heavier and the lifetimes shorten. Another point of note is the fact that a minimum of 40 frequencies (that are within the phase-dependent frequency range of sample) were required for accurate fits to the complex decay profiles. Heavy crude oils exhibit noisy phase modulation responses because they tend to be weak emitters, leading to low signal to noise ratios. An additional factor is the fact that the lifetimes are very short (tending to 1 ns or less) due to quenching, and the FLIM system we used is only capable of generating accurate modulation frequencies up to ~200 MHz. The phase and modulation data therefore do not span a wide enough range; leading to relatively poor data fitting. It would be possible to obtain better quality data with a system capable of higher modulation frequencies (up to 1 GHz).

The choice of model used to calculate an average fluorescence lifetime of these complex fluids is critical. The fact that there are very large numbers of interacting fluorophores produces very complex decay behaviour. In

previous work from this laboratory [9–14] the intensity averaged lifetime calculated from a multiple discrete lifetime model was used. However, it should be noted that while this model is not an accurate descriptor of the emitting species, it had utility in describing general trends in the photophysics of crude oils. Part of the reason for undertaking this study was to evaluate the different models available for FD lifetime calculations.

All phase-modulation data were fitted using the discrete and distribution models with multiple lifetime components. The normalised distributions from three representative oils are shown in Fig. 5. As one would expect the Lorentzian distribution gives a narrower distribution of lifetimes when compared to the Gaussian case. In some cases the Lorentzian model fits incorporate very narrow peak widths as can be seen in the top distribution of Fig. 5. Intrinsicly one would expect that a broader distribution would be a better description of the photophysical behaviour and because of this, determination of average lifetime for the distribution of lifetimes in the oil may not be valid. A detailed analysis of all the fit data for the oils (Table 3) shows some interesting features.

First, most of the light to medium oils can be fitted to a simple mono-modal Gaussian (or Lorentzian) distribution, i.e., when the API¹ gravity is above 36, or where the average lifetime is ~3 ns or longer). The mono-modal lifetime values are all reasonably short compared to the average lifetimes generated from a multi-exponential discrete decay model. This can be very significant in some cases up to ~2 ns. A comparison of the confidence intervals from the surface plot-derived limits, indicate that the lifetimes from the mono-modal distribution are more accurate than the discrete lifetime models. This may directly represent the simpler distribution of fluorophores found in the lighter crude oils. These results indicate that this simpler distribution model is a more accurate representation of the oil photophysics and should be used in preference to the average lifetimes generated by multi-exponential models.

The shorter lifetime oils in general required multi-modal distributions (Gaussian or Lorentzian) to accurately model the fluorescence decay. This introduced significant variances in the calculated average fluorescence lifetimes, and in certain oils this difference was as much as 3.0 ns. A comparison of the confidence intervals provides no guidance as to which is the correct lifetime. The uncertainty in the average lifetime value is generally greater for the multimodal distribution models and the long lifetime component has the most significant impact on this value. These results confirm that extreme caution should be applied in comparing fluorescence lifetimes of complex fluids such as crude oils.

¹ API gravity is defined as: $((141.5/\text{specific gravity at } 15.6\text{ }^\circ\text{C}) - 131.5)$.

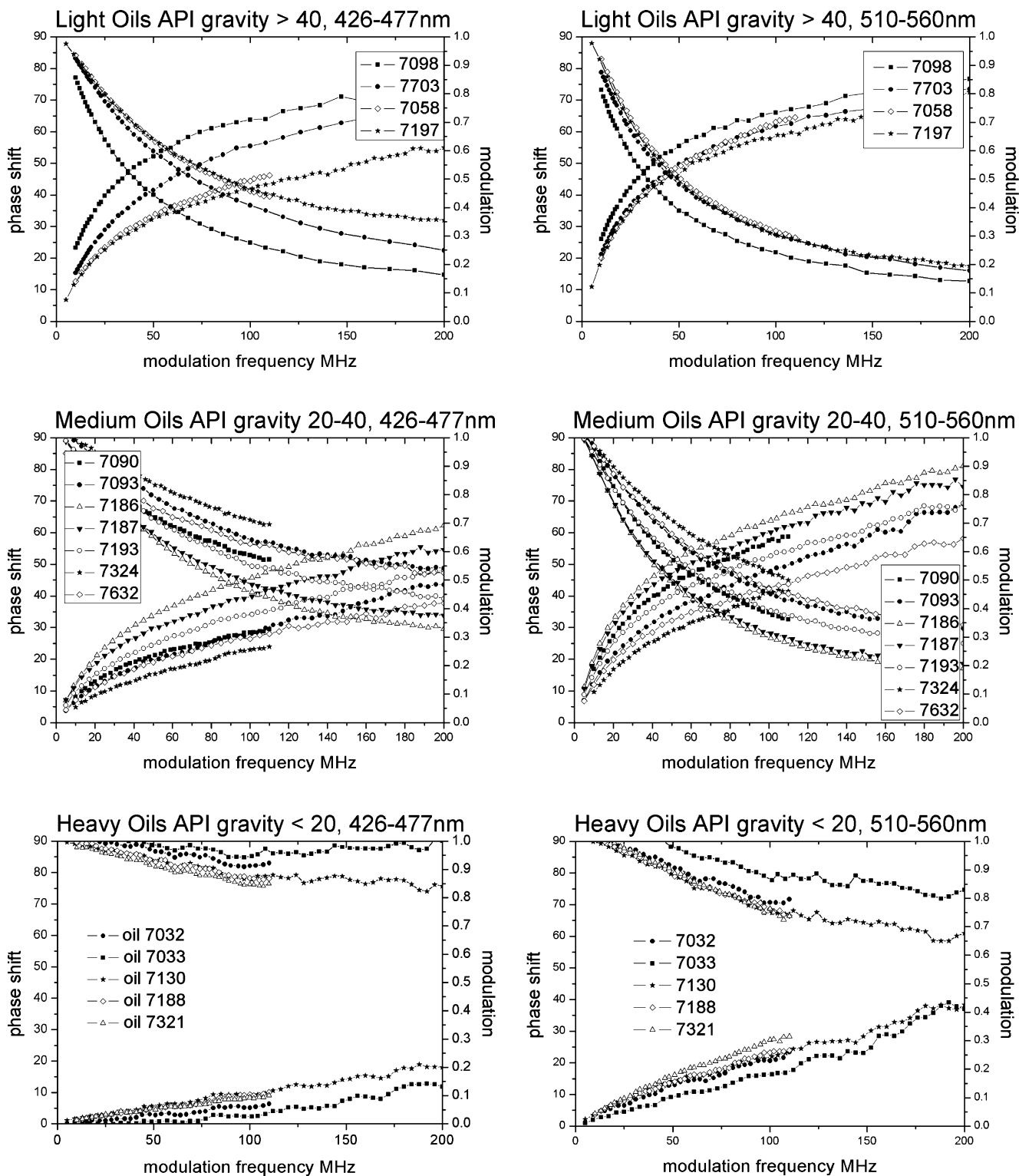


Fig. 4 Phase and modulation responses for light (*top*), medium (*middle*), and heavy (*bottom*) crude oils at two different emission wavelength bands. The increased noise in the data from the heavy oils

is due to the much lower signal to noise ratios resulting from the weak emission and from the very short lifetimes (near to 1 ns)

In essence the average lifetime value is only valid for a particular model and measurement method.

The average lifetime (irrespective of the fit model) increases with increasing emission wavelength which is in

agreement with literature studies [9, 12] (Fig. 6). This curved lifetime/wavelength response is due to the fact that fluorescence lifetimes are affected by processes such as collisional quenching, energy transfer, and excited state complex

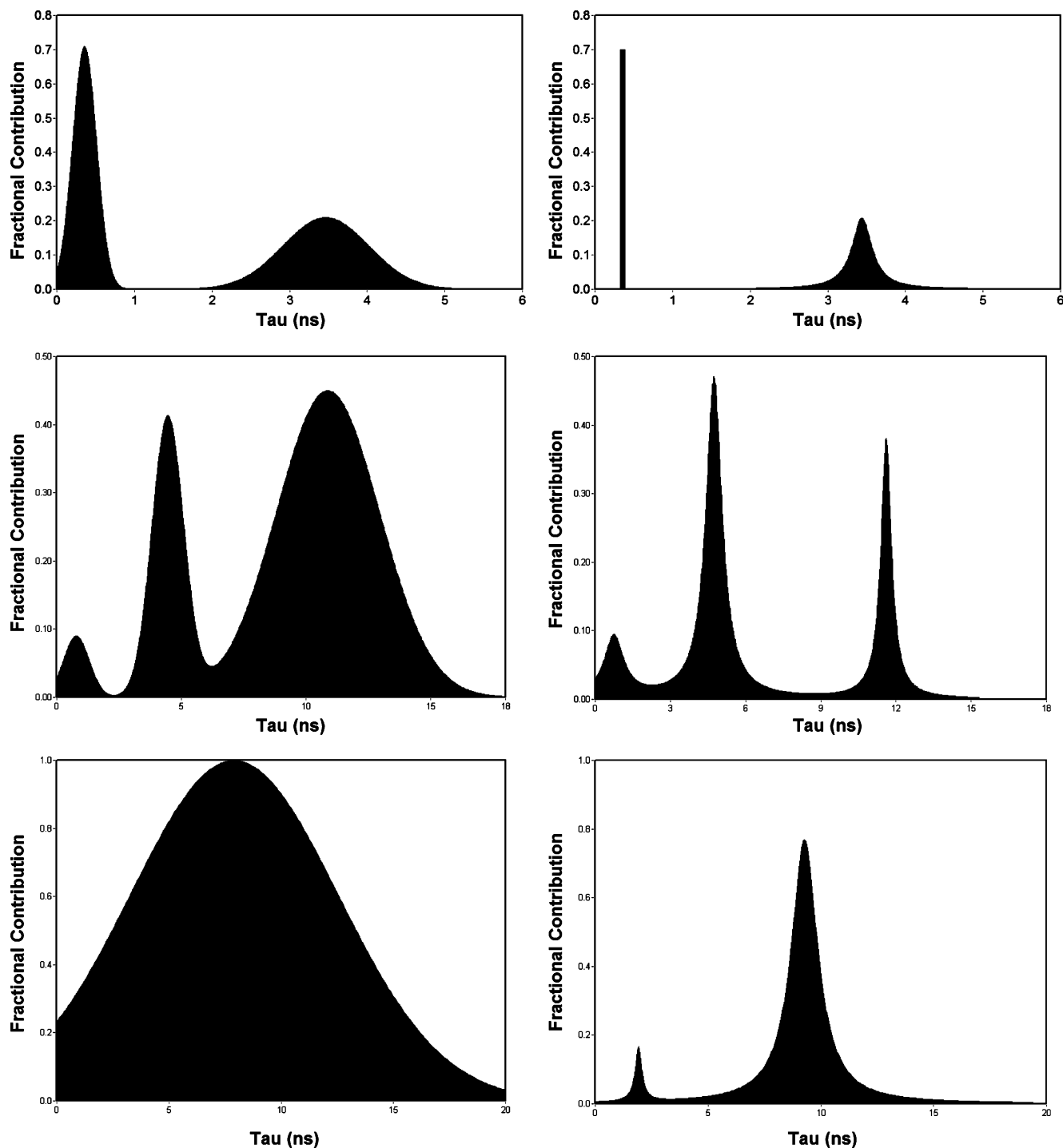


Fig. 5 Gaussian (*left*) and Lorentzian (*right*) lifetime distributions for a heavy oil, 7032 (*top*), a medium density oil, 7058 (*middle*), and a light crude oil, 7098 (*bottom*). The *single bar* in the top right figure indicates a peak width too narrow to display

formation. Each emission wavelength range represents a different population of emitting fluorescent species. At shorter wavelengths the emission largely occurs from smaller aromatics with relatively large HOMO–LUMO band gaps. At longer wavelengths the emission is largely due to the response of larger molecules with smaller HOMO–LUMO

band gaps. There is a net decrease in the quantity of energy transfer at longer wavelengths and hence the lifetime increases. Lifetimes are generally shorter for heavy oils and longer for low density oils because heavy oils contain greater proportions of polar and asphaltic compounds which cause fluorescence quenching leading to shorter lifetimes. Lighter

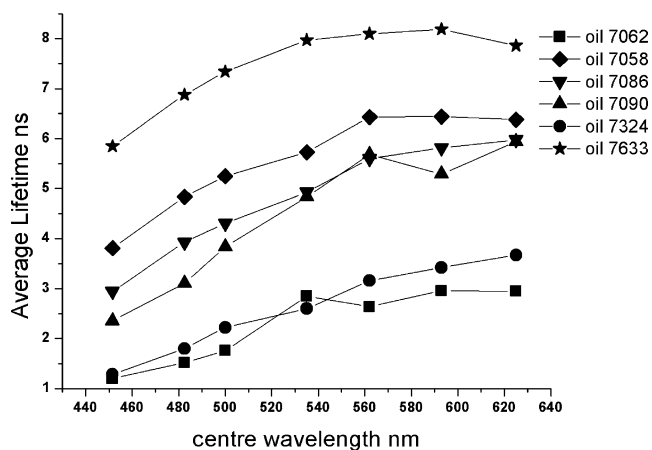


Fig. 6 Average lifetimes (discrete lifetime model) for some selected medium density crude oils. A general increase in lifetime is observed with increasing emission wavelength. A similar trend occurs with heavy and light crude oils

oils have higher alkane content and less heavy asphaltic molecules which give rise to longer lifetimes.

In order to test the lifetime values obtained from the different models, correlations were made with bulk composition parameters of the oils. Previous studies at this laboratory [14] have showed that there was a positive linear correlation between average fluorescence lifetime and API gravity but with a high degree of scatter. Figure 7 plots the API gravity–lifetime correlation for the FD and TCSPC data, showing a similar degree of scatter and no major improvement in correlation. Following on from this, a comparison in correlations of the FD average lifetimes across the emission wavelength range is shown in Table 4,

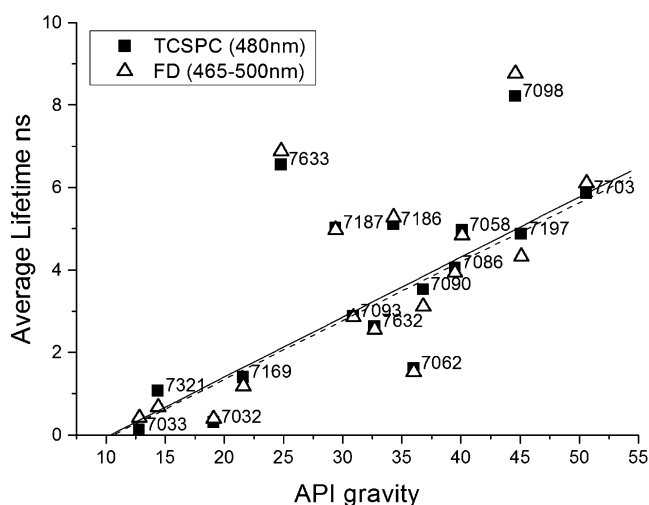


Fig. 7 Correlation between API gravity and TCSPC/FD average lifetimes. All data was measured at a *centre wavelength* of 480nm and average lifetimes were calculated using the discrete multiple decay model. Correlation coefficients were calculated without the outliers 7633 and 7098. (line TCSPC linear fit $r^2=0.73$; dashed line FD linear fit, $r^2=0.74$)

where the 542–582 nm range shows marginally better correlations. In [14], it was determined that the TCSPC average lifetimes recorded in the 540 nm emission range gave the best correlations (in terms of r^2 values) to the bulk oil composition parameters. Thus the 542–582 nm data set was selected for comparison of average lifetimes between the fitting models (Fig. 8).

The alkane and aromatic plots (not shown) showed a high degree of scatter and no clear trend. A better correlation was made with corrected (normalised in order to take account of the column losses) alkane and the best correlations were obtained with % Polar and also with API gravity. The outliers evident in Fig. 8 are oils with unusual characteristics such as abnormally high water, wax, or polar concentrations relative to their API gravity [9–14]. This highlights the difficulties in dealing with crude oil samples, namely the large non-linear variations in chemical composition encountered. The correlation coefficients determined from the plots in Fig. 8 are shown in Table 5 which indicate that there is no significant improvement over previously reported correlations [14]. This indicates that the compositional parameters of crude petroleum oils generated by conventional SARA analyses do not correlate linearly with fluorescence lifetime irrespective of measurement method and analysis model.

Conclusions

Frequency Domain (FD) methods were used to measure the fluorescence lifetimes of a series of crude oils. It was found that the calculated average lifetimes vary significantly depending on the fit model used. For light crude oils with long fluorescence lifetimes, a relatively simple mono-modal Gaussian or Lorentzian distribution was sufficient to accurately describe the fluorescence decay. For heavier oils, with shorter lifetimes, more complex multi-modal distributions were required to adequately fit the data. This

Table 4 Correlation coefficients (r^2) associated with best linear fits for the 20 crude oils recorded at varying wavelength ranges

Emission wavelength (nm)	Corrected alkane	Polar	Corrected polar	API gravity
426–477	0.66	0.77	0.77	0.72
465–500	0.72	0.81	0.86	0.74
510–560	0.72	0.83	0.88	0.76
542–582	0.76	0.86	0.85	0.79
573–613	0.76	0.81	0.81	0.81
575–650	0.74	0.83	0.85	0.74

All values have been determined using the discrete multi exponential model with outliers removed

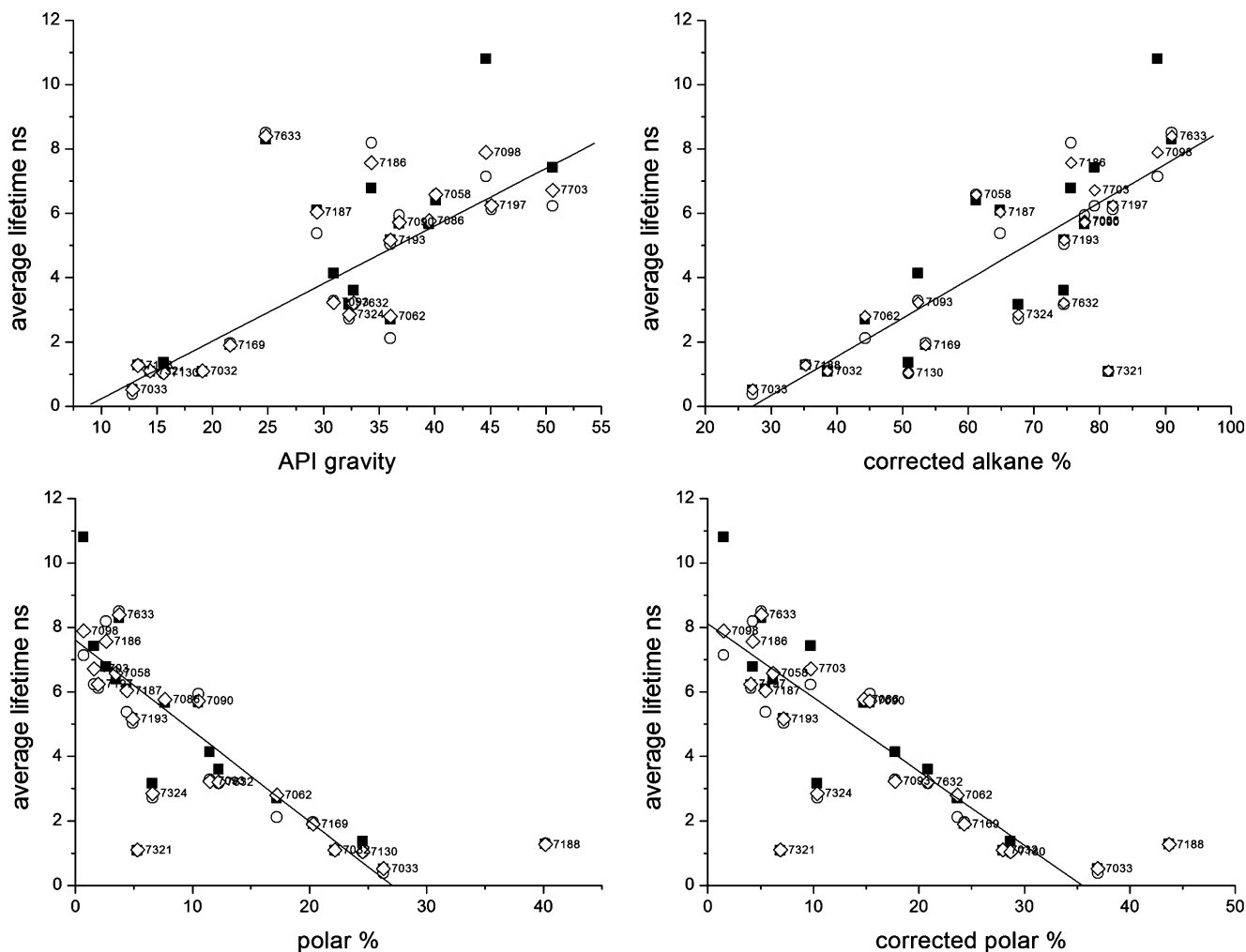


Fig. 8 Correlations between average lifetimes and gross chemical composition parameters (%corrected alkane, polar and corrected polar %) and API gravity for the 20 crude oils. The regression lines

are based on the Gaussian model average lifetimes. Emission wavelength was 542–582 nm (filled square Discrete, empty circle Lorentzian, empty diamond Gaussian)

may mirror the increased complexity of the composition and photophysical processes underway. When a discrete multi-exponential decay model was used to fit the FD data it was found that the majority of lifetimes differed significantly (by at least 0.2 ns) from the values obtained using TCSPC methods. This underlines the need to specify

precisely both the data acquisition method and the exact fit model when quoting fluorescence lifetimes of complex fluids such as crude petroleum oils. In practical terms, data collection times for both FD and TCSPC methods are comparable, although the shorter acquisition times for single frequency phase and modulation measurements is a distinct advantage for rapid imaging or sensing applications. Data fitting in this particular case of complex crude oils was on balance, found to be quicker for FD than for TCSPC. It is also concluded, that neither TCSPC nor FD derived fluorescence lifetimes correlate quantitatively with gross chemical compositional parameters as generated by SARA analysis.

Table 5 Correlation coefficients (r^2) associated with best linear fits for the 20 crude oils recorded at 542–582 nm as shown in Fig. 8

Fitting method	Corrected alkane	Polar	Corrected polar	API gravity
Discrete	0.76 (0.77)	0.86 (0.86)	0.85 (0.81)	0.79 (0.7)
Lorentzian	0.76	0.86	0.86	0.83
Gaussian	0.76	0.90	0.90	0.86

Figures in brackets indicate the best reported correlation coefficients from [12]

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