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

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Abstract:
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 petroleum oils. A better approach may be to use the Total Synchronous Fluorescence Scan (TSFS) method to fully interrogate the complex chemical composition of the oils. We present the TSFS spectra from 18 crude petroleum oils of varying composition, sourced from around the world. The TSFS of these oils are very complex, with the bands being spread out for wavelengths near 250-700 nm (Fig. 1). For the two crude oil concentrates at 119% (api 55.6, 150-250 mm) and 197% (api 78.2, 200-400 mm) the first feature represents fluorescence emission originating from energy transfer with the second, longer wavelength feature being generated by direct fluorescence emission without energy transfer. The topography of the TSFS contour maps 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.

Introduction:
Crude petroleum oils (CPOs) are complex mixtures of diverse hydrocarbons, in widely varying compositions, that originate from a variety of geological sources. The non-destructive, non-contact, qualitative/quantitative analysis of CPOs is desirable in both the oil exploration and processing industries. Fluorescence based methods offer high sensitivity, good diagnostic potential, relatively simple instrumentation, and are well suited for macro- and micro-scale analysis. 46 CPOs fluorescence derives largely from the aromatic hydrocarbon content of oils, and is strongly influenced by the precise chemical and physical composition. Unfortunately the physical and chemical diversity of CPOs complicates the development of analytic fluorescence methods. In general, light oils (high API gravity) 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 emission are due to the higher concentration of fluorophores and quenchers present in the heavier oils, which leads to a higher energy transfer and quantum yield. Increasing excitation wavelength results in a significant effect on CPO emission spectra, with a narrowing of the emission band. Reductions in the Stokes shift, quantum yield, and fluorescence lifetime are observed. The decrease in the complex interaction of energy transfer and quenching processes. At short excitation wavelengths, energy transfer processes dominate because the absorbing chromophores tend to have large bandgaps allowing energy transfer to smaller bandgap molecules. For longer excitation wavelengths, the excited fluorophores have smaller bandgaps, reducing the rate of energy transfer so most collisions result in quenching and a reduction in C. Furthermore, as the bandgap decreases, there is a reduction in the contribution to the emission reduction in lifetime. We are studying various steady state and time-resolved fluorescence methods with a view to developing qualitative and quantitative CPO analysis methods.

Materials & Methods:
The crude petroleum oils originated from several sources worldwide and all crude oils measurements were made using the same, non-diluted oil, in 1 mm pathlength quartz cuvettes. The refined oil (Edwards high vacuum oil) was sampled in a 1 ml pathlength cell. Fluorescence measurements were made using a PE LS50B fluorescence spectrometer fitted with a front surface, or 90° sampling accessories, and a red sensitive (HR28) PMT detector. All spectra were recorded with a scan speed of 1500 nm min⁻¹ over the synchronous excitation wavelength range of 250-700 nm and a wavelength interval of 40-60 nm and sits set at 15 nm excitation and 20 nm emission. Each TSFS plot was normalised with respect to the point of maximum fluorescence intensity, and then plotted with 0.2 equally spaced contour lines from 0.9 to 50.

Results & Discussion:
Synchronous excitation wavelength (nm)
Wavelength interval (nm)
Fig. 1: TSFS plots for Edwards High Vacuum Oil (HR, H110-03.026) with: (A) 90° geometry (B) front surface sampling. In both cases the oil was placed in a 1 cm cuvette.

Fig. 2: TSFS plots for 9 heavy, medium weight crude oils from 150-200 mm with a 1 x 10⁻³ nm band pass and a Δλ = 40-200 nm in a front surface sampling geometry.

Fig. 3: TSFS plots for 9 medium to light weight crude oils recorded from 250-700 nm over a Δλ = 40-200 nm in a front surface sampling geometry.

Acknowledgements:
This work was supported by the Irish Government’s National Development Plan, the Irish Research Council for Science, Engineering and Technology and Science Foundation Ireland. This work was also funded by the National Centre for Biomedical Engineering Science as part of Higher Education Authority’s Programme for Research in Third Level Institutions.

Conclusions & Future plans:
- TSFS spectra for crude oils must be measured with a front surface or backscattering geometry.
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