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Assessing the Maturity of Crude Petroleum Oils Using Total Synchronous Fluorescence Scan Spectra

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There have been many applications of fluorescence methods for the analysis of crude petroleum oils down through the years. However, none of these studies has yielded a robust qualitative or quantitative method for quantifying the chemical composition, or assessing the maturity of crude oils. Simple fluorescence parameters such as lifetime, intensity, and intensity ratios do not correlate well with chemical composition particularly for medium weight crude oils [A. G. Ryder, T. J. Glynn, and M. Feely (2003). *Proc. SPIE-Int. Soc. Opt. Eng.* **4876**, 1188–1195.]. A better approach may be to use the Total Synchronous Fluorescence Scan (TSFS) method to fully interrogate the complex chemical composition of the oils [D. Patra and A. K. Mishra (2002). *Anal. Bioanal. Chem.* **373**, 304–309.]. We present TSFS spectra from 18 crude petroleum oils of varying composition, sourced from around the world. The TSFS plots of these oils are very complex, with the contours being spread over the full 250–700 nm wavelength range (λ_{ex}) and 40–200 nm wavelength interval ($\Delta\lambda$) sampled. The 3-D contour maps tend to two contour concentrations one at $\lambda_{em} < 300$ nm, $\Delta\lambda = 120$–200 nm, and a second near $\lambda_{ex} \sim 380$–400 nm, $\Delta\lambda = 40$–60 nm. The first feature represents fluorescence emission originating mainly from energy transfer processes with the second, longer wavelength feature originating from fluorescence emission generated by a higher proportion of direct excitation as opposed to emission resulting from energy transfer. The topography of the 3D contour plots is therefore influenced by the balance between energy transfer and direct fluorescence emission, which is governed by the chemical composition of the crude oils. We discuss how the gross chemical composition affects TSFS spectra and how TSFS can be used to assess oil maturity with a view to developing quantitative methods.

KEY WORDS: Fluorescence; spectroscopy; crude oil; petroleum; energy transfer; quenching.

INTRODUCTION

Crude petroleum oils (CPOs) are complex mixtures of different hydrocarbon compounds. They are obtained from an extensive range of different geological sources and their chemical composition and physical properties can vary enormously. The non-destructive, non-contact, quantitative analysis of crude oils is desirable for applications within the oil exploration and processing industries, on both the macro- and microscopic scale [3,4]. Satisfying the need for both macroscopic and microscopic non-destructive methods is not easy, however, fluorescence based methods offer a convenient route to achieving these goals. Fluorescence based techniques offer high sensitivity, good diagnostic potential, relatively simple instrumentation, and suitability for either microscopy or portable instrumentation. CPO fluorescence derives from the aromatic hydrocarbon component of oils, and this fluorescence is strongly influenced by the precise chemical and physical composition. Unfortunately the wide range of physical and chemical characteristics found in CPOs makes the fluorescence analysis rather complex [5,6].

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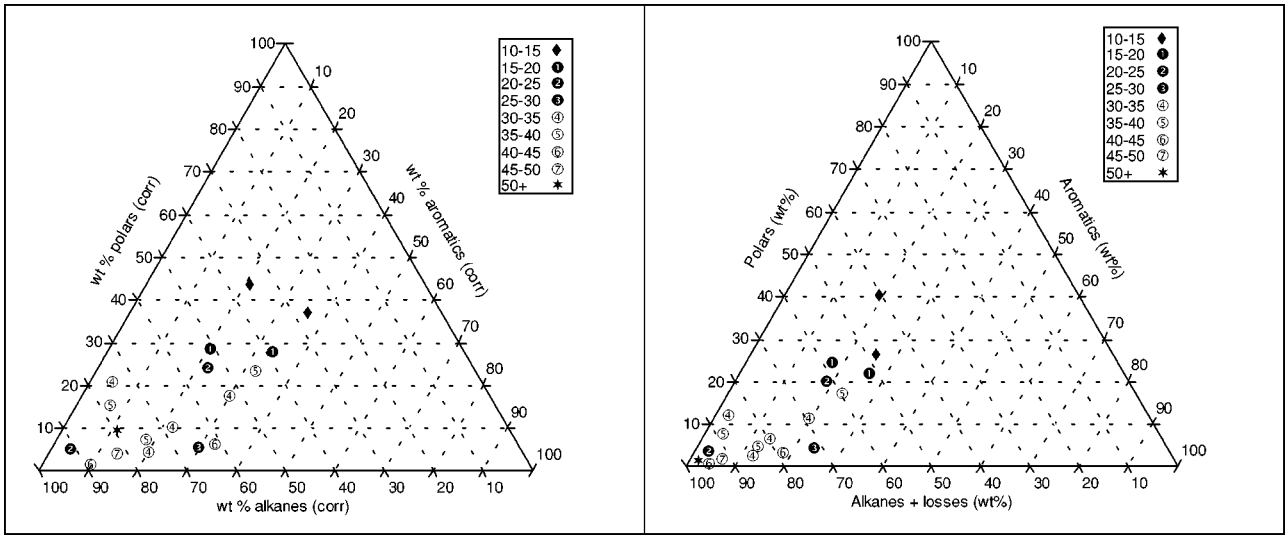

Fig. 1. (A) Ternary plot of API gravity versus the gross chemical composition (corrected for column losses) of 18 crude petroleum oils. (B) Ternary plot of API gravity versus the gross chemical composition (uncorrected for column losses).

In general, light oils (high API gravity)[3] tend to have relatively narrow, intense fluorescence emission bands with small Stokes shifts when compared to heavy oils (low API gravity) where the emission tends to be weaker, broader, and red shifted. These changes in fluorescence emission are due to the higher concentration of fluorophores and quenchers present in the heavier oils, which leads to a higher rate of energy transfer and quenching, producing a broader, weaker, red shifted emission [7,8]. The fluorescence lifetime of a CPO is also governed by the combination of energy transfer and quenching, with heavy oils having shorter lifetimes on average, than lighter oils [9–11]. The fluorescence lifetime (for any given excitation wavelength) is also emission wavelength dependant, since each emission wavelength represents a different population of fluorophores. In general, the wavelength at which the maximum average lifetime for a heavy crude oil is measured occurs at longer wavelength than it does for a light oil [10,11]. The excitation wavelength also has a significant effect on the emission spectra of CPOs, with a narrowing of the emission band [7], and reductions in the Stokes shift, quantum yield [8], and average fluorescence lifetime [6,10], being noted as the excitation wavelength increases. This decrease is caused by a complex interaction between energy transfer and quenching processes. At short excitation wavelengths, energy transfer processes dominate since most of the absorbing chromophores have large bandgaps and can transfer energy to the large numbers of smaller bandgap molecules. At longer excitation wavelength, the excited fluorophores have small bandgaps and there are fewer molecules with smaller bandgaps for energy transfer, so most collisions result in quenching and a reduction in the fluorescence lifetime. Furthermore, as the bandgaps of the excited fluorophores decreases there is an increased rate of internal conversion, which also contributes to a reduction in the average lifetime [8,10,12].

Recently Patra and Mishra [2] demonstrated the use of Total Synchronous Fluorescence Scan (TSFS) method as an alternative method for presenting the fluorescence response of complex hydrocarbon systems. Our goal is to develop accurate quantitative fluorescence based analytical methods for CPOs. In this work we present a preliminary investigation of the TSFS behaviour for a very diverse sample set of crude oils. We also examine how suitable TSFS 3-D spectra normalised at the point of maximum fluorescence emission are for classifying oil maturity.

MATERIALS & METHODS

The crude petroleum oil samples (Fig. 1) originate from several sources worldwide and were kindly provided by Robertson Research International of North Wales, who also measured the chemical composition in-house [13]. The ternary plots give a good visual indication of the compositional diversity of the samples. Figure 1A shows the plot of API gravity versus the corrected aromatic,

[3] API gravity of oil is inversely related to the density by the formula: API gravity = ((141.5/specific gravity at 15.6°C) − 131.5).

alkane, and polar concentration. There is a weak trend with the lighter oils placed towards the apex (0% polar–100% alkanes) of the ternary plot. However, there is still a large degree of scatter indicating that the physical parameter (API gravity) does not correlate very well with the corrected compositional data. One point of note is that the corrected concentration refers to the fact that the alkane/aromatic/polar concentration is measured using column chromatography. In these analyses it is usual for the sum of the individual concentrations to be less than 100%. This occurs because either the very light alkane fractions are lost by evaporation or some of the very heavy components (asphaltenes etc) are retained on the column. Column losses for these oils varied from 8.1 to 84% with the lighter API gravity oils having the higher losses. In Fig. 1B the column losses are added to the alkane concentration and is a slightly better correlation with API gravity.

The refined oil analysed was an Edwards high vacuum oil and it was sampled in a 1 cm pathlength cell. All measurements on the crude oils were made using the neat, non-degassed oil held in 1 mm pathlength quartz cuvette at room temperature (20–22°C). Fluorescence measurements were made using a Perkin-Elmer LS-50B fluorescence spectrometer fitted with a front surface, or 90° sampling accessories, and a red sensitive (R928) PMT detector. All spectra were recorded with the excitation slit set to 15 nm and the emission slit at 20 nm, and a scan speed of 1500 nm per min. These settings were chosen to maximise light collection efficiency and reduce sampling times. For comparison purposes each TSFS plot was normalised with respect to the point of maximum fluorescence intensity, and then plotted with 9 equally stepped contour lines from 0.1 to 0.9.

RESULTS AND DISCUSSION

For crude petroleum oils (CPOs) there is a large variation in chemical composition, which results in CPOs having very different optical and fluorescent properties. Typically CPOs vary in colour from black to pale straw colour, which can make fluorescence based analysis methods problematical [13]. In the recent TSFS study of refined petroleum oil products, 1 cm pathlength cells and a 90° sampling geometry was employed [2], and as such there are considerable inner filter effects. This is illustrated in Fig. 2, which shows TSFS plots for a typical lubricating oil recorded under the two different sampling geometries. Figure 2A shows the 90° case, with the contour lines concentrated at an excitation wavelength (λ_{ex}) around 500 nm, with the maximum fluorescence at shorter wavelength intervals ($\Delta\lambda$) (<110 nm for 50% or greater intensity). In contrast, Fig. 2B shows considerably more variation with more contour lines at shorter λ_{ex}, and a blue

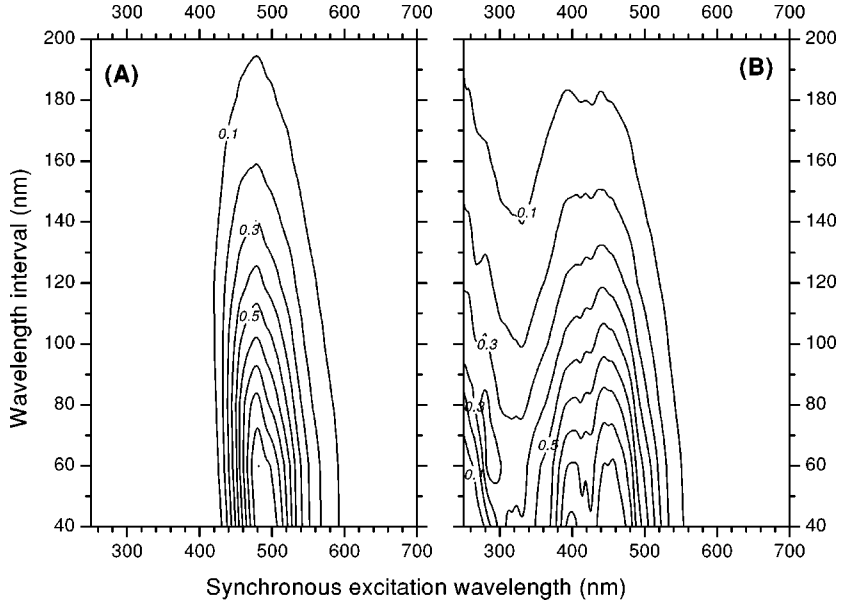

Fig. 2. TSFS plots for a typical refined lubricating oil (Edwards High Vacuum oil 16, H110-03-026) recorded from 250 to 700 nm over a wavelength interval of 40–200 nm with: (A) sample analysed in a 90° geometry, and (B) sample analysed in a front surface sampling accessory. In both cases the oil was placed in a 1 cm pathlength quartz cuvette.

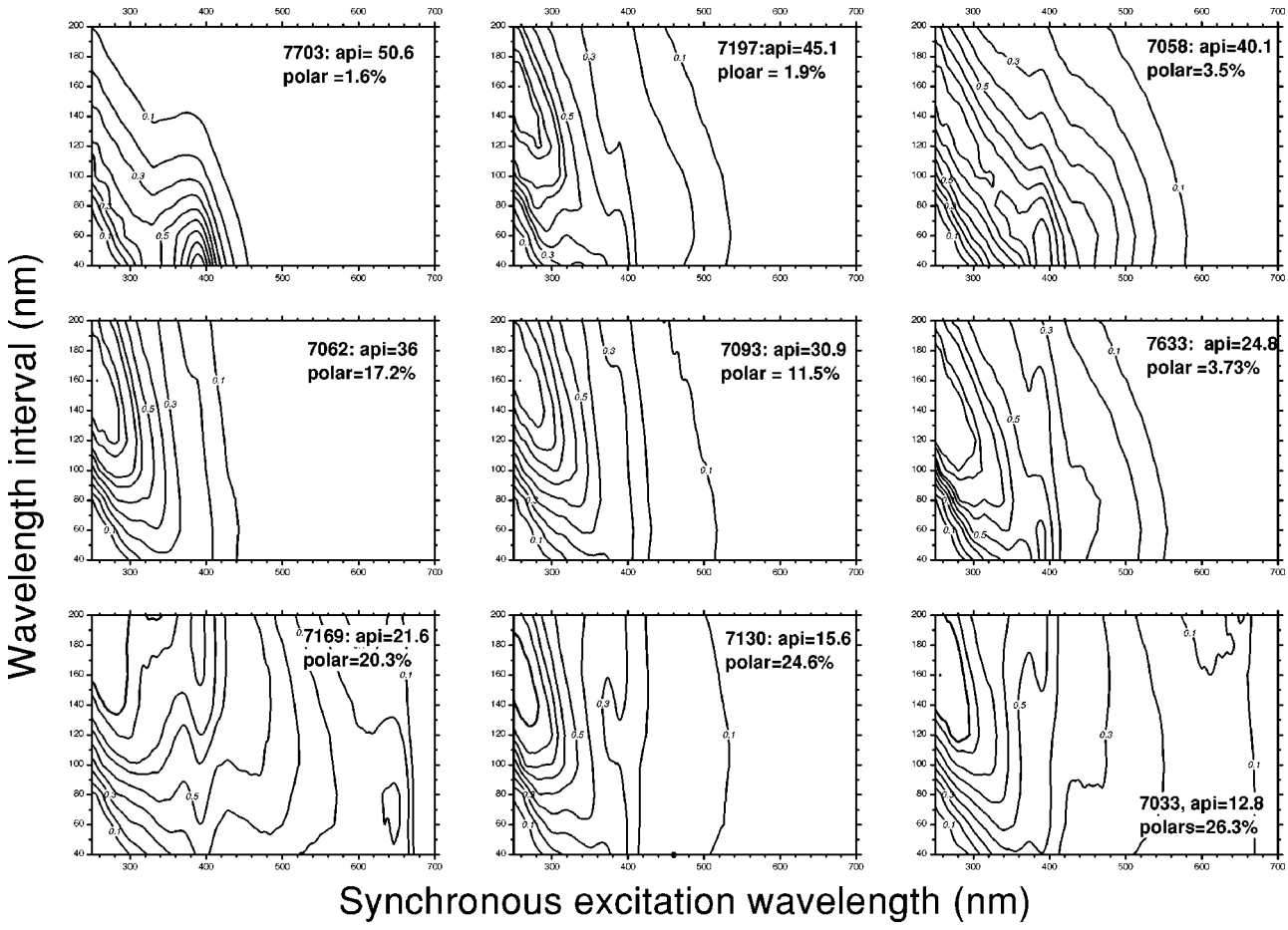

Fig. 3. TSFS plots for 9 different crude petroleum oils recorded from 250 to 700 nm over a wavelength interval of 40–200 nm in a front surface sampling geometry.

shift of ∼50 nm for the λ_{ex} maximum. This detail is absent from Fig. 2A because the shorter wavelength fluorescence emission is being reabsorbed due to a very *large inner filter effect*. The diagonal feature (250–350 nm) in Fig. 2B is symptomatic of emission resulting from collisional energy transfer between the short wavelength absorbing species (small aromatics) and lower bandgap large polycyclic aromatics. As λ_{ex} increases, the TSFS contour lines concentrate at shorter wavelength intervals indicating that the proportion of the observed fluorescence originating from directly excited species is greater than that resulting from energy transfer. The concentration of contour lines in the 380–480 nm λ_{ex} range indicates that the fluorophores are primarily 4, 5, and 6 ring polycyclic aromatics [14]. It is obvious therefore that considerable diagnostic potential is lost by inner filter effects when petroleum oils are sampled at right angles in 1 cm pathlength cells. In addition, most crude oils are opaque liquids which makes the 90° sampling geometry impractical for crude oils. This is important in the context of our ongoing research effort to develop a fluorescence-based method for the analysis of microscopic (<100 μm diameter) petroleum containing fluid inclusions, which can only be effectively studied in a back scattering geometry using microscopy.

The compositional diversity of crude petroleum oils results in a wide range of TSFS plots as seen in Fig. 3 where the TSFS spectra of 9 different CPOs are displayed. For comparison purposes, and to account for instrument instability/sampling effects, each TSFS plot was normalised to the point of maximum fluorescence intensity. This allows a general comparison between the different CPOs on the basis of the identity of the emitting species. All the crude oil TSFS plots show a general diagonal contour trend from short λ_{ex}/large $\Delta\lambda$, to long λ_{ex}/short $\Delta\lambda$ which represents a maximum fluorescence emission in the 350–500 nm range for these excitation wavelengths. This diagonal trend represents the extensive impact energy transfer processes have on crude petroleum oil fluorescence.

The top row of Fig. 3 shows the TSFS plots of 3 light oils (API $> 40^{\circ}$) with low concentration of polar components ($<$4%). There are considerable differences in the plot topology and this is due to changes in the concentration (as measured) of the aromatic component. The measured aromatic concentration increases across the row from 1.8 to 6.6%, and then to 18.2% for 7058. The oil 7703 is classed as a late maturity oil and as such most of the larger polyaromatic species will have been broken down to alkanes and small aromatic species. This results in a very tight TSFS contour plot centred at $\lambda_{ex} = 390$ nm, $\Delta\lambda = 40$ nm, indicating a fairly homogenous, and restricted mixture of fluorophores, with an emission maximum around 430 nm. The more diverse and wider ranging contour plot of oil 7197 cannot be explained just on the basis of a $\sim$4% increase in aromatic concentration, but also by a change in the type of aromatic species present. Since most fluorophores in CPOs are aromatic, it follows that the increase in aromatic concentration causes the TSFS contours to spread out over a larger parameter space. The primary process driving this is the increased rates of collisional energy transfer from small to large aromatic species. Generally as a crude oil matures, the aromatic fraction is gradually reduced and it would seem possible to assess the maturity of the oils by measuring the changes in TSFS topography. Unfortunately, this would only be applicable to oils from a single source, because the second row of Fig. 3 shows that the TSFS plots for oils with similar aromatic concentrations as 7058 (7062 & 7093) the topography of the contour plots are very different. This is caused by a relatively high polar concentration which results in increased rates of collisional quenching, with the greatest effect being observed at $\lambda_{ex} \sim 400$ nm and $\Delta\lambda$ of $<$100 nm. In the TSFS plot for 7633 the contours extend further out into the red because this oil has a relatively low polar concentration leading to a reduced quenching rate.

The bottom row of Fig. 3 shows the TSFS plots for 3 heavy oils, all of which have relatively large concentrations of polar constituents. This results in much weaker fluorescence intensity, but apart from 7169, the TSFS topography does not appear to be all that different from the TSFS in the preceding rows. 7169 is a unique case in that it is heavily degraded which has resulted in the formation of a much wider range of fluorophores as evidenced by the spread of high intensity contours into more of the parameter space.

The large degree of similarity between the TSFS plots for the very diverse oils sampled is largely due to the fact that normalisation was done at the point of maximum fluorescence intensity and this obscures the huge differences in fluorescence intensity observed for the various samples. The difference in intensity between the weakest emitting heavy oil and the most intense emission from the light oil 7703 is a factor of $\sim$200. This reduction of the data can be seen very clearly in Fig. 4A which shows the plot the integrated area for the normalized TSFS plots against

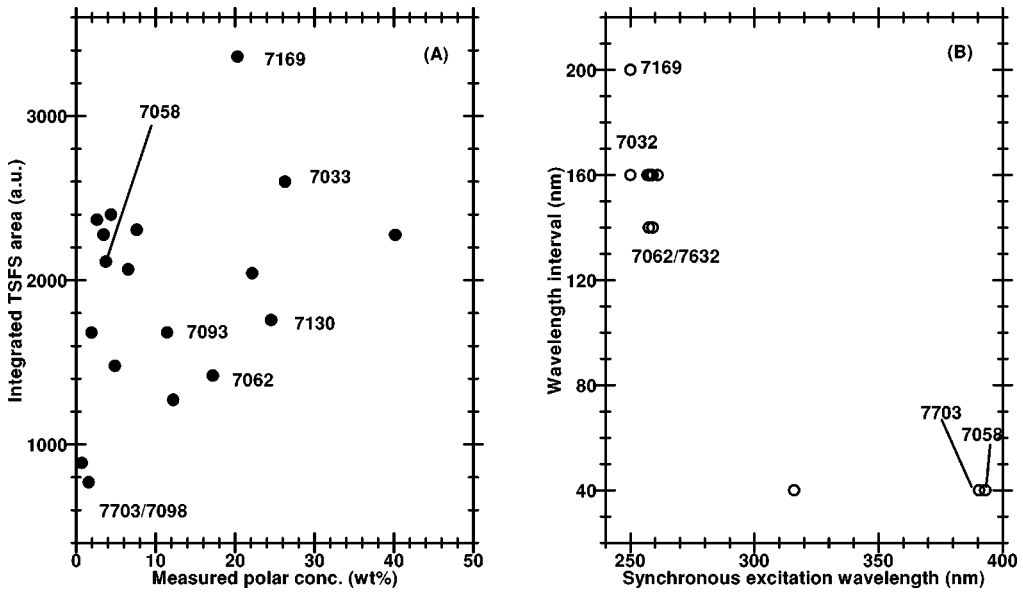

Fig. 4. (A) Plot of measured polar concentration (wt%) versus the integrated area of the normalised TSFS plots. (B) Plot of position of point of maximum fluorescence intensity as a function of synchronous excitation wavelength and wavelength interval.

the measured polar concentration. It is obvious that the integrated area increases with polar concentration, which is the opposite of what is expected since the components of the polar fraction tend to act as very efficient fluorescence quenchers [1,13]. However, Fig. 4A does support the view that the more mature, lighter oils contain fewer types of fluorophores since the integrated area is reduced compared to that of the heavier oils.

Figure 4B summarises the TSFS data for all 18 oils by plotting the position of maximum fluorescence intensity as a function of the synchronous excitation wavelength and the wavelength interval. It is clear that using the position of maximum fluorescence intensity can only discriminate the oils into two distinct populations, but neither has any clear correlation with the chemical compositional data. However, some form of normalisation is required for CPO TSFS because of the very large differences in the magnitude of fluorescence intensity between the light and heavy oils. This coupled with the inherent difficulties associated with steady-state measurements means we need to examine TSFS methods using different normalisation points which may improve the qualitative and/or quantitative accuracy of the method for CPO analysis.

CONCLUSIONS

TSFS spectra for crude petroleum oils have to be collected using a front surface or backscattering sampling geometry in order that optically dense samples can be analysed. This ensures an accurate picture of the fluorescence parameter space (the TSFS plot) is obtained. All the crude oil TSFS plots show a general diagonal contour trend from short excitation wavelength/large wavelength interval, to long excitation wavelength/short wavelength interval which is a largely result of energy transfer processes. The choice of the normalisation point for TSFS plots is of vital importance for the classification of different oil types. In this study the choice of the maximum emission intensity point was found to be inadequate for classifying oils according to their chemical composition, other than discriminating the light mature oils from all other types. We are continuing our investigations by studying the use of different normalisation points, from which a better classification method may be developed.

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