Determination of Synchronous Fluorescence Scan Parameters for Certain Petroleum Products

Digambara Patra, K Lakshmi Sireesha and A K Mishra*
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036
Tel (044) 4458251, Fax (044) 2352545, E-mail: mishra@acer.iitm.ernet.in

Received: 21 October 1999; accepted: 25 January 2000

Synchronous fluorescence scan (SFS) technique is a promising tool for polycyclic aromatic hydrocarbon analysis. For analytical purposes the SFS parameters that are needed to be optimized are $\Delta \lambda$ ($\lambda_{em} - \lambda_{ex}$) and synchronous fluorescence maximum. In the present work, conventional petroleum products available in Indian market like kerosene and petrol, and added lubricant namely 2T oil have been studied with respect to their SFS parameters. For these multilfluorophoric systems conventional electronic absorption and fluorescence spectroscopy is of limited use. The effect of dilution (5 - 100 per cent, v/v in cyclohexane) on the SFS parameters has been examined. In these multilfluorophoric systems, excitation energy transfer results in shifting of synchronous fluorescence maxima with increasing concentration of the petroleum product. The correlation of this shift with concentration shows the possibility of using it as an analytical method to quantify the petroleum products in the environment.

Introduction

Petroleum products usually contain a host of polycyclic aromatic hydrocarbons with high fluorescence efficiency. Fluorescence studies of crude oils have provided valuable insight into their fundamental and dynamic properties. Fluorescence obtained from these crude oils comes from the different polycyclic aromatic hydrocarbons present in these systems. In spite of their complexities and differences, crude oils often exhibit systematic behaviour, particularly with fluorescence properties. Total fluorescence scanning gives a systematic spectral fingerprint for different crude oils obtained from different sources. Therefore, fluorescence properties of crude oils and related organic matter have been used in various applications. Evolution of organic material in source rock can be monitored by fluorescence. Ralston et al. have shown the dependence of fluorescence quantum yield with the excitation wavelength, which is similar for different crude oils. Downare and Mullins have observed that energy transfer produces large red shifts and large widths in the fluorescence emission spectra for long wavelength excitation of different crude oils. They have also found that the fraction of emission resulting from collisional energy transfer relative to nascent emission is almost independent of oil types and quantum yields are lower for higher fluorophore concentrations (heavy crude oils) and higher for light crude oils.

Use of fluorescence for characterization of different crude oils has led to the development and commercial use of new kind of fluorescence instruments. Out of these, synchronous fluorescence scan gets preference because of its narrower spectral band, high selectivity and simplified spectrum. The technique was initially developed by Lloyd to identify many polynuclear aromatic hydrocarbons and refined petroleum products. In this technique, both excitation and emission monochromators are scanned simultaneously, keeping a constant wavelength difference inbetween them. Parameters needed to be optimized in the synchronous fluorescence scan based analytical methods are $\Delta \lambda$ and $\lambda_{sfs}^{max}$.

Taylor and Patterson have analyzed the excitation resolved synchronous fluorescence of aromatic compounds and fuel oil. Lloyd has successfully characterized petroleum products of high relative molecular mass for forensic purposes using SFS. He has also characterized rubbers obtained from tyre prints using this technique. John and Soutar have identified different types of crude oils obtained from different sources using this technique. They have studied the effect of factors like

*Author for correspondence
wavelength increment, concentration, temperature, and frequency bandpass on synchronous fluorescence spectra of different crude oils. It is found that there is a little difference in the synchronous fluorescence spectra of different crude oils obtained from different sources, which shows a small variation in the relative amounts of aromatic components in each crude oil. Shaver and McGown have successfully analyzed the complex coal liquid samples using lifetime synchronous spectrum. However, conventional petroleum products like petrol, kerosene, and lubricant like 2T oil have never been subjected to evaluation of their synchronous fluorescence properties. The present study is aimed at evaluation of synchronous fluorescence parameters for petrol, kerosene, and 2T oil that are commonly available in Indian market. The effect of dilution on these multifluorophoric systems has been studied.

Experimental Procedure

Kerosene, petrol (leaded), and 2T oil (Servo) were collected from the local market in Chennai. Particulate matter in the products was removed by centrifugation at 4000 rpm. Cyclohexane (HPLC grade, Ranbaxy) was used as solvent after purification and was subjected to blank experiments to ensure its fluorimetric purity. A known volume of pure sample was pipetted out and was made up to the corresponding concentration (in per cent) with cyclohexane.

Absorption spectra were recorded on a Shimadzu spectrophotometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorimeter. For fluorescence as well as synchronous fluorescence measurement the scan speed was 240 nm/s and PMT voltage was at 700 V. Excitation and emission slit width were 5 nm. Excitation source was 100 W Xenon lamp. The corrected fluorescence spectrum was recorded in the range 200–600 nm and synchronous fluorescence spectra were plotted in the excitation scale. The spectral shifts were measured by taking the first derivative of synchronous fluorescence spectra. Three independent experiments were performed for samples obtained from different sources.

Results and Discussion

Generally, petroleum products like petrol, kerosene and 2T oil contain a large amount of organic molecules, which absorb light strongly in UV range. The absorption spectra of neat samples of petrol, kerosene and 2T oil are shown in Figure 1.

Figure 1 shows that petrol and kerosene absorb strongly in the UV range from 200 to 350 nm, whereas 2T oil absorb strongly in the range 200 to 480 nm. However, in the absence of any structure, absorption spectrometry has no analytical use for these systems.

Conventional Fluorescence of Petroleum Products

Kerosene shows the cut-off line of excitation wavelength in the range 250 to 350 nm. No change was ob-
served in the emission maximum of kerosene in the excitation range 250 to 330nm. The excitation wavelength was fixed at 330nm, for which the emission intensity was maximum. No fluorescence emission was observed when petrol was excited in the wavelength below 300nm and above 400nm. 2T oil shows an excitation maximum of 470nm and emission maximum at around 510nm.

The conventional fluorescence spectra of kerosene, a representative sample, at various dilutions (5 – 100 per cent, v/v in cyclohexane) is given in Figure 2. The spectra are generally broad with some degree of structuring. An enhancement of fluorescence intensity with a red shift of emission maximum is observed with increasing concentration. The plot of variation of fluorescence intensity at 344nm with concentration is shown in Figure 3(a).

Comparison of these spectra with the conventional fluorescence spectrum shows that there is a significant band compression (less FWHM) in the SF scan. The maximum intensity was found at $\Delta \lambda = 15$nm for kerosene and was chosen as optimized $\Delta \lambda$. Similar optimization was done for petrol and 2T oil. The optimized $\Delta \lambda$ for petrol and 2T oil were 40nm and 35nm, respectively. The synchronous fluorescence spectra of kerosene at various dilutions (in cyclohexane) are shown in Figure 5.

The overall shift of 10nm on going from 5 per cent kerosene to neat kerosene is comparable to the shift of maximum observed in conventional fluorescence spectrum (Figure 2). However the narrower SF bands make it possible to observe the variation of SF spectral shift with concentration more clearly. The first derivative of
Figure 4—Synchronous fluorescence spectra of kerosene (neat) at various \( \Delta \lambda (\lambda_{ex} - \lambda_{em}) \). The values are shown in the figure.

Figure 5—Synchronous fluorescence spectra and first derivative synchronous fluorescence spectra of kerosene at various concentrations in cyclohexane (in per cent, v/v). \( \Delta \lambda = 15 \text{nm} \) synchronous fluorescence spectrum provides a more accurate value of the maximum. Representative first derivative spectra for kerosene are given in Figure 5 from which the value of SF maxima were obtained. Figure 6(a) shows the shift of these SF spectral maxima with concentration.

It is observed that there is a shift of spectral maximum to longer wavelength. The spectral shift is more rapid in the lower concentration range as compared to the higher ranges. The overall variation, however, is quite regular. It may be noted that the shoulder that appears towards shorter wavelength in 5 per cent solution, rapidly diminishes in intensity. SF spectra of petrol (Figure 7) and 2T oil (Figure 8) show similar trends.

Figure 6—Plot of first derivative synchronous fluorescence maximum \( (\lambda_{ex}^{max}) \) with concentration (in cyclohexane in %, v/v). (a) Kerosene \( (\Delta \lambda = 15 \text{nm}) \), (b) Petrol \( (\Delta \lambda = 40 \text{nm}) \) and (c) 2T oil \( (\Delta \lambda = 35 \text{nm}) \). In Figure 6(c) the \((x-x-x)\) line refers to the shift of shorter wavelength band and the \((*-*)\) line refers to the shift of longer wavelength band.

The extent of synchronous fluorescence spectral shift for petrol was 20 nm and for 2T oil it was much more, i.e., 72 nm. For 2T oil, it is observed that the synchronous fluorescence spectrum at lower concentration is essentially an overlapping two band system; the shorter wavelength band which is the predominant band at 5 per cent rapidly decreases in intensity with increasing concentration and at \( \geq 20 \) per cent only longer wavelength band persists. Figure 6(c), therefore, shows the shift of shorter wavelength band maximum up to 20 per cent and that of longer wavelength maximum above that concentration.

The other important observation that is made is that the intensity of SF maximum does not vary much with concentration for kerosene but for petrol and 2T oil, intensity keeps on decreasing with increasing concentration. This trend was already observed for conventional fluorescence spectral intensity too (Figure 3). The linearity of electronic spectral parameters like optical density and fluorescence intensity with concentration is usu-
Figure 7–Synchronous fluorescence spectra of 5, 10, 20, 30, 40, 50, 60, 80 per cent petrol in cyclohexane and petrol (neat, 100 per cent). Δλ = 40nm

genually expected only at quite low concentration ranges of the sample. In the chosen concentration range for our study (5–100 per cent) intensity based estimation techniques are not available. However the regularity of shift of SFS maximum offers such a possibility. The narrow spectral bands of SF technique makes it possible to obtain the spectral shifts to a fairly high degree of accuracy. Therefore spectral shift based calibration curves given in Figure 6 provide reliable estimation method for petroleum products at high concentration ranges. Even the error ranges of data, such estimations for kerosene and petrol for which the overall spectral shift is low, can be made within 10 per cent accuracy. For 2T oil the accuracy is much better at ±1.5 per cent.

Almost every petroleum product contains various polycyclic aromatic hydrocarbon fluorophores. Low-boiling products like petrol and kerosene predominantly contain one- and two-ring systems17 whose absorption and fluorescence spectrum appears at higher energy (<350 nm). A higher boiling product like 2T oil contains polycyclic aromatic hydrocarbons of various ring sizes ranging from one-ring system to 4- and 5-ring systems. Non-radiative resonance energy transfer between molecules occurs by a Foster type mechanism when the emission spectrum of the energy donor overlaps with the acceptor absorption spectrum18. The efficiency of such energy transfer is given by the formula:

\[ k_e = (R^6 / K^2 \times n^4 \times \alpha) \times 8.71 \times 10^7 \text{ s}^{-1} \]

where \( R \) is the distance between the donor and acceptor in Å, \( J \) is the overlap integral which expresses the degree of spectral overlap between the donor emission and the acceptor absorption and its units are \( M^2 \text{ cm}^2 \), \( K \) is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor, \( n \) is the refractive index of the medium and \( \alpha \) is the emissive rate of the donor which can be expressed as \( \Phi_d / \tau_d \) where \( \Phi_d \) is the quantum yield of the donor in the absence of acceptor and \( \tau_d \) is the life time of the donor in the absence of acceptor. For randomly oriented donor and acceptor molecules in solution the orientational factor contributes an averaged value of 2/3. The efficiency is then governed by the spectral overlap integral and the mean distance between the donor and acceptor molecules. Petroleum products invariably containing multiple fluorophores absorbing and emitting in a broad wavelength range, is expected to have extensive spectral overlap of absorption and emission spectra of various species. The efficiency of energy transfer then becomes only a function of the mean distance of separation between the donor and acceptor pairs. This distance decreases with increasing concentration of the petroleum product sample. In neat samples, \( R \)'s of various donor and acceptor pairs being minimum the most efficient and multiple Foster type energy hopping would be observed the energy being nonradiatively transferred from higher electronic energy states (lower ring system polycyclic aromatic hydrocarbon) to the lowest energy sink (higher ring system polycyclic aromatic hydrocarbons) through multiple hopping. Emission can then be observed mostly from species emitting at longer wavelengths. With increasing dilution the mean distance of separation increases, thus resulting in less efficient resonance energy
transfer which is reflected in progressive blue shift of the emission maximum. This phenomenon which is observed for conventional fluorescence spectra (Figure 2) is quite clearly observable for synchronous fluorescence spectrum due to the extensive narrowing of spectral bands. It is appreciable that the identity of individual fluorophores that could be present in the sample and their absolute concentration are unimportant for developing an estimation method based on shift of spectral maximum; what is important is the regularity of the shift with concentration.

Acknowledgement

The authors gratefully acknowledge the financial support extended by Council of Scientific and Industrial Research, New Delhi, to carry out this project.

References