

Light emissions from oil

A valuable information source for petroleum analysis

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Il greggio, liquido tipicamente di colore nero, se illuminato con luce ultravioletta, può risultare in molti casi fluorescente. La fluorescenza, che si origina dalla presenza di composti aromatici, è fortemente influenzata dalla composizione chimica. Ciò ha permesso di utilizzare la fluorescenza per la caratterizzazione e l'analisi sia di greggi, sia di prodotti di raffinazione. Vari aspetti delle caratteristiche di fluorescenza degli oli (intensità, colore, distribuzione di lunghezze d'onda e tempi di vita) sono state correlate con fattori come la composizione chimica del petrolio e la densità (°API). I metodi basati sulla fluorescenza hanno diversi vantaggi: possono essere "non a contatto" (per esempio possono impiegare fibre ottiche per misure "remote sensing"), hanno un'elevata sensibilità alla presenza di idrocarburi aromatici e sono facilmente miniaturizzabili. La fluorescenza è spesso usata per rilevare la presenza di petrolio durante le operazioni di perforazione mediante l'osservazione dei cuttings. Esistono, però, possibili interferenze dovute agli additivi dei fanghi o ai fanghi a base olio, che devono essere superate per fornire risultati accurati. In questo articolo sono presentati brevemente i principi della fluorescenza del petrolio e viene mostrato come un metodo sviluppato in EniTecnologie, basato sulla "Total Scanning Fluorescence" (TSF), può essere utilizzato per discriminare gli oli dagli additivi e per quantificare la densità.

Despite the fact that most crude oils are dark coloured liquids, many are observed to be strongly fluorescent when illuminated with UV light. This fluorescence, which originates from the presence of aromatic compounds, is strongly influenced by chemical composition. This has led to the use of fluorescence techniques as tools for the characterisation and analysis of crude and refined oils. Various aspects of the fluorescence behaviour of oils (intensity, colour, wavelength distribution, and lifetime) have been correlated with factors such as petroleum chemical composition and density (API gravity). Fluorescence based methods have several advantages, including: they are non-contact (e.g. can employ fibre optic probes for remote sensing), high sensitivity to the presence of aromatic hydrocarbons and easily miniaturised instrumentation. Fluorescence is often used to detect the presence of crude oil during drilling operations by observing the fluorescence of the cuttings. However, there are possible interferences from mud additives or oil-based muds, and these need to be overcome to provide accurate results. In this article we outline the basics of petroleum fluorescence and discuss how a "Total Scanning Fluorescence" (TSF) method, developed in EniTecnologie, can be used to discriminate drilling additives from crude oils, and to quantify the API gravity (density) of crude oils.

Light and molecules

The Perrin-Jablonski diagram (figure 1) is convenient for visualizing the different processes involved in the

interaction of a molecule with light: photon absorption, internal conversion, fluorescence, intersystem crossing and phosphorescence [1].

The electronic states of most organic molecules can be divided into singlet (S) and triplet (T) states, depending on the spin of the electrons and each of these states has many vibrational energy levels. When a molecule is excited from the ground state to an upper excited singlet state (S_n) by absorption of a photon of light {1}, it usually ends up in one of the upper vibrational levels of that state. A molecule in a high vibrational level will quickly fall to the lowest vibrational level of this state by a process called "vibrational relaxation", which does not involve any light emission {4}.

When the molecule has attained the lowest vibrational level in the excited state, one of three things can happen:

- return to the singlet ground state by the emission of a photon of light (fluorescence) without changing the spin state {2}. The lifetime of this process is very short (nanoseconds);
- decay back to the ground state through vibrational collisions (radiationless decay) with other molecules {6};
- the spin of the excited electron reverses, leaving the molecule in an excited triplet state (T_1); this mechanism is called "InterSystem Crossing" (ISC)

{5}. The T_1 state is of a lower electronic energy than the excited singlet state. The T_1 state can decay to the ground state by photon emission in a process called "phosphorescence", but the transition is forbidden and this results in very long excited state lifetimes (up to 10's of seconds).

In the case of petroleum fluorescence, only the first two processes are significant (see table 1).

Process	Characteristic average times (seconds)
Absorption	10^{-15}
Vibrational relaxation	$10^{-12} - 10^{-10}$
Lifetime of the excited state S_1	$10^{-10} - 10^{-7}$
Intersystem crossing	$10^{-10} - 10^{-8}$
Internal conversion	$10^{-11} - 10^{-9}$
Lifetime of the excited state T_1	$10^{-6} - 10$

Table 1: characteristic times of the processes involved in the fluorescence process

Crude oil fluorescence

In order to be fluorescent, a molecule must be highly absorbing, and possess the appropriate structure and electronic energy levels. For organic materials, fluorescence species tend to be highly conjugated non-aromatic, aromatic, or heterocyclic compounds. Crude oils are fluorescent because they contain a wide variety of aromatic species, from the simplest single ring structures (benzene/toluene) to very complex, high molecular weight species such as asphaltenes. If a molecule is fluorescent can be easily assayed by fluorescence at levels below 1 ppm. The nature of the emitted fluorescence is strongly influenced by the chemical composition and to a lesser degree the physical properties of the oil.

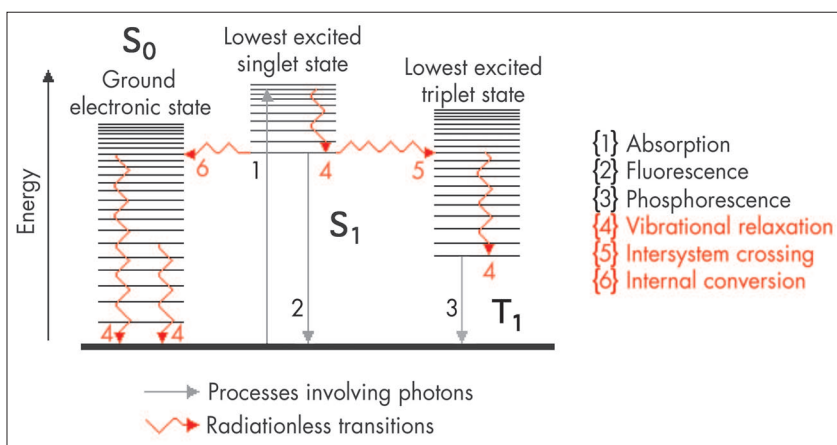


Figure 1: Perrin-Jablonski diagram

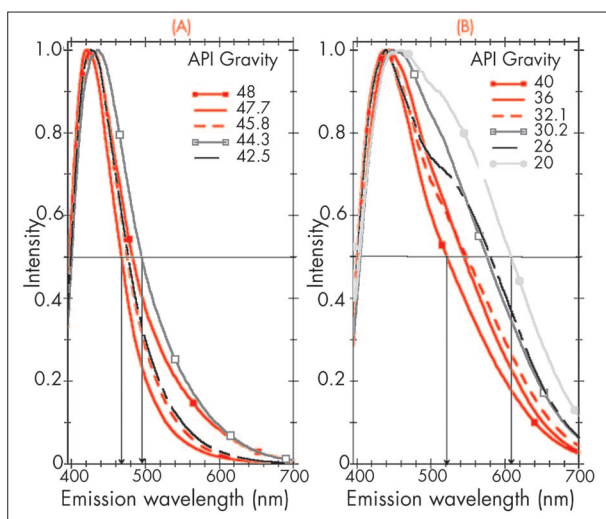


Figure 2: normalized fluorescence emission spectra for a series of crude North Sea oils, showing the differences between light (A) and medium-heavy (B) oils. Data obtained with 380 nm excitation [adapted from ref. 2]

In general, heavy oils (low API gravity) tend to have relatively broad, red shifted, less intense fluorescence emission bands, and shorter fluorescence lifetimes when compared to light oils (high °API). These changes are seen in figure 2 where the light oils (figure 2A) have narrow emission bands compared to the medium and heavy oils (figure 2B) [2].

The differences in emission spectra are largest when UV excitation sources are used, because of the effect of energy transfer and the fluorophore population distribution. Increasing the excitation wavelength results in a narrowing of the fluorescence emission bands, and a reduction in Stokes' shifts¹, fluorescence lifetime, and quantum yields. This is due to the excitation of different populations of lower energy fluorophores causing a reduction in energy transfer rates.

The analysis of crude oils

There are many different fluorescence-based methods used for the analysis of crude petroleum oils

¹ The Stokes' shift is the difference between the excitation and emission maxima for any given fluorophore (fluorescent species).

in a variety of environments. Fluorescence is used for the analysis of bulk oil, to oil spills at sea, to microscopic hydrocarbon bearing fluid inclusions (HCFI) found in rock.

The most rigorous approach is to look at the spectral distribution of the fluorescence emission, which contains much more diagnostic potential. Spectral data (spectral width, position of maximum fluorescence, λ_{max}) have been found to correlate with API gravity or aromatic concentration for various restricted sets of crude oil samples or synthetic HCFI. The red-green quotient Q ($Q = \text{intensity}_{650\text{nm}}/\text{intensity}_{500\text{nm}}$), and λ_{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. Synchronous fluorescence excitation-emission spectroscopy has been used since the 1970's for identifying crude oils [3] and has also been applied to the fingerprinting of oils entrapped 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.

Steady-state fluorescence based measurements such as those described above 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 [1]. The apparent fluorescence intensity and spectral distribution can also be influenced by factors such as sampling geometry, physical properties of the crude oils (opacity, sample turbidity) and in the case of microscopic HCFI the scattering properties of both the actual inclusion and host mineral. One way in which these factors can be overcome is to use Time Resolved Fluorescence (TRF) techniques, and in particular, fluorescence lifetimes [4]. TRF methods also provide information that is lost in the time-averaging process inherent in steady-state

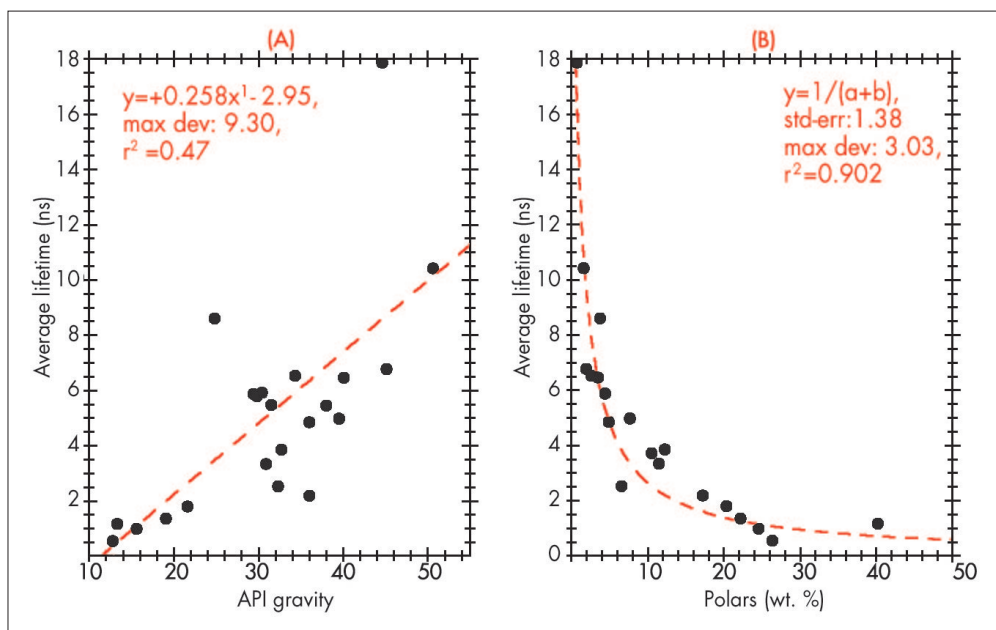


Figure 3: fluorescence lifetime plotted against: (A) API gravity, and (B) measured polar concentration for a series of crude oils from different geological locations and source rocks. The data was obtained with 380 nm excitation and measured at an emission wavelength of 500 nm

methods and this can be used to study the photophysics and weathering of crude oils. In the case of crude oils, time-resolved fluorescence measurements offer the best approach for fully revealing the influence of quenching and energy transfer processes on fluorescence behaviour. The use of TRF (particularly fluorescence lifetime) methods has been proposed as a tool for monitoring oil pollution at sea, and for the analysis of HCFI. Recently, researchers at NUI-Galway in Ireland have obtained TRF data from individual HCFI and correlated the results with data obtained from a bulk oil model. The results indicate that TRF can discriminate small changes in oil composition for HCFI from a single geographical source. One of the most significant results from this work is that API gravity is not a particularly good parameter to try and correlate with fluorescence lifetime data [2] for widely different oil types that do not originate from the same source. However, it has been found that the concentrations of the polar and alkane constituents have a greater influence on the fluorescence emission than density (API gravity), since they directly influence the quenching rate. Figure 3 shows API gravity and polar concentration

plotted against fluorescence lifetimes for a set of very diverse crude oils.

The cores and cuttings analyses

Fluorescence is currently used by geologists for the identification of oil: the cuttings, placed under an ultraviolet light source (Woods lamp), are directly observed by sight. This quick visual evaluation allows only a qualitative estimation of the presence of hydrocarbons but gives no information about the oil nature or composition. Moreover, problems can arise when fluorescent minerals and/or certain drilling mud additives are present in rock cuttings. A more rigorous method was developed by Texaco, the QFT II, where fluorescence is measured using two different emission wavelengths. This method, nevertheless, fails to discriminate possible interfering species [5].

In EniTecnologie, a "Total Scanning Fluorescence" (TSF) approach was tested to discriminate crude petroleum oils from drilling mud additives and to predict the API gravity of the oils.

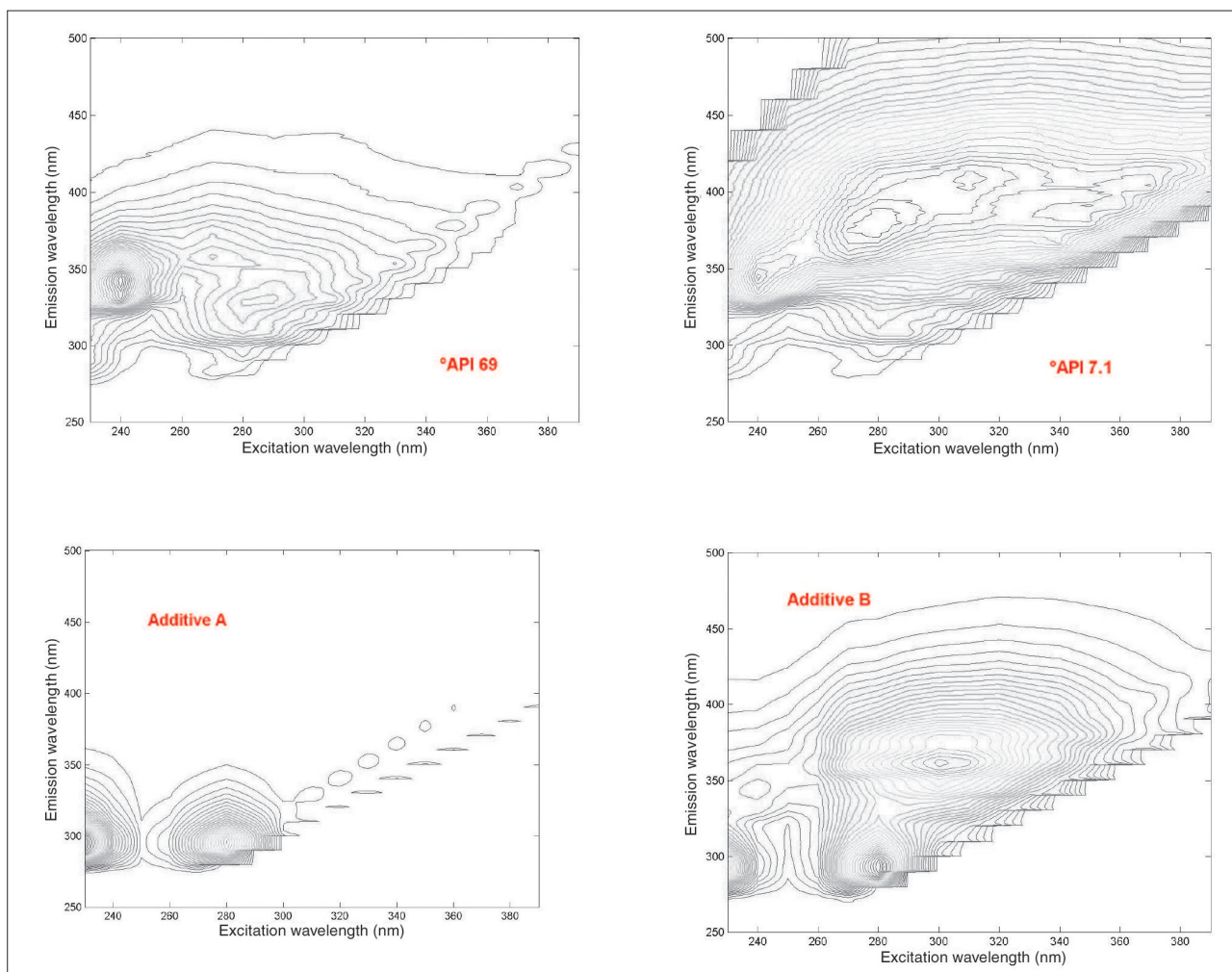


Figure 4: TSF maps (contour plot) of high and low °API crude oils and of two commercial lubricating additives (A, B)

A test set of 49 crude oils, with °API in a range from 7 to 70, and 5 lubricating additives used in water based muds (WBM) was used. TSF maps were obtained by extensively diluting the samples in cyclohexane, a non-fluorescing solvent. Figure 4 shows some example of TSF maps obtained from very different °API crude oils and two additives, diluted in cyclohexane. The broader and more extensive contours of the heavy oil are indicative of the presence of a wider distribution of fluorophores. The fact that the contours extend out into the visible

region of the spectrum indicates the presence of a greater concentration of higher molecular weight aromatic compounds. The narrower and more compact contours of the light oils indicate a narrower fluorophore distribution, with significantly fewer large aromatic species. The fact that the contour is clustered at short emission wavelengths proves that these fluorophores are mainly smaller aromatic species. These differences in the contour topology offer a potential method for characterising and quantifying crude oils and additives.

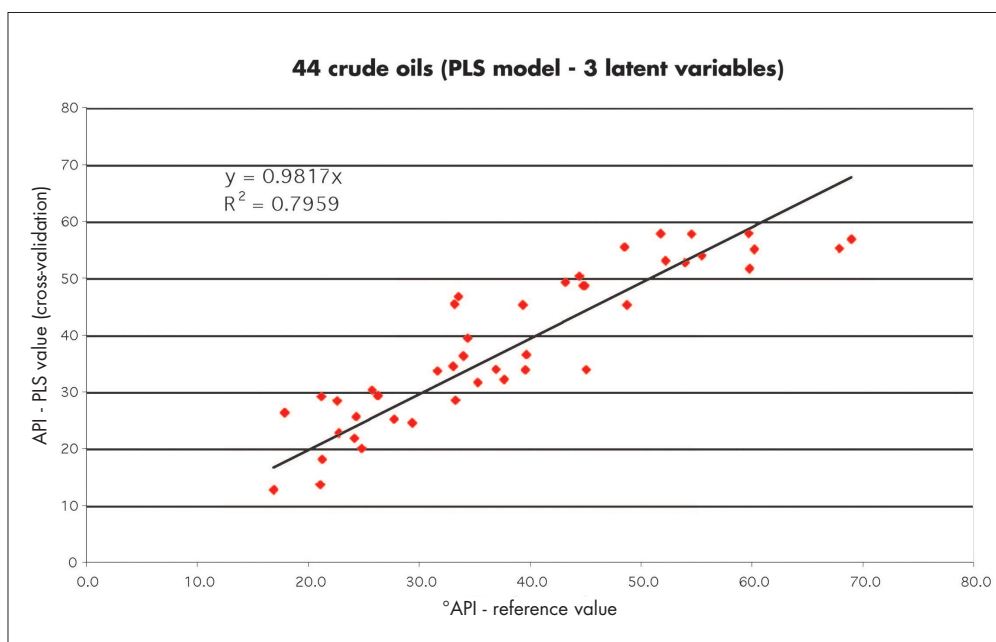


Figure 5: predicted °API plotted against reference values

Multivariate analysis methods can be employed to interrogate the full TSF datasets, either to discriminate the different types (oils or additive), or to calibrate oil parameters such as density (API gravity).

Multidimensional PLS (Partial Least-Squares) regression was tested to predict the API gravity using TSF maps, on the samples having density higher than 15 °API (44 samples). Figure 5 shows the plot of predicted API gravity versus the reference values, and there is a reasonably good correlation (R^2 is nearly 0.8), indicating that PLS and TSF methods can be used to estimate crude oil API gravity. The standard error of prediction, calculated by means of cross-validation is ± 6.5 °API.

The TSF method has the potential to offer an accurate method to detect the presence of crude oils during drilling operations. TSF can overcome the difficulty of distinguishing crude oil fluorescence from that of the contaminants in drilling cuttings, such as pipe dope and other mud additives, particularly lubricating oils containing aromatic compounds.

References

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Alan Ryder's profile

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