Abstract  Extending the two-dimensional synchronous fluorescence scan to a three-dimensional total synchronous fluorescence scan (TSFS) spectral measurement gives the total synchronous fluorescence characteristics of a multifluorophoric sample at various possible wavelength intervals (\(\Delta \lambda\)), which could help to characterize multifluorophoric systems better. TSFS spectra of petroleum products such as diesel, kerosene, petrol, engine oil etc., available in the Indian market, are reported. Fluorescence in these samples is due to the presence of polycyclic aromatic hydrocarbons (PAHs) of various ring sizes. The TSFS contour plot profiles of the neat samples measured at right-angle geometry is a result of various energy-degrading photophysical processes such as inner filter effect, light attenuation, resonance energy transfer, collisional quenching etc. TSFS plots make it easy to obtain the optimized \(\Delta \lambda\) of an unknown sample of analytical interest. TSFS and the excitation-emission matrix (EEM) techniques are similar, but the contour profiles generated are different. The response of the TSFS contour profiles to dilution is different from that in the EEM contour profiles. Thus, TSFS can provide an alternative way of presenting the fluorescence response of concentrated multifluorophoric samples.

Keywords  Total synchronous fluorescence scan · TSFS · EEM · Petroleum products · Fluorescence

Introduction

Spectroscopic characterization of multicomponent systems such as petroleum products have been a topic of great interest, where chemical species are analyzed with respect to the overall spectral characteristics of the system. Common spectroscopic techniques such as UV-visible, IR, Raman, NMR etc. need tedious separation procedures for characterization of multicomponent/complex mixture systems. However fluorescence techniques have higher selectivity for such systems [1, 2].

Petroleum products contain traces of polycyclic aromatic hydrocarbons (PAHs) that are highly fluorescent. Therefore, the fluorescence properties of petroleum products have been studied intensively for devising fluorescence-based analytical methods [1, 2, 3, 4, 5, 6]. For multifluorophoric samples at higher concentrations, despite the presence of factors such as light attenuation (LA), self-absorption, energy transfer (ET) and collisional quenching (CQ), it has been observed earlier that the use of right-angle sample geometry is capable of providing better analytical utility, as compared to front-face or 45°-angle sample geometry [6, 7]. Synchronous fluorescence scan (SFS) gives a narrower and simpler spectrum and is of extensive use for multi-fluorophoric analysis [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. In this method, both excitation and emission monochromators are scanned simultaneously keeping a fixed wavelength interval (\(\Delta \lambda\)) between them (constant \(\Delta \lambda\) mode). The parameter \(\Delta \lambda\) needed to be optimized in SFS and this optimization can be carried out by measuring the SFS spectra at various \(\Delta \lambda\).

In the present work we have extended the two-dimensional synchronous measurement to total synchronous fluorescence scan (TSFS) spectra measurement, where the TSFS spectra is obtained by plotting fluorescence intensity as a combined function of the excitation wavelength and of the difference between the emission and excitation wavelengths (\(\Delta \lambda\)). Such TSFS plots are very similar to the well-known EEM (excitation-emission matrix) plots [4], the difference being that here data are collected along diagonals (\(\lambda_{em} = \lambda_{ex} + \Delta \lambda\)) instead of lines (\(\lambda_{ex}\) = constant). Consequently, the iso-intensity contour plots of TSFS are expected to be different from those of EEM. The synchronous fluorescence spectral features are usually sharper than the corresponding conventional fluorescence spectra due to the compression of spectral bandwidth. The corresponding feature expected in TSFS is that the contour
plots of TSFS would be better resolved than those of EEM. Earlier, in combination with a selective fluorescence quencher, Ayala et al. [21] have used TSFS to obtain better resolution of an analyte present in a mixture. The three-dimensional total synchronous fluorescence scan (TSFS) spectral measurements for different multifluorophoric petroleum products such as diesel, kerosene, petrol, engine oil etc., commonly available on the Indian market, have been presented here.

Materials and methods

Samples

Diesel, engine oil (Mobil), kerosene, and petrol (unleaded) were collected from the local market in the Chennai. Kerosene (PDS) was collected from the Public Distribution System, Government of India. Cyclohexane (HPLC grade, Ranbaxy) was used as solvent after purification and checking that it was completely non-fluorescent. A known volume of pure sample was pipetted out and made up to the desired concentration (in %, v/v) with cyclohexane. Measuring a known volume of the desired petroleum product (neat sample) and mixing them in different proportions, the synthetic mixtures were prepared. To check the spectroscopic consistency, test samples from ten different places in Chennai were collected in their pure form within a time gap of 6 months. Except for some minor changes in fluorescence intensity, no variation in other fluorescence properties was observed for these samples.

Experimental technique

Fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. For synchronous fluorescence scan measurement, the scan speed was 240 nm/s and PMT voltage was 700 V. Excitation and emission slit widths were 5 nm. Excitation source was a 100 W Xenon lamp. Right-angle geometry was used for measurement because for fluorophores at higher concentrations it gives larger linear dynamic range [22], lower detection limit [22] and larger shift in synchronous fluorescence maximum [6, 7] as compared to the front-face or 45°-angle sample geometry. The dimension of the cell used was 1 cm². For neat samples where the optical densities are high, the spectra reflect a combined effect of fluorescence and inner filter effect. The synchronous fluorescence scans were obtained in the excitation wavelength range of 250 nm to 700 nm at various wavelength interval from 10 nm to 200 nm. The synchronous fluorescence scan spectrum at each wavelength interval was measured in 10 nm steps. The three-dimensional total synchronous fluorescence scans (TSFS) were obtained by plotting the fluorescence intensity (z-axis) as a function of synchronous excitation wavelength (x-axis) and wavelength interval (Δλ) (y-axis). A Windows-based software, ORIGIN, was used for plotting the 3D topographical surface diagrams and contour maps.

Results and discussion

Characterization of neat samples

The TSFS technique allows plotting of synchronous emission intensities at all combinations of synchronous fluorescence scan (SFS) and wavelength interval (Δλ) in a single three-dimensional array either as a contour diagram or as a topographical surface. The total synchronous fluorescence scan (TSFS) spectra of a neat sample of diesel at right-angle sample geometry are given in Fig. 1. It shows that the TSFS contour map of diesel spreads in the synchronous excitation wavelength (λSFS max) 440–580 nm and in the wavelength interval (Δλ) region 10–140 nm. The contours are concentrated in the synchronous excitation wavelength 500–520 nm and wavelength interval 30–50 nm. The maximum fluorescence intensity for neat sample of diesel is observed at Δλ=40 nm, which has been found earlier to be the optimized Δλ for diesel [6]. Thus, TSFS can be conveniently used to find the optimized Δλ for an unknown sample. The 3D topographical plot for neat diesel shows two fluorescence maxima, one at ~420 nm and the other at ~510 nm. Generally, the PAH fluorescence maxima shift to longer wavelengths with increasing ring size [6, 23]. PAHs having lower aromatic ring size give a shorter λSFS max band and higher aromatic ring size give a longer λSFS max [6]. For example, two-ring PAHs like naphthalene emit around 300–340 nm, three-ring PAHs (like anthracene) at around 360–390 nm and five-ring PAHs (likeperylene) at around 420–480 nm [24]. Thus, the two λSFS max of neat diesel originate from larger ring (5/6) PAHs [6] present in diesel. In contrast, for kerosene,