

IDENTIFICATION OF PETROLEUM OILS BY FLUORESCENCE SPECTROSCOPY

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ABSTRACT

A simple and rapid method for the identification of weathered petroleum oils (passive tagging) by fluorescence spectroscopy is described. The approach used takes advantage of the three-dimensional character of the oil fluorescence spectra. Oil identification methods of other investigators that use fluorescence spectroscopy are also reviewed within the context of the three-dimensional system. Our method involves excitation of the oils at 15 wavelengths, between 220-500 nanometers (nm), at 20-nm intervals. The emission monochromator is rapidly scanned at each excitation wavelength to obtain an emission spectrum. The maximum emission intensities are then plotted versus the excitation wavelengths to derive silhouette profiles. These are used as fingerprints for passive tagging petroleum oils. The influence of weathering, quenching, and solvent effects on our method are also examined.

INTRODUCTION

The discharge of petroleum products into the marine environment has caused extensive environmental damage in the past. The current increasing transportation and offshore production of petroleum is, therefore, of vital concern to the U.S. Environmental Protection Agency. Effective legislation, with adequate analytical support for enforcement, should reduce this damage, and methodology for the identification of the source of discharged oil is needed.

Fluorescence spectroscopy is a rapid and promising tool for the source identification of weathered oil (passive tagging). While in the past few years many laboratories have used this tool for passive tagging both crude and refined petroleum products, few innovations in the technique have come about. Although three parameters are inherent to the fluorescence technique, only two of them have been commonly used. This can be explained more clearly within the context of a three-dimensional system. Because fluorescence spectroscopy entails three parameters (excitation wavelength, emission wavelength, and fluorescence intensity), the total spectrum of an oil can be presented as a topographical map of a mountainous region. Figure 1 depicts the total fluorescence spectrum of an oil with three fluorescence maxima; the excitation wavelength, emission wavelength, and fluorescence intensity represent the x , y , and z axes, respectively.

Most publications on the identification of oils by fluorescence spectroscopy do not mention the three-dimensional character of oil fluorescence spectra. Their authors limit themselves by using only two of the three parameters. Within the context of the three-dimensional system, the approach of these investigators can be described as taking "cuts" through figure 1 in planes that are parallel to the y axis and at specific points along the x axis. Figure 2 illustrates this; each cut is an emission spectrum at one excitation wavelength.

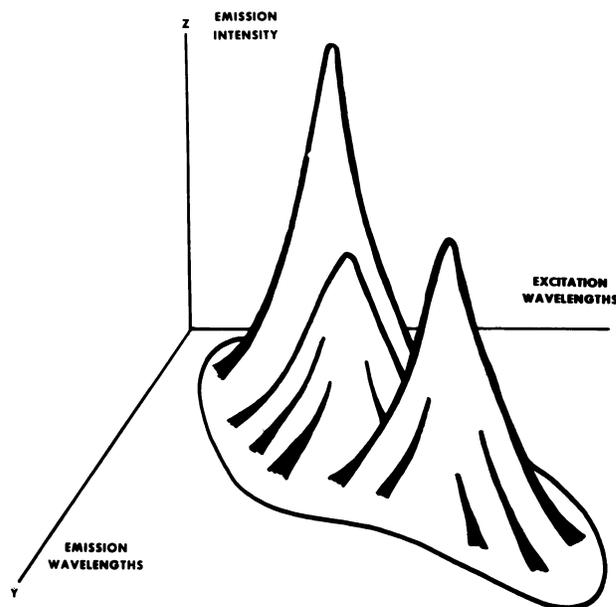


Figure 1. Three-dimensional presentation of the total fluorescence spectrum of an oil

Thus, Thruston and Knight [1] utilize 340 nanometers (nm) as the excitation wavelength for oil solutions in cyclohexane at three concentration levels. They then ratio the 386-nm and 440-nm emission maxima to one another. A similar approach is taken by Coakley [2] who excites each oil at a discrete wavelength. He selects for each oil the excitation wavelength that yields the maximum emission for that oil. His wavelengths are usually in the range 290-320 nm. Jadamec [3], in a more recent method, uses 254 nm as the excitation wavelength. He generates emission spectra for passive tagging 8 oil spill samples.

All of these methods utilize the same basic approach. The oils are excited at specific wavelengths and their emission spectra are obtained. The methods differ only in their wavelength of excitation.

Other fluorescence methods are available or have been proposed for passive tagging oils, but their utility for this purpose has not been established. Lloyd [4,5] describes a method whereby cross-sectional cuts are taken at 45° angular planes to the x and y axes. This is accomplished by simultaneously scanning the excitation and emission monochromators of the fluorescence instrument. Another method by Freearge et al. [6] proposes the analysis of oils by constructing contour maps. While this approach somewhat simulates a three-dimensional system, it is extremely time consuming and requires computer services for data manipulation.

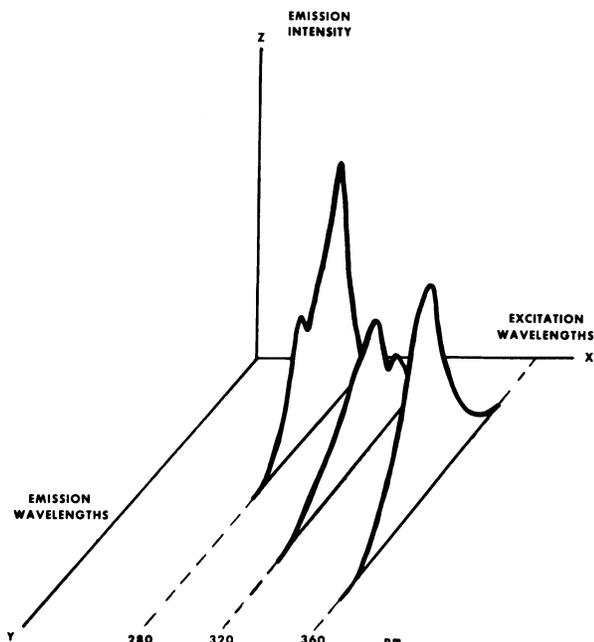


Figure 2. Three-dimensional presentation of the emission spectra of the oil in figure 1 excited at three wavelengths

Our method circumvents these limitations; sample analysis and data handling are rapid and commensurate with the other commonly used fluorescence techniques [1,2,3,]. We use all three fluorescence parameters, and thereby exploit the advantages that derive from the three-dimensional system that is illustrated in figure 1. We obtain in our method a silhouette profile of an oil's total three-dimensional spectrum as it is observed in a plane that parallels the *x* axis. Figure 3 illustrates how a simplified silhouette profile of an oil is obtained from the three-dimensional spectrum that is illustrated in figure 1. In actual practice, we excite each oil at 20-nm wavelength intervals between 220 nm and 500 nm. The emission monochromator is rapidly scanned at each excitation wavelength, and the maximum emission intensity of each scan is recorded. These maximum intensities are then plotted manually versus the excitation wavelengths, and the silhouette profiles of the oils are obtained by connecting the points with straight lines.

We evaluated the ability of the method to identify weathered oils, i.e., to correlate weathered oils with unweathered portions of the same oils (passive tagging). Pertinent environmental factors such as photodecomposition, evaporation, dissolution, and biodegradation were considered separately and in combination. Quenching and solvent effects that may influence the accuracy of our method were also examined.

Weathering effects

Previous investigators indicate that weathering may drastically degrade petroleum oils. Thruston and Knight [1], Coakley [2], and Freearde et al. [6] surmised that significant changes in the intensity and shape of the emission spectrum can occur when oils are exposed to sunlight. Two studies were therefore conducted in order to establish our method's ability to cope with weathering effects. The first study dealt primarily with photodecomposition effects, and the second study examined the combined effects of water, radiation, heat, and bacteria.

Quenching effects

Thruston and Knight [1] found that the intensity and shape of oil fluorescence spectra substantially depend on the concentrations of the solutions that are measured. Fluorescence quenching is a phenomenon that occurs at high solution concentrations and is

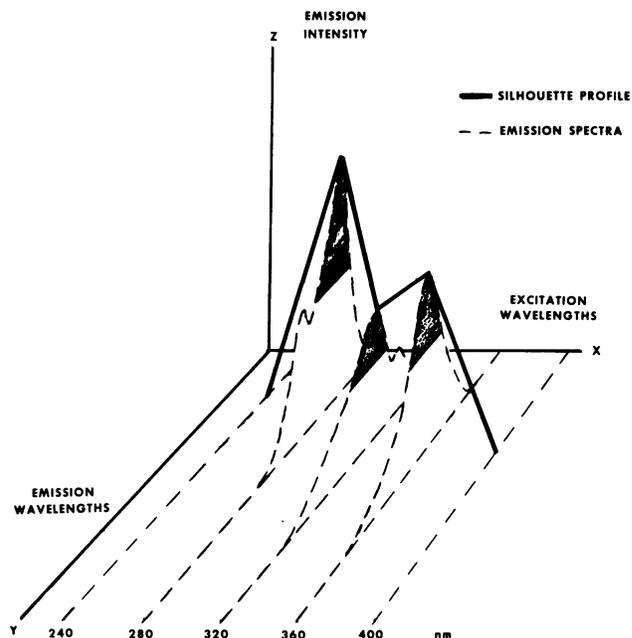


Figure 3. Three-dimensional presentation of the derivation of the silhouette profile from the oil in figure 1

characterized by the formation of excimers. These are combinations of excited molecules. Excimer formation and their effect on fluorescence spectra was first noted by Forster and Kasper [7], who demonstrated that while a polynuclear aromatic compound (PNA) yielded a fluorescence emission maximum at 390 nm, a hundredfold increase in the concentration of this compound shifted its fluorescence maximum to 480 nm. Other PNAs, exhibit similar behavior. Because other investigators [8,9] have demonstrated that petroleum oil fluorescence is primarily attributable to PNAs, we maintain that the distortion of high concentration oil fluorescence spectra is due to excimer formation.

Excimer formation is considered important to our method because its effects can combine with or can be confused with the effects of weathering. Also, losses of volatiles by spilled oils invariably result in increased concentrations of PNAs in the weathered residues; the PNAs are higher boiling materials that do not readily volatilize. As a consequence, excimer formation can become quite prominent and can cause ambiguities during passive tagging analyses. Therefore, the oil solution concentrations at which substantial quenching appears must be known before our method can be successfully used.

Solvent effects

Cyclohexane, our solvent of choice, presents two problems: (1) interference by Raman scatter, and (2) interfering emissions by solvent impurities. Raman scatter is caused by the interaction of excitation radiation with the bonds of the cyclohexane molecules. It reveals itself as an emission band that appears 0.3 microns^{-1} from the Rayleigh band in cyclohexane [10]. Also, impurities in cyclohexane yield spectra that can coincide with those of oils. The effects of these interferences on our method are also examined in this paper.

Experimental

Apparatus. A Perkin-Elmer model MPF-3 Fluorescence Spectrophotometer,¹ with a constant temperature cell bath (P.E. Part No. 220-1419) was used. The cell (10 mm pathlength, quartz; P.E. Part No. 990-2711) was maintained at $20^\circ \pm 0.5^\circ\text{C}$.

¹Mention of trade names or commercial products does not constitute endorsement by the U.S. Government.

Procedure. The silhouette profile of a typical oil was obtained in the following manner:

A stock solution with an accurately known concentration approximating 1000 mg/l oil in cyclohexane was prepared. An aliquot of this solution was then diluted to obtain a final concentration of 5 mg/l. This was measured in a cell which was placed into the constant temperature cell holder for a five-minute equilibration period. The analysis was performed at a constant temperature of 20°C.

In order to prevent the recorder pen from going off scale during a run, the excitation wavelength that yielded the maximum emission response was determined. This was performed by manually scanning the excitation and emission monochromators until a maximum pen deflection was obtained. Next, the instrument settings were adjusted to yield ca. 90% recorder scale deflection at this excitation wavelength.

The oil was then excited at 15 wavelengths, 20 nm apart, in the range 220 to 500 nm (i.e. 220, 240, 260, ..., 480, 500 nm), to obtain the maximum emission at each wavelength. This was accomplished by setting the excitation monochromator at each excitation wavelength and rapidly scanning the emission monochromator over the entire fluorescence spectral region of the oil. Fifteen compressed emission spectra were thereby obtained. A cyclohexane "blank" was similarly analyzed by exciting at the 15 wavelengths to determine its contributions to the oil spectra. None were found at the instrument settings used.

The silhouette profiles were prepared by manually plotting the maximum emission intensity of each spectrum versus its excitation wavelength and then connecting these points with straight lines. Two criteria were used to compare one profile with another: (1) shape, and (2) the excitation wavelength of the maximum emission intensity.

Weathering effects. Photodecomposition effects were examined by placing four oils (No. 2 and No. 6 fuel oil; South Louisiana and Bachaquero crude oil) as surface slicks in wide-mouth, quart-size jars, containing ocean water. The jars were exposed to the elements on a building roof during the entire month of August.

The other environmental effects were examined by subjecting five other crude oils to weathering conditions which simulate typical oil spill incidents. The weathering was performed by the Department of Environmental Protection, State of Maine, at the facilities of the TRIGOM laboratory, South Portland, Maine, as part of a U.S. Environmental Protection Agency (EPA) sponsored grant. The oils were weathered by spilling one pint of oil on salt water in 500-gallon fiberglass tanks. Seawater drawn from Casco Bay, Maine, was constantly circulated through the tanks whose geometry was such that the outlets were located at the bottom and the inlets at the top. All weathering was performed under ambient outdoor conditions, during the summer months, and for periods of 7-14 days. The weathered oils were skimmed from the water surface, dissolved in cyclohexane, and centrifuged in order to separate the oil from particulate matter and residual water. The solutions were then decanted, and the solvent stripped off with the aid of an air stream at room temperature. Silhouette profiles of the weathered and unweathered oils were then prepared and compared.

Quenching effects The concentration at which quenching phenomena became apparent was determined for four representative crude and refined oils. A No. 2 fuel oil (a low-viscosity distillate), a No. 6 fuel oil (a high-viscosity residual), a South Louisiana crude oil (a low-viscosity crude), and a Bachaquero crude oil (a medium-viscosity crude) were examined. Solutions having accurately-known concentrations of these oils in cyclohexane were prepared. Emission spectra in the range 220-600 nm were obtained by exciting at 290 nm and 340 nm, and fluorescence intensity versus concentration plots were prepared. The maximum concentration within the linear region of each plot was designated at the onset of quenching (figure 4).

Solvent effects. The emission spectra of ten oils were examined in order to demonstrate the effects of solvent Raman scatter on the fluorescence spectra of the oils. Solutions having concentrations of 1 mg/l and 10 mg/l oil in cyclohexane were excited at 290 and 340 nm. A cyclohexane blank measurement was obtained concurrently

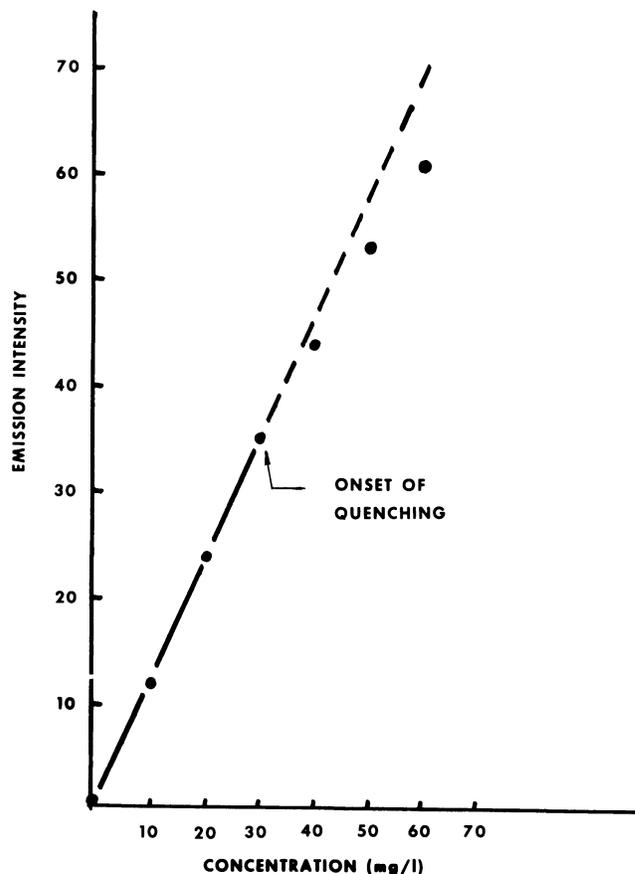


Figure 4. Emission intensity versus concentration plot of No. 2 fuel oil in cyclohexane demonstrating the onset of quenching. The maximum concentration within the linear region is 30 mg/liter

with each oil measurement using the same instrument settings. The emission spectra of two solvents (Fisher Scientific Co., Spectro-analyzed and 99 Mol % Pure cyclohexanes) were also checked for the presence of fluorescing impurities.

Results and discussion

Weathering effects. The criteria that are used to judge the efficacy of a method for passive tagging oils are: (1) whether the method can correctly correlate weathered and unweathered portions of the same oils, and (2) whether it can distinguish between oils. Our first weathering study, i.e., the study of photodecomposition effects, demonstrates that the profiles of four oils remain relatively unchanged despite weathering (figure 5) and that the method distinguishes between the oils (figure 6). Four discrete silhouette shapes and excitation wavelength maxima were obtained, yet the profiles of the weathered and unweathered portions of each oil were quite similar. We therefore conclude that our method not only discriminates between oils but also that exposure of the oils to sunlight did not adversely affect our method.

The results of our second weathering study, i.e., the study of other environmental effects, also support the contention that our method is adequate for passive tagging oils. The silhouette profiles of the weathered and unweathered portions of five crude oils are shown in figure 7. Each weathered oil is again uniquely matched with its unweathered counterpart.

Quenching effects. The optimum solution concentration for fluorescence measurement was found to be 5 mg/l oil in cyclohexane. Table 1 illustrates our reasons for selecting this concentration by listing the concentrations of the oils at which the onset of quenching occurs (figure 4). Oil solutions that exceeded this

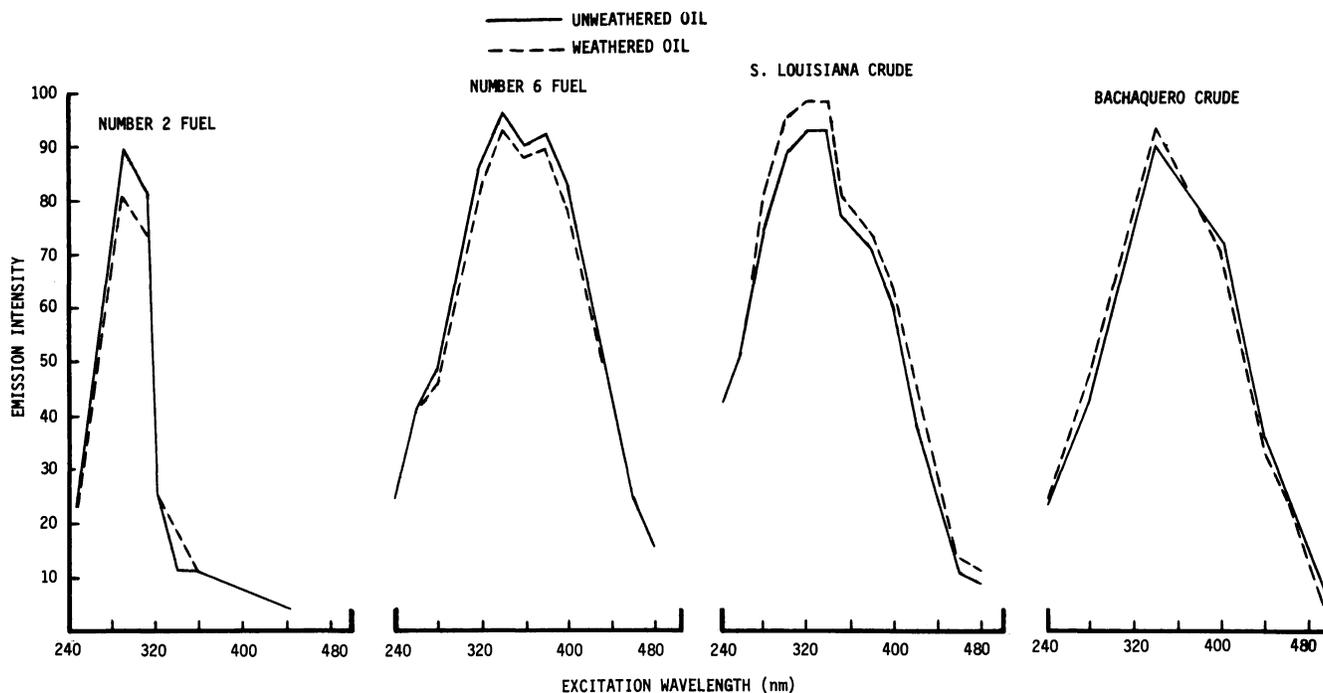


Figure 5. Silhouette profiles of weathered and unweathered portions of four crude and processed oils

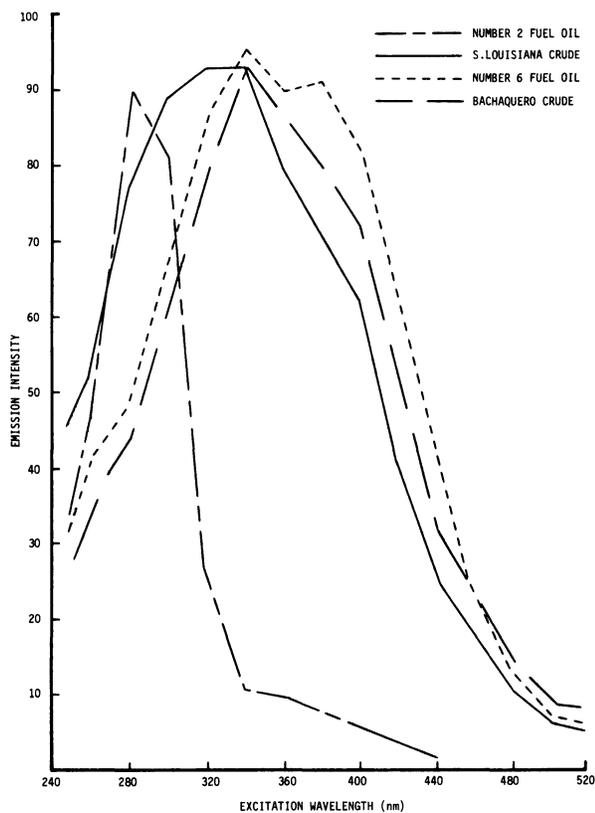


Figure 6. Overlay of the silhouette profiles of the unweathered oils in figure 5

concentration yielded fluorescence spectral envelopes that changed with solution concentration. The spectral envelopes of less concentrated solutions remained constant despite concentration changes.

We, therefore, suggest that it is vital to use solution concentrations that are within the linear portion of figure 4 to avoid spectral distortion by quenching effects.

Solvent effects. Raman scatter can be quite prominent in cyclohexane at concentrations below 10 mg/l oil in solvent. Its impact depends on the excitation wavelength that is used and on the fluorescence efficiency (emission intensity) of the oil. Typical Raman band interference with a spectrum of oil is illustrated in figure 8. Two excitation wavelengths are used, and they produce different effects. This figure demonstrates the importance of measuring neat solvent prior to oil analysis. Fortunately, most petroleum oils have such a high fluorescence efficiency that this solvent Raman band overlap does not handicap our ability to achieve oil identification.

The presence of fluorescing impurities in the solvent is a factor that must also be taken into account. Two grades of cyclohexane were examined: Spectroanalyzed and 99 Mol % Pure cyclohexane (Fisher Scientific Company). Impurities in the spectroanalyzed grade solvent yielded substantial interfering fluorescence envelopes, but the 99 Mol % Pure solvent was essentially free of these interferences. We successfully purified the spectroanalyzed cyclohexane, however, by simple distillation [11].

Summary

We have described the three-dimensional character of oil fluorescence spectra and reviewed within this context the pertinent work of previous investigators. We have also presented a straightforward method for identifying the source of discharged petroleum oil, i.e., correlating a weathered oil correctly with an unweathered portion of the same oil (passive tagging). Our method utilizes the three-dimensional aspect of fluorescence spectra, and requires only simple data manipulation. In order to validate our method for passive tagging oils, we tested its ability to match weathered with unweathered portions of nine petroleum oils and to discriminate among them. Each oil yielded a unique and different profile in these tests, and the profiles remained substantially unchanged despite weathering. We also demonstrate that some common phenomena such as fluorescence quenching, Raman scatter, and solvent impurities do not handicap our method.

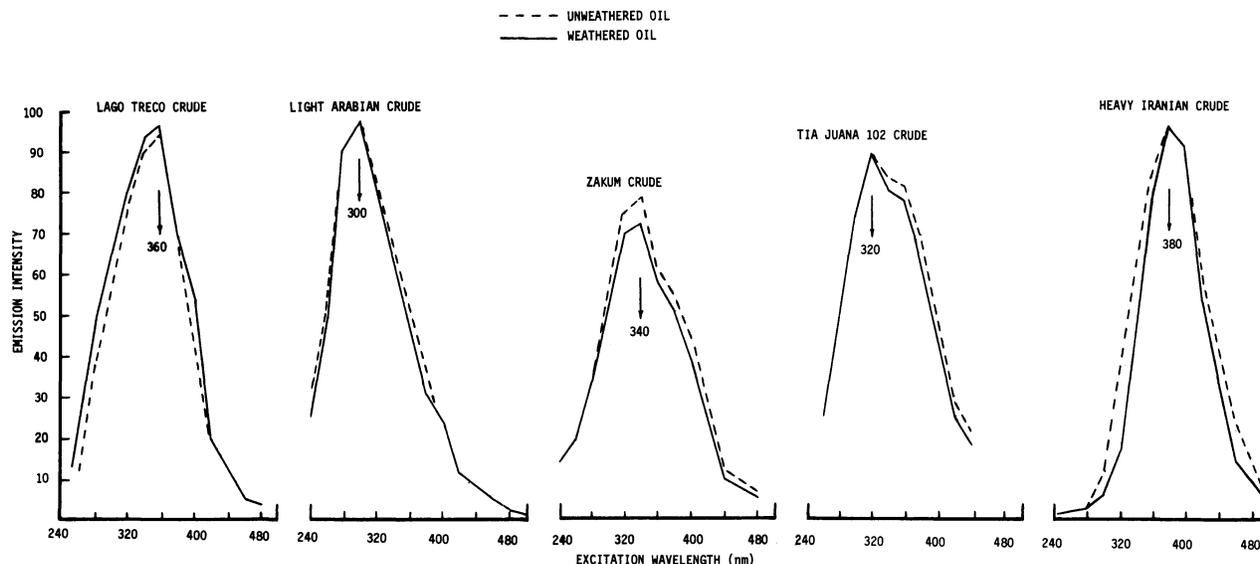


Figure 7. Silhouette profiles of weathered and unweathered portions of five crude oils

Table 1. Concentrations of oil in cyclohexane at which the onset of quenching appears for 4 crude and refined oils

OIL	CONCENTRATION (mg/l)	
	Ex 290 nm	Ex 340 nm
Number 2 Fuel Oil	30	No Emission
Number 6 Fuel Oil	6	7
Bachaquero Crude	6	18
Iran - Gach Crude	16	25

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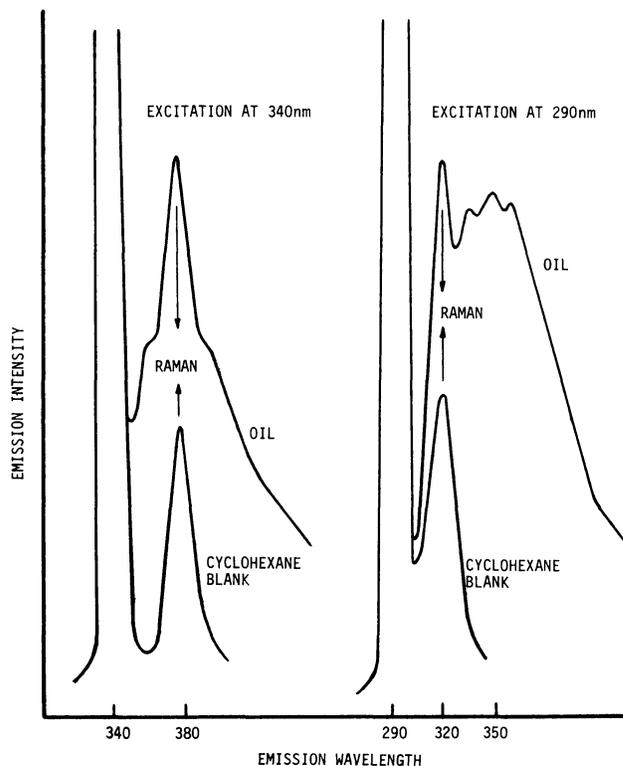


Figure 8. Raman band interference with the emission spectra of a La Rosa crude oil. The concentration 1 mg/l oil in 99 Mol % Pure cyclohexane is used

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