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Effect of sample geometry on synchronous fluorimetric analysis of petrol, diesel, kerosene and their mixtures at higher concentration

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A comparison of synchronous fluorescence scan (SFS) spectra of petrol, diesel and their mixtures with kerosene in front surface, 45° and 90° angle sample geometry as obtainable from a commercial fluorimeter reveals that 90° angle sample geometry provides certain distinct characteristics to SFS spectra. The presence of extensive inner filter effects and resonance energy transfer in petroleum products are the major causes of the distinctive characteristics of these spectra. These characteristics enable the development of calibration plots for mixture samples (petrol–kerosene and diesel–kerosene) based on the shift in λ_{SFS}^{max} and SFS intensity. This novel method shows promise in detecting and estimating the contamination of petrol and diesel by kerosene. Calibration graphs obtained from SFS intensity measurement are found to be efficacious in the whole range 0–90% v/v of kerosene, and give a good linearity in the adulteration range generally found in the field (0–50% v/v) for petrol and diesel. The method is simple, rapid and superior both in terms of sensitivity (0.1% v/v) and accuracy to other analytical methods used for petroleum product analysis.

1. Introduction

The contamination of diesel and petrol by kerosene is known to be a serious problem in South Asia and the development of suitable methods for their analysis has been the topic of much interest.[1–7] These petroleum products contain many polycyclic aromatic compounds (PACs) which are highly fluorescent. Therefore fluorescence, in contrast to conventional methods, can be used to analyse them directly. Fluorescence also gives sensitivity, selectivity and simplicity. Synchronous fluorescence scan (SFS) spectroscopy, developed by Lloyd[8] in 1971, has been successfully used for the simultaneous determination of polycyclic aromatic compounds in the environment.[9–14] In this method both excitation and emission monochromators are scanned simultaneously keeping a fixed wavelength interval between them (constant $\Delta\lambda$ mode).

Conventional commercial fluorimeters usually employ a right angle geometry. For analytical fluorimetry it becomes necessary to use a concentration of fluorescent samples at a level where light absorption is low enough to avoid inner filter effects. Mutifluorophoric petroleum samples usually have very high optical densities and sample dilution becomes necessary for conventional fluorescence measurements at right angle geometry.[15–21] In the literature, a front surface illumination has generally been preferred for fluorescence measurement of petroleum products at higher concentrations.[18–22]

For an undiluted petroleum sample with multiple fluorophores, each fluorophore having its own distinct absorption spectrum, the inner filter effect in right angle geometry is strongly excitation wavelength dependent. At and below an excitation wavelength where complete saturation occurs the sample will be completely opaque showing no fluorescence.

Yet another characteristic of such a sample will be the presence of extensive resonance energy transfer due to strongly overlapping absorption and emission spectra.[15,21–24] These two characteristics effectively render conventional analytical fluorimetry at right angle geometry, which relies on a linear dependence of fluorescence intensity with concentration, completely useless. However, they could impart a certain distinctive uniqueness to the fluorescence spectrum of a petroleum product at right angle geometry.

In this work, we have compared the synchronous fluorescence spectra of petrol, diesel, kerosene and their mixtures at three sample geometries: front surface, 45° angle with a triangular cell and 90° angle. A synchronous fluorimetric analysis of petrol, diesel and kerosene has been carried out using these three sample geometries. An attempt has also been made, for the first time, to use the synchronous fluorimetric technique to check for the contamination of petrol and diesel by kerosene.

2. Experimental

2.1 Sample

Petrol (unleaded), diesel and kerosene were obtained from Madras Refinery Limited, Chennai, India. A known volume of neat kerosene was pipetted out and was made up to the corresponding concentration (in % v/v) with petrol/diesel to prepare the desired synthetic mixture.

2.2 Instrumentation

Fluorescence spectra were measured using a Hitachi (Tokyo, Japan) F-4500 spectrofluorimeter. Three different sample geometries (front surface illumination, 45° angle and 90° angle) were used for analysis as shown in Fig. 1. For SFS measurement, the scan speed was set at 240 nm s^{-1} and the photomultiplier tube (PMT) voltage at 700 V. The excitation source was a 100 W xenon lamp. The synchronous fluorescence scan was measured at an excitation wavelength range of 250 to 600 nm. The optimized $\Delta\lambda$ for petrol and diesel were found by scanning the neat sample at various $\Delta\lambda$ (with a difference of 10 nm). A $\Delta\lambda$, which gave the maximum fluorescence intensity at the corresponding synchronous fluorescence maximum
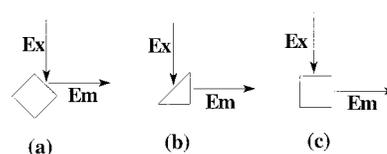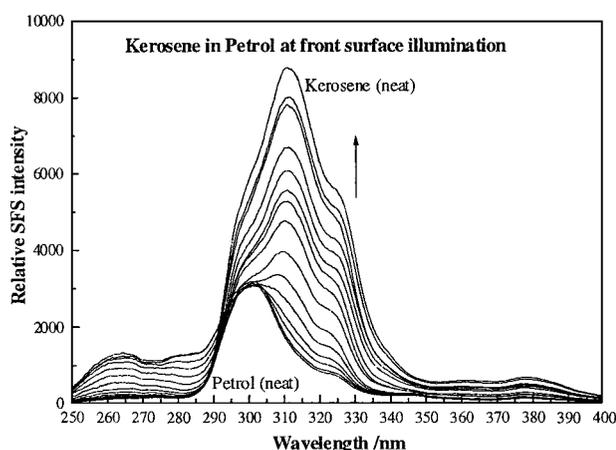

Fig. 1 Sample geometries used for analysis of petrol, diesel, kerosene and their mixtures. (a) Front surface illumination, (b) 45° angle sample geometry with a triangular cell and (c) 90° angle sample geometry.
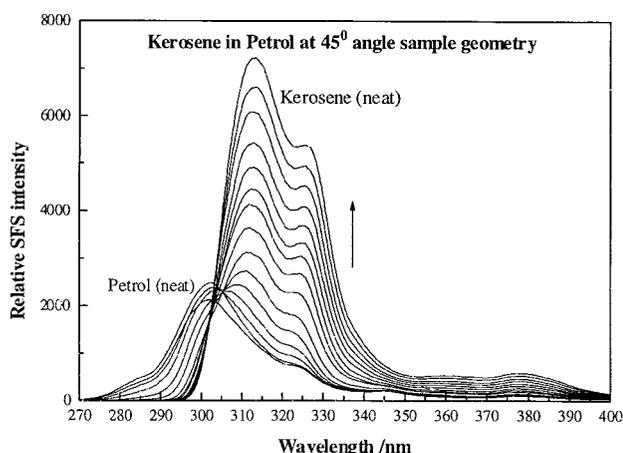
(λ_{SFS}^{max}) was chosen as the optimized $\Delta\lambda$ for that sample. The optimized $\Delta\lambda$ for petrol and diesel was found to be 30 nm. This $\Delta\lambda$ was used for further analysis of contaminated samples.

3. Results and discussion

Fig. 2 shows the SFS spectra of neat and mixture samples of petrol with kerosene at front surface illumination. Fig. 3 and Fig. 4 show SFS spectra for 45° and 90° angle sample geometries respectively. The synchronous fluorescence maximum of a sample as plotted on the excitation spectral range was chosen as the λ_{SFS}^{max} of that sample. With progressive increase in kerosene proportion, λ_{SFS}^{max} shifts from 301.6 nm (neat petrol) to 313.4 nm (neat kerosene) with front surface illumination. With 45° angle sample geometry (Fig. 3), the position of λ_{SFS}^{max} remains more or less the same. Small differences found are loss of spectral features at shorter wavelengths and a relatively more pronounced shoulder at ~ 322 nm. With reference to Fig. 1(b), it is clear that reabsorption of fluorescence at shorter wavelengths (~ 250 nm)

is responsible for this loss of fluorescence. The spectral features at 90° sample geometry (Fig. 4) are markedly different for other geometries. The appearance of fluorescence starts only above 290 nm, which is clearly a result of inner filter effects. Neat petrol shows a maximum at 312.2 nm (red shift compared to other geometries), and has a more pronounced shoulder at ~ 322 nm. This maximum keeps decreasing in intensity and progressively shifts to red on addition of kerosene and completely vanishes by 30% v/v kerosene. The spectral features at longer wavelengths (350–400 nm) are more pronounced than those for other geometries, but do not show much shift. Comparison of Fig. 2, 3 and 4 suggests that measurement at 90° geometry offers a larger range of shift in spectral features due to the presence of substantial inner filter effects.

Fig. 5, 6 and 7 give the SFS spectra of diesel–kerosene mixtures at front surface, 45° and 90° angle geometries respectively. The general observations are similar to those for petrol–kerosene mixtures. In fact geometry effects are much more pronounced here as diesel contains fairly significant amounts of higher polycyclic aromatic compounds. With increasing addition of kerosene the shift in spectral maxima (diesel: 387 nm, kerosene: 312 nm) is nominal for front surface illumination (Fig. 5), highly pronounced for 90° geometry (Fig. 7) and shows an intermediate trend at 45° angle geometry
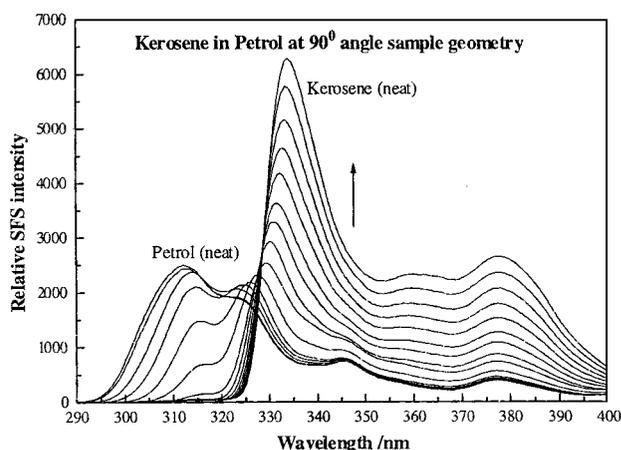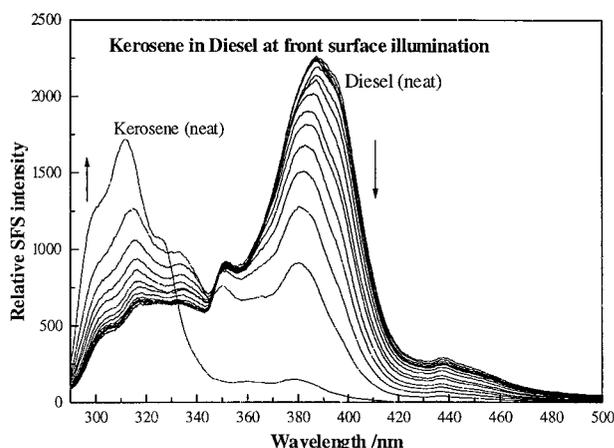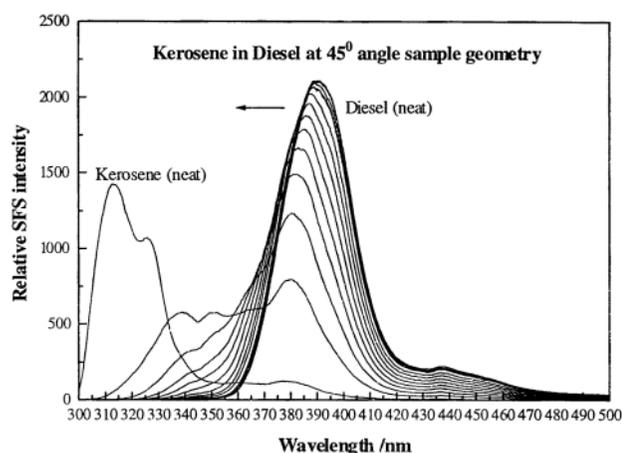

Fig. 2 Synchronous fluorescence scan spectra of a neat sample of petrol, petrol contaminated by kerosene at 0.1, 1, 2.4, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90% v/v and a neat sample of kerosene at front surface illumination. $\Delta\lambda$ = 30 nm. The excitation and emission slit widths were kept at 2.5 nm and 5.0 nm respectively.

Fig. 4 Synchronous fluorescence scan spectra of a neat sample of petrol, petrol contaminated by kerosene at 0.1, 1, 2.4, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90% v/v and a neat sample of kerosene at 90° angle sample geometry. $\Delta\lambda$ = 30 nm. The excitation and emission slit widths are kept at 5.0 nm.

Fig. 3 Synchronous fluorescence scan spectra of a neat sample of petrol, petrol contaminated by kerosene at 0.1, 1, 2.4, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90% v/v and a neat sample of kerosene at 45° angle sample geometry. $\Delta\lambda$ = 30 nm. The excitation and emission slit widths were kept at 2.5 nm and 5.0 nm respectively.
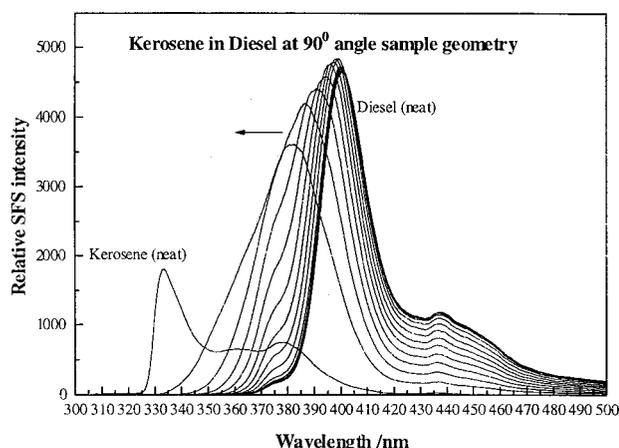

Fig. 5 Synchronous fluorescence scan spectra of neat kerosene, diesel contaminated by kerosene at 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, 2.4, 1, and 0.1% v/v and neat diesel at front surface illumination. $\Delta\lambda$ = 30 nm. The excitation and emission slit widths are kept at 2.5 nm.

(Fig. 6). Right angle geometry measurement seems to show a much greater sensitivity in spectral shift for diesel samples, in which both inner filter effects and resonance energy transfer are appreciable.

The shift in maxima with 90° angle geometry measurement could possibly provide a method for detecting kerosene contamination in petrol and diesel. Moreover a novel calibration plot based on $\lambda_{SFS}{}^{max}$ shift can, in principle, be developed for estimating the extent of contamination. Based on $\lambda_{SFS}{}^{max}$ shift at 90° angle sample geometry a calibration plot for estimating kerosene present in petrol and diesel is shown in Fig. 8. It is to be noted that this $\lambda_{SFS}{}^{max}$ shift based calibration is feasible only at 90° angle sample geometry. The most striking observation in Fig. 8a is the remarkable shift of SFS maximum even with small additions of kerosene ($\leq 5\%$ v/v) to petrol. This could provide both a method for detection of kerosene contamination as well as a highly sensitive quantitative method. The calibration curve at 5–100% v/v is a fairly regular one with pronounced curvature. The calibration plot for diesel Fig. 8b shows a fairly regular blue shift in the range 0–90% v/v kerosene and is fairly sensitive with an overall 20 nm shift from 400.8 nm to 380.8 nm. The marked change of SFS maxima between 90 to 100% v/v kerosene is analytically not important unless one is looking for contamination of kerosene by diesel.

SFS intensity based calibration plots have been constructed by monitoring the SFS intensity at 312 nm for frontal surface illumination, at 313.4 nm for 45° angle sample geometry and at 333.6 nm for 90° angle sample geometry. Fig. 9 gives the plots for petrol–kerosene mixtures and Fig. 10 for diesel–kerosene mixtures. The slopes of the curve tend to decrease in the order, front surface illumination > 45° > 90° angle geometry, however 90° angle geometry appears to provide much flatter curves, which in principle should impart better accuracy.

Results are presented in Table 1 for other traditional measurement, API (American Petroleum Institute) gravity, refractive index and viscosity, of neat and contaminated
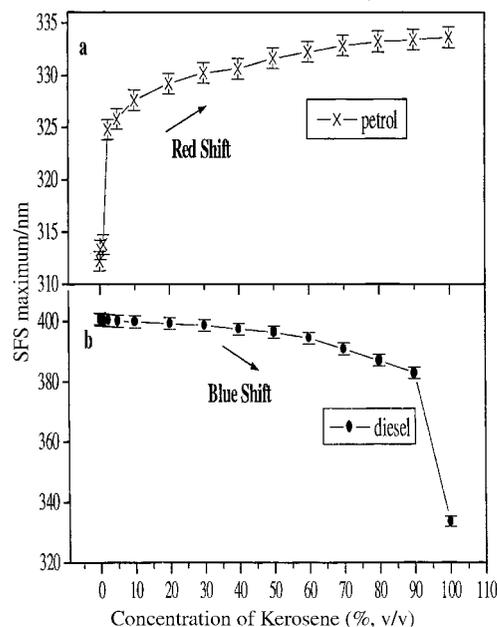

Fig. 6 Synchronous fluorescence scan spectra of neat kerosene, diesel contaminated by kerosene at 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, 2.4, 1 and 0.1%, v/v and neat diesel at 45° angle sample geometry. $\Delta\lambda = 30$ nm. The excitation and emission slit widths are kept at 2.5 nm.

Fig. 7 Synchronous fluorescence scan spectra of neat kerosene, diesel contaminated by kerosene at 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, 2.4, 1 and 0.1% v/v and neat diesel at 90° angle sample geometry. $\Delta\lambda = 30$ nm. The excitation and emission slit widths are kept at 2.5 nm and 5.0 nm respectively.

Fig. 8 Calibration curve based on shift in $\lambda_{SFS}{}^{max}$ for quantitative analysis of contamination of (a) petrol ($\times$) and (b) diesel ($\bullet$) by kerosene in the concentration range 0 to 100% v/v at 90° angle sample geometry.
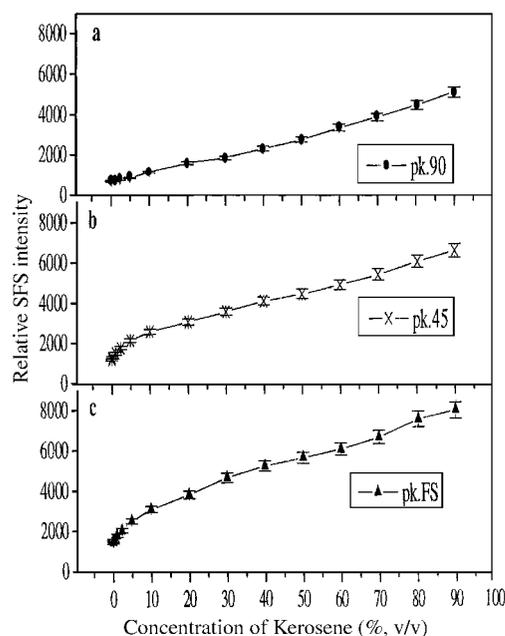
Fig. 9 Calibration curve based on fluorescence intensity measurement for quantitative analysis of contamination of petrol by kerosene (pk.) in the concentration range 0 to 90 % v/v. (a) 90° angle sample geometry ($\bullet$), (b) 45°angle sample geometry ($\times$) and (c) front surface illumination ($\blacktriangle$). The $\lambda_{SFS}{}^{max}$ used for frontal surface illumination, 45° and 90° angle sample geometry are 312 nm, 313.4 nm and 333.6 nm respectively.

Table 1 Variation of API gravity, refractive index and viscosity of petrol with kerosene concentration

Sample code	Concn. of kerosene (% v/v)	API gravity	Refractive index	Viscosity (centipoise) at 25 °C
A	0 (Neat sample of petrol)	63.67	1.418	0.75
B	0.1	63.67	1.418	0.75
C	1	63.67	1.418	0.752
D	2.4	63.13	1.418	0.76
E	5	62.33	1.419	0.777
F	10	62.07	1.42	0.806
G	20	61.54	1.421	0.874
H	30	61.01	1.425	0.941
I	40	58.68	1.427	0.998
J	50	55.91	1.43	1.103
K	60	55.17	1.431	1.176
L	70	54.19	1.433	1.304
M	80	52.5	1.435	1.42
N	90	52.26	1.438	1.57
O	100 (Neat sample of kerosene)	51.31	1.44	1.725
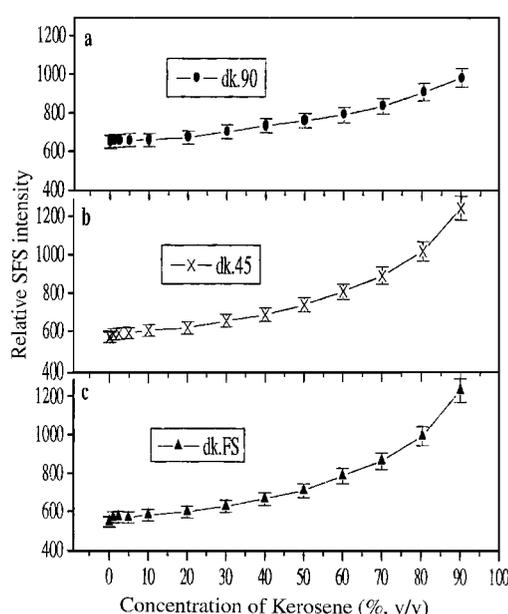
Fig. 10 Calibration curve based on fluorescence intensity measurement for quantitative analysis of contamination of diesel by kerosene (dk.) in the concentration range 0 to 90% v/v. (a) 90° angle sample geometry (●), (b) 45° angle sample geometry (×) and (c) front surface illumination (▲). The λ_{SFS}^{max} used for frontal surface illumination, 45° and 90° angle sample geometry are 312 nm, 313.4 nm and 333.6 nm respectively.

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samples of petrol by kerosene. It should be noted that these methods fail below 5% v/v of kerosene concentration and, measurements of API gravity and refractive index are inaccurate. Our SFS measurement was found to be independent of temperature unlike viscosity measurement. Moreover, the traditional methods are useful only for quantitative analyses, qualitative detection can not be carried out using this methods.[1] On the other hand in addition to 0.1% v/v sensitivity of contaminated sample present in petrol/diesel, the method gives a good linearity for petrol and diesel in the range 0 to 50% v/v of kerosene, in which range contamination is a common practice. The combination of right angle geometry and SFS spectroscopy shows promise in the analysis of petroleum products and their mixtures.