

Fluorescence Spectroscopy

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Identification of Oils Using Synchronous 2D and 3D Fluorescence Spectroscopy for Environmental Monitoring and Oil Exploration

Introduction

Synchronous fluorescence spectroscopy provides a useful tool to produce a simplified “fingerprint” for complex mixtures of fluorescent compounds

such as crude oil and its distillates. This technique provides a rapid method for analyzing environmental samples in fresh or sea water to identify the type of oil involved and to help include or exclude a suspected source of contamination. It can also be used to characterise oils in drilling fluids as part of hydrocarbon exploration.

Synchronous Fluorescence Spectroscopy

Synchronous fluorescence spectroscopy involves scanning the sample using both monochromators simultaneously with a constant difference between them. This difference may be in terms of wavelength - Constant Wavelength Synchronous Luminescence* (CWSL) or in terms of energy (frequency – in cm^{-1}) – Constant Energy Synchronous Luminescence* (CESL). The latter offers the advantage that it is possible to “tune out” some constant energy artefacts such as Raman bands that are associated with fluorescence spectra in order to give a “cleaner” 2D spectrum.

3D Synchronous Spectra

It is possible to generate a 3D matrix of synchronous spectra with the X axis showing the excitation monochromator wavelength, the Y axis for fluorescence intensity and the Z axis showing the incremented "Delta" value - either wavelength (in nanometers) or frequency (in cm^{-1}) depending on which synchronous mode is being used. For crude oils and their distillates, this provides a much more powerful technique than a 3D "EEM" plot where the emission (or excitation) spectra are incorporated into a 3D matrix by incrementing the fixed wavelength (which forms the Z axis). For oils – which all excite around 280 nm – it is very difficult to use EEM plots to make an accurate identification. EEM plots also feature a "ridge" where the two monochromators are at the same wavelength (or multiples thereof).

Sample Preparation

Oils readily dissolve in hexane and cyclohexane and so there are the most commonly used solvents. Quartz fluorescence cuvettes (which have four clear sides) should be used. Disposable cuvettes are unsuitable on grounds of both wavelength range and solvent resistance. For aqueous samples the samples can be solvent extracted into the cyclohexane. For neat samples a 30000-fold dilution into cyclohexane should be considered. Only high purity solvents should be used as other grades often contain aromatic impurities which also fluoresce. The solution concentration may require adjusting in order to get the readings within the range of the instrument.

Measurement

3D synchronous spectra can be measured on both the FL 6500 (pulsed xenon lamp) and FL 8500 (continuous 150 W xenon lamp) models. The FL 8500 has higher sensitivity and this means that it is able to scan the sample faster. The maximum scan speed on the FL 6500 is 24,000 nm/min whereas on the FL 8500, it is 60,000 nm/min. In this application note the FL 6500 nm was used.

The spectra were scanned between 220 and 450 nm (as defined by the excitation monochromator) and the delta wavelength was incremented from 5 nm in 2 nm steps. A 5 nm slit was used on both the excitation and emission.

Results and Discussion

Three samples – aviation fuel (kerosene), fuel oil and Kuwaiti crude were scanned as 3D CWSL plots and the results are shown below. The 2D synchronous graph is shown in the bottom right hand corner of each data set and this has been optimized for the delta wavelength at the highest peak position.

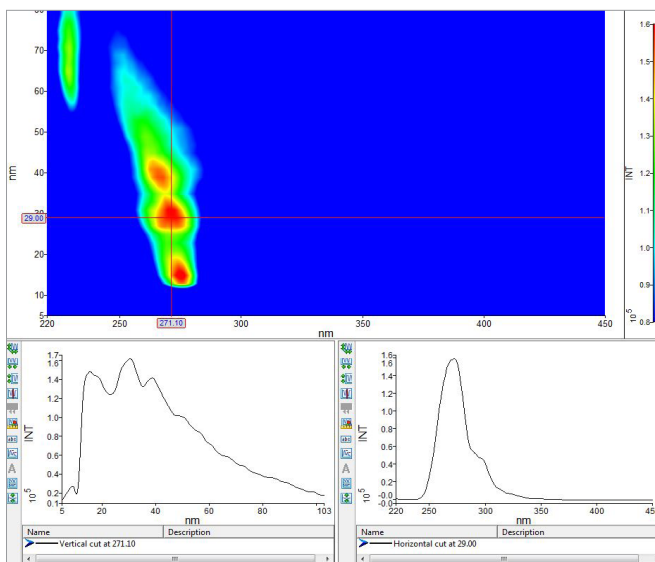


Figure 1. 2D and 3D Constant Wavelength Luminescence (Fluorescence) Spectra of Aviation Fuel (Kerosene) in cyclohexane.

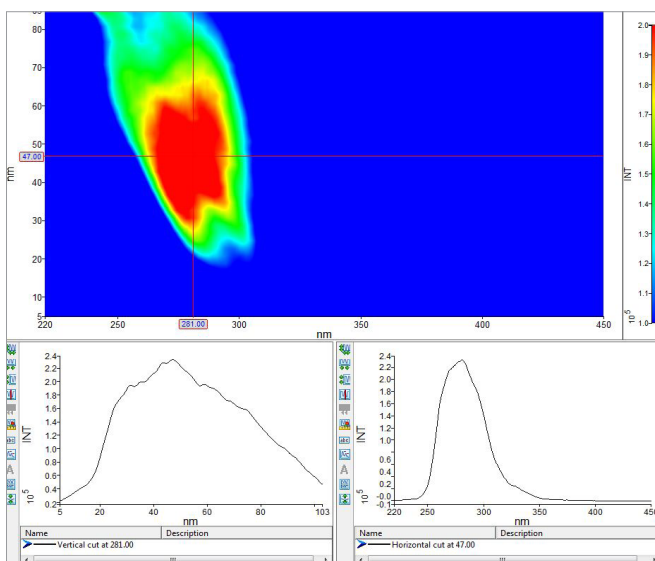


Figure 2. 2D and 3D Constant Wavelength Luminescence (Fluorescence) Spectra of Fuel Oil in cyclohexane.

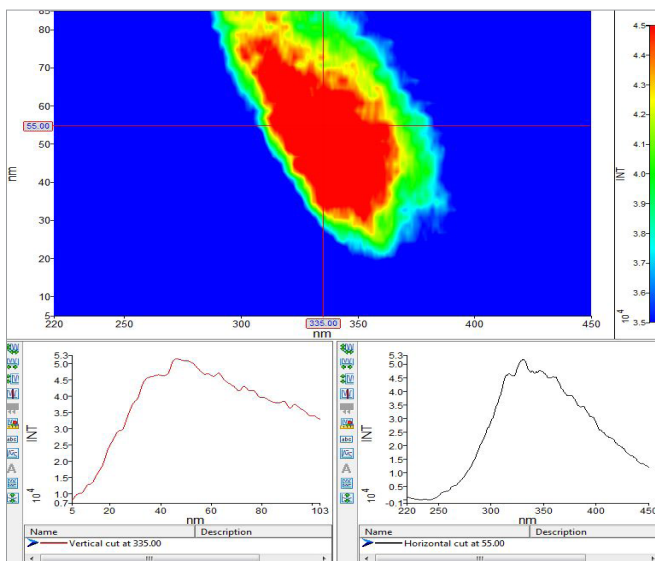


Figure 3. 2D and 3D Constant Wavelength Luminescence (Fluorescence) Spectra of Crude Oil in cyclohexane. Please note shift in position of 3D feature compared to refined oil products.

Conclusion

2D and 3D synchronous fluorescence plots provide a simple to measure and rapid method to characterise oil samples as encountered in environmental spills. The technique can also be used in oil exploration for the analysis of drilling fluids. Other sample types with complex mixtures, including PAH's (polyaromatic hydrocarbons) and drug ingredients, can also be measured. Both the FL 6500 and FL 8500 instruments are ideal for this purpose. The FL 8500 is particularly suited for high throughput laboratories by virtue of its very high scanning speed.

() Please note that the term "luminescence" is used here in its correct usage. It relates to photoluminescence – either fluorescence (singlet excited state) or phosphorescence (triplet excited state) where excitation is produced using monochromatic light produced by the instrument's excitation monochromator. It does not relate to chemical or biochemically induced excitation which is often incorrectly thought to be the only form of "luminescence". Synchronous spectroscopy is not possible with either chemi- or bioluminescence and its derivatives.*