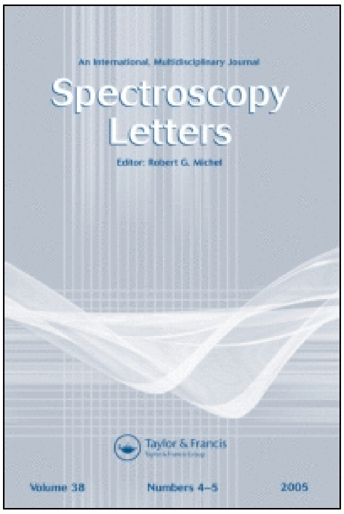

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Synchronous Fluorescence Method to Check Adulteration of Petrol and Diesel by Kerosene

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Synchronous Fluorescence Method to Check Adulteration of Petrol and Diesel by Kerosene

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Abstract: Commercial automotive fuels available on the Indian subcontinent like petrol and diesel are heavily adulterated with kerosene. Kerosene is used as a cooking fuel among the vast rural and urban populations in India. It is heavily subsidized in the local markets; hence, it becomes a cheap and commonly available adulterant. Intelligent mixing of this product with automotive fuels escapes detection. In this work, we report the synchronous fluorescence scan (SFS) technique as a direct tool to both identify and quantify the amount of adulterant present in commercial petrol and diesel mixtures across the city of Pune. The assay reported here promises to be an efficient tool for such detection purposes (kerosene as low as 1% v/v) within a limited geographical area using conditions of calibration with local components.

Keywords: Adulteration, contaminants, diesel, kerosene, petrol, synchronous fluorescence scan

INTRODUCTION

Adulterated fuels make exhaust gases more poisonous, worsening the pollution crisis and causing acute respiratory infections and other ailments. For example, when kerosene is mixed with petrol, it does not burn completely

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and releases more cancer-causing hydrocarbons, nitrous oxides, and carbon monoxide instead of the less-harmful carbon dioxide.[1] Adulteration of diesel with kerosene lessens diesel's lubricating function, leading to faster wear and tear of the pistons and higher maintenance costs. In addition, the soot particles carried by diesel exhausts also have unburnt and harmful hydrocarbons from the kerosene. Because fuel adulterants belong to similar hydrocarbon families as that of automotive fuels, though of varying composition, some amount of mixing is possible without changing the overall parameters of the fuel specifications.[2] Both kerosene and light diesel fuel, which are the most popular adulterants for petrol and diesel, are so similar in chemical structure to petrol and diesel that these mix with almost no aberration in the properties of automotive fuel.[3,4] Intelligent mixing of common adulterants like kerosene and light diesel fuel with diesel or naphtha and other solvents with petrol may not show up in routine analytical tests [5–7] but still satisfy the required octane number. Most petroleum products are mixtures of several polycyclic aromatic compounds (PACs) and their compositions with respect to the source of the crude oil and the types of distillation processes in terms of their hydrocarbon content and distribution.[8] Therefore, a globally invariant calibration plot to check for adulteration cannot be made. The common methods such as specific gravity and refractive index measurement suffer significant inaccuracy in their measurement, whereas viscosity of the adulterated sample is generally recovered by adding a small amount of high-viscosity lubricating oil. Most of the methods used to check adulteration on a quantitative basis fail below 5% v/v of kerosene concentration.

Fluorescence spectroscopy has been used extensively as an analytical technique to study petroleum products.[9–19] However, undiluted petroleum samples with multiple fluorophores suffer from high optical density values and broad featureless fluorescence spectra; several-folds of dilutions are required before any meaningful data can be obtained from them. Yet another characteristic of these samples will be the presence of extensive resonance energy transfer due to strongly overlapping absorption and emission spectra. These characteristics effectively render the conventional fluorimetry at right angle geometry completely useless. In the literature, front face illumination has generally been preferred for fluorescence measurements of petroleum samples at higher concentrations. But when it comes to detection of adulterants in petrol and diesel, identical spectral characteristics between the fuels and the adulterant renders conventional fluorescence useless as a detection tool. Front face geometry coupled with synchronous excitation has been used to identify a number of polynuclear hydrocarbons and refined petroleum products.[20] The advantage of this technique is simplification of the complex quasilinear spectra in a multicomponent mixture. Mishra and co-workers have successfully used the synchronous fluorescence scan (SFS) technique to address the problem of adulteration in automotive fuels.[13–19] In this work, SFS technique has been used to develop a calibration plot, which can then be used effectively to identify as well as quantify the amounts of kerosene present in commercial petrol and diesel.[21] However, because the composition of the automotive fuels varies widely depending on the source of the crude oil, this method will be applicable only to a limited geographical area and has to be subjected to calibration using local standards.

MATERIALS AND METHODS

Authentic and pure samples of petrol, diesel and kerosene were a gift from Indian Oil Corporation (IOC; Pune, India). Commercial samples of petrol and diesel were bought from vendors at different petrol stations across the city of Pune. Cyclohexane (obtained from Merck, Mumbai, India) was distilled and purified prior to use.

Sample Preparation

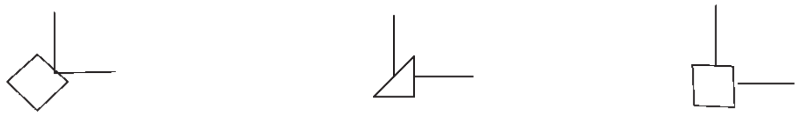
A known volume of pure and authentic sample of kerosene was pipetted out and was mixed in different ratios with pure and authentic petrol or diesel to give (in % v/v) the desired adulterated synthetic mixture. Likewise, pure petrol and diesel were also diluted using cyclohexane in the range 0.1% to 90% v/v to be used as controls.

Absorption Spectra

Absorption studies were done in the ultraviolet and visible regions of the optical spectrum (Shimadzu model 220A UV-Vis spectrophotometer, Mumbai, India) for spectroscopic characterization of the samples in the ground state. The optical path length of the cuvette used in all the experiments was a 1-cm cell. The absorption spectra were recorded at room temperature (23–25°C). The absorption spectrum of neat, as well as diluted petrol, diesel, and kerosene (1% to 90% v/v in cyclohexane) was also recorded with an appropriate solvent blank.

Sample Geometry

In our preliminary experiments, the fluorescence emission spectra and the synchronous spectra of all the samples were recorded at three different geometries (front surface, 45° angle with a triangular cuvette, and 90° angle). The sample geometry affected the results quite considerably. The effects were quite pronounced for the front face, intermediate for the 45° angle and least for the 90° angle. All the fluorescence scans reported in this work were done with front face geometry (Scheme 1).



Front face

45° Angle

90° Angle

Scheme 1.

Fluorescence Spectra

Steady-state fluorescence spectra (Hitachi model F-4500 spectrofluorimeter, Mumbai, India) taken were all corrected. While recording the fluorescence spectra, unpolarized light from the xenon lamp was used. Narrow excitation and emission slit widths (2 nm) were chosen for both the excitation and the emission sides. Because the absorption spectra were broad and structureless for the neat samples, excitation wavelength was varied between 250 to 330 nm, and emission spectra were recorded for different excitation

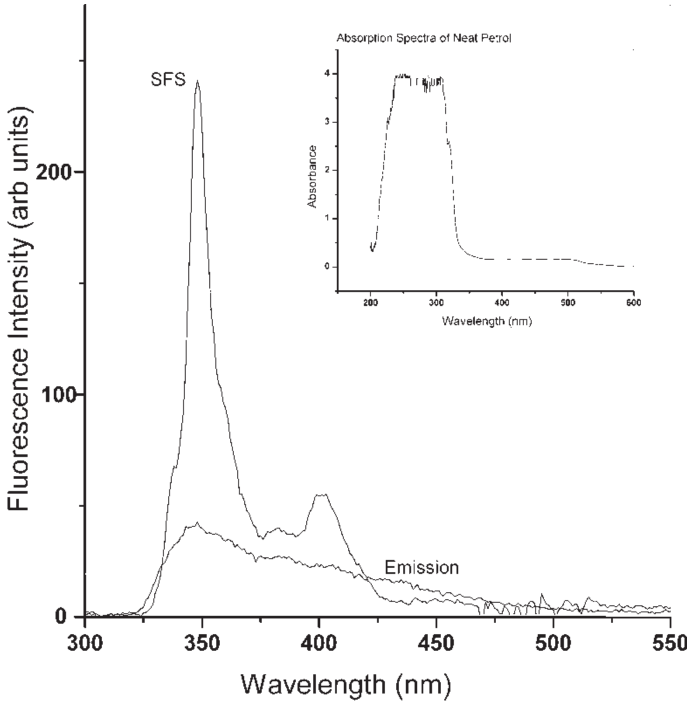


Figure 1. Absorption, emission, and synchronous spectra of pure petrol without any dilution. $\Delta\lambda$ for SFS = 20 nm.

wavelength. Changes in fluorescence intensity as well as emission peak position were studied as a function of dilution for different excitation wavelength. Each emission scan is an average of five acquisitions.

Synchronous Fluorescence Scan

Synchronous spectra were recorded by scanning both the excitation as well as emission monochromators with a fixed difference between them. For an excitation wavelength range (250 to 600 nm), synchronous spectra were taken varying the $\Delta\lambda$ (in nm) between the excitation and the emission monochromator (say $\Delta\lambda$ of 5, 10, 20, 30, 40, 50 nm, etc). The $\Delta\lambda$ difference for which the intensity of the SFS peak is maximal for each sample was found out, and this $\Delta\lambda$ was fixed for all subsequent SFS measurements. Each synchronous scan is an average of five acquisitions. SFS for the neat samples are shown in Figs. 1 to 3. Cyclohexane was used to dilute (0.1% to 90% v/v) neat petrol and diesel, and the corresponding SFS were recorded to study the effect of dilution (spectra not shown, see ratio metric plots of Figs. 6 and 7).

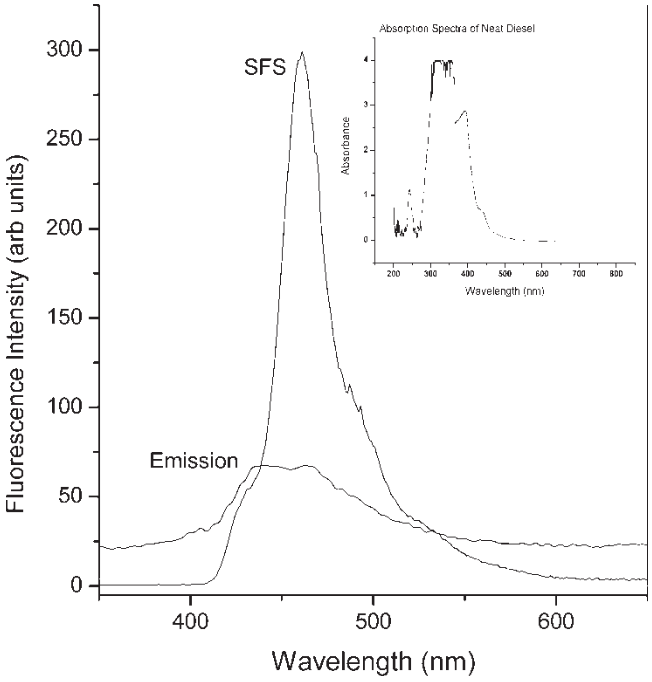


Figure 2. Absorption, emission, and synchronous spectra of pure diesel without any dilution. $\Delta\lambda$ for SFS = 20 nm.

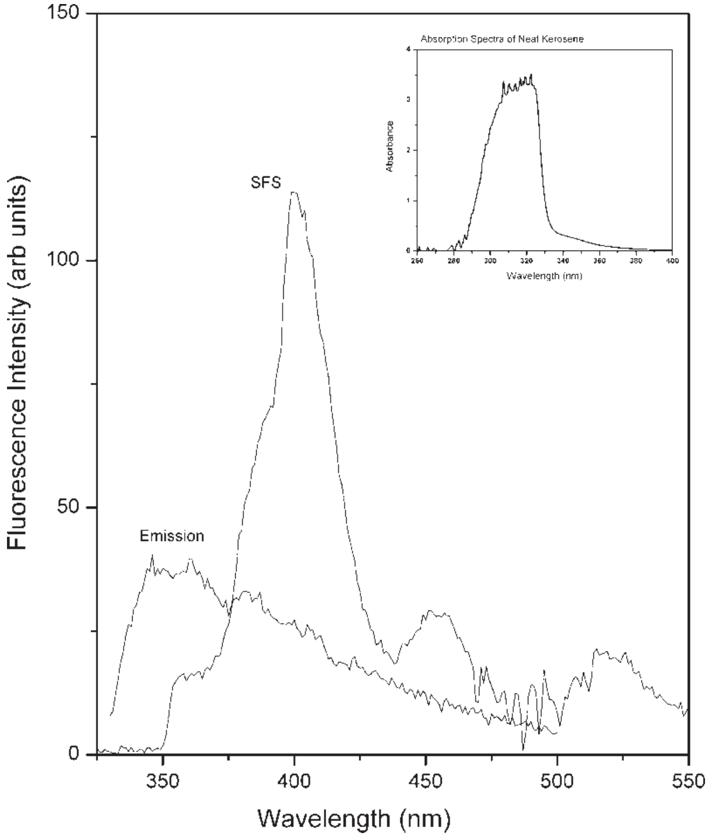


Figure 3. Absorption, emission, and synchronous spectra of pure kerosene without any dilution. $\Delta\lambda$ for SFS = 30 nm.

Calibration Plots

Four independent experiments were performed in constructing the calibration graphs by obtaining different batches of pure and authentic samples from Indian Oil Corporation over a period of 6 months. The standard deviations are indicated on some of the figures.

RESULTS AND DISCUSSION

Conventional Fluorescence Analysis

The absorption and emission spectra of pure and authentic petrol, diesel, and kerosene as obtained from IOC were recorded (Figs. 1, 2, 3 and insets). The absorbance is very high for the pure samples in all the three cases, indicating very high concentrations of polyaromatic hydrocarbons (PAHs). The samples were then diluted using a nonfluorescent hydrocarbon solvent like cyclohexane to ensure good mixing. Fluorescence emission scans were recorded at different excitation wavelengths (250–330 nm). The emission spectra were also very broad and quenched, in all the cases, as expected. The variation of absorbance or fluorescence intensity as a function of concentration doesn't show linearity in any of the three cases. The changes seen in absorbance and fluorescence intensity are very non linear (data not shown), and with an increase in concentration of the constituents fluorescence intensity goes down, because of inner-filter effects and extensive energy transfer between the hydrocarbons. Föster type resonance energy transfer takes place between higher and lower hydrocarbons. Hence, conventional absorption and fluorescence techniques fail as a quantitative tool for analysis of petrol

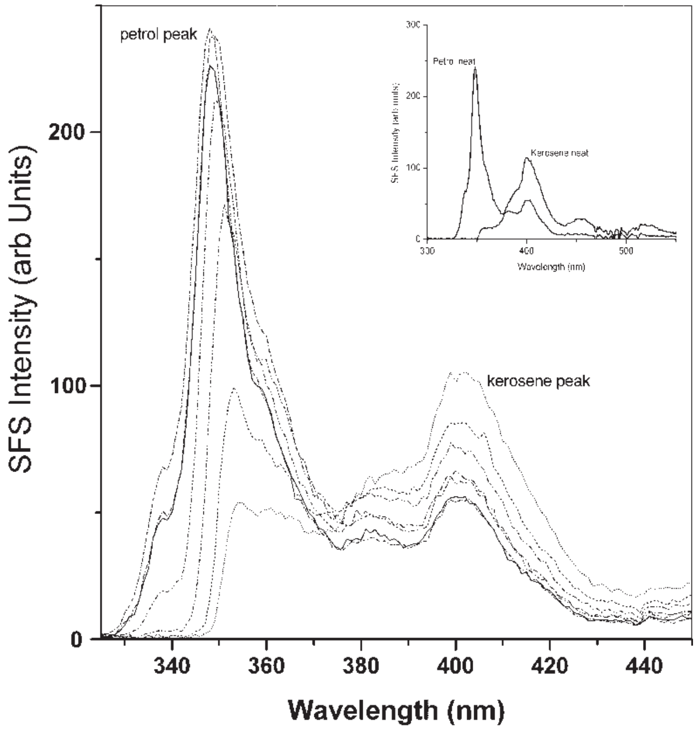


Figure 4. Synchronous fluorescence spectra of 0.1% to 90% v/v of kerosene in petrol scanned with $\Delta\lambda$ of 20 nm. Spectra of 0.1%, 1%, 5%, 15%, 30%, 40%, 50%, 60%, 70%, 80% and 90% v/v of kerosene-contaminated pure petrol are shown. The excitation and emission slit widths were 2.5 nm, respectively. The SFS peak intensity of petrol decreases ($\lambda = 350$ nm) with a concomitant increase of the kerosene peak ($\lambda = 400$ nm) with increase in kerosene concentration.

and diesel samples. More complicated were the samples when they were adulterated with kerosene, which is again a mixture of hydrocarbons.

Synchronous Fluorescence Scans

The synchronous fluorescence spectra of pure petrol, diesel, as well as kerosene were taken at different shift in wavelength (delta lambda, $\Delta\lambda$). The SFS shows a characteristic narrow band for all the three neat samples. The $\Delta\lambda$ (in nm) that gave the maximum intensity for the 0–0 bands was chosen thereafter for all further studies. For neat petrol and diesel, a SFS scan with $\Delta\lambda$ of 20 nm and for kerosene $\Delta\lambda$ of 30 nm gave the maximum intensity for the 0–0 bands. The SFS of pure petrol, diesel, and kerosene all have one prominent peak around 350, 450, 400 nm, respectively (shown as SFS peaks in Figs. 1, 2, and 3, respectively). Petrol + kerosene mixtures, as well as diesel + kerosene

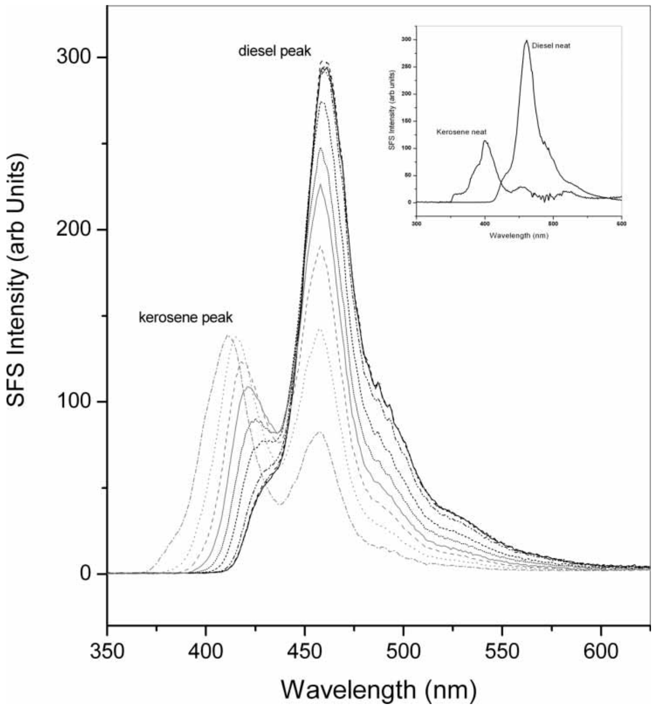


Figure 5. Synchronous fluorescence spectra of 0.1% to 90% v/v of kerosene in diesel scanned with $\Delta\lambda$ of 20 nm. Spectra of 0.1%, 1, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90% v/v of kerosene-contaminated pure diesel are shown. The excitation and emission slit widths were 2.5 nm, respectively. The SFS peak intensity of diesel decreases ($\lambda = 450$ nm) with a concomitant increase of the kerosene peak ($\lambda = 400$ nm) with increase in kerosene concentration.

mixtures, were prepared ranging from 0.1% to 90% v/v, and their corresponding SFS were recorded. Looking at the SFS for these synthetic mixtures of petrol and kerosene (Fig. 4), as well as diesel and kerosene (Fig. 5), the two prominent peaks in the spectra are obtained. These can be broadly classified as a petrol-like peak around 350 nm and a kerosene-like peak around 400 nm (see Fig. 4, inset); similarly, the diesel-like peak is around 450 nm and the kerosene-like peak is around 400 nm (see Fig. 5, inset). As more and more kerosene was added into neat petrol or diesel, the intensities of the petrol and diesel-like peaks decrease while the intensity of the kerosene-like peak increases. The ratio between peak intensities of petrol to kerosene follows a trend. A plot of ratio of the two peak intensities against the concentration of kerosene (% v/v) yields a linear relationship, which can be used as a quantitative tool to estimate amounts of kerosene present in pure petrol and diesel (Figs. 6 and 7, respectively). To account for the dilution factor in mixing kerosene into the neat samples, a control-dilution plot with cyclohexane was constructed. With dilution, the peak intensity of petrol and

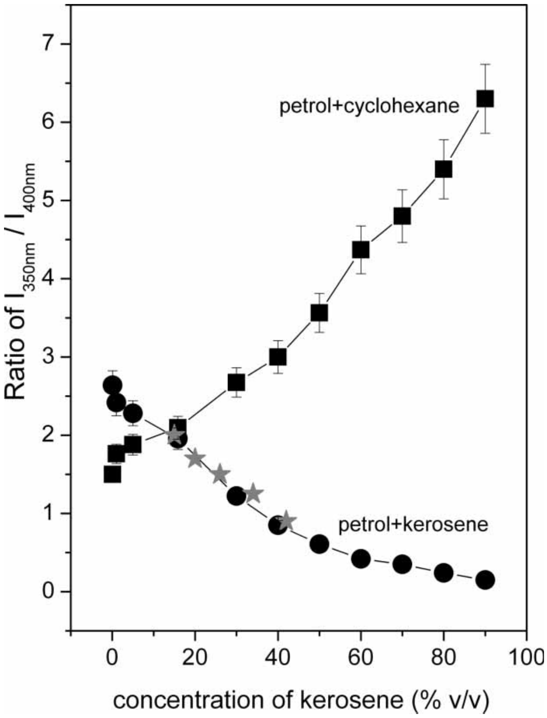


Figure 6. Calibration plot showing ratios of peak intensity of petrol to kerosene (I_{350nm}/I_{400nm}) as a function of concentration of kerosene (%v/v). -■- line refers to the effect of dilution of petrol by cyclohexene. -●- refers to the effect of adding kerosene to petrol. Stars are the commercial samples procured from local gas stations.

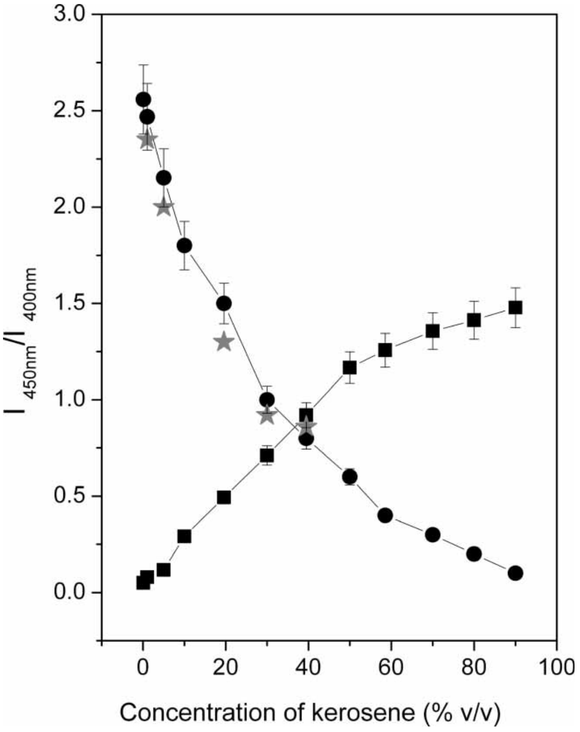


Figure 7. Calibration plot showing ratios of peak intensity of diesel to kerosene (I_{450nm}/I_{400nm}) as a function of concentration of kerosene (%v/v). -■- line refers to the effect of dilution of diesel by cyclohexene. -●- refers to the effect of adding kerosene to diesel. Stars are the commercial samples procured from local gas stations.

diesel both showed an increase due to reduction of quenching effects. Hence, the effect of dilution and addition of kerosene to the pure samples had opposite effects on the ratios of peak intensities.

SFS of Commercial Samples

Several commercial petrol and diesel samples were procured from the local gas stations across the city of Pune. These samples were used as procured. SFS analysis was done on these samples. The SFS spectra showed two prominent peaks as expected (one pertaining to petrol or diesel and the other to kerosene) (data not shown). The ratios of the petrol-to-kerosene peaks as well as diesel-to-kerosene peaks are interposed in the calibration graphs (see stars on Figs. 6 and 7). Each star in the figure refers to a commercial sample procured from different gas stations at different locations across the city of Pune, and the amount of adulterant kerosene present in them was estimated directly from their *y*-intercept. It is worth noting that the commercial samples sold at different local petrol stations show substantial amounts of kerosene contamination (20% to 40%), as revealed by the current analysis.

CONCLUSIONS

Kerosene is a very cheap and common contaminant used in adulteration of commercially available petrol and diesel. Petrol samples usually vary greatly in composition with respect to the source of the crude oils and the cracking procedure. Most of the methods currently available for purity checks cannot identify 5% (v/v) of contaminants in the test sample. In this work, we have studied kerosene contamination in petrol and diesel under a small geographical area (Pune, Maharastra, India) over a period of 6 months using SFS technique. The results obtained have proved that SFS can be effectively used to identify contaminants in petroleum samples under conditions of local calibration. A minute amount of adulterant present in petrol and diesel was easily detected by the method described in this report. A calibration graph has been constructed for synthetic adulterant mixtures (obtained by mixing pure kerosene with pure petrol). This calibration graph, obtained from the SFS method, was found to be effective in the whole range of 1% to 90% v/v of kerosene. Several commercial samples from various local petrol stations were subjected to the SFS analysis, and the results from the test analysis were interposed into the calibration graphs. This directly gives an estimate of the amount of kerosene present in the commercial samples. The method is simple, reliable, and gives advantages in terms of both sensitivity (1% v/v) and accuracy compared with any other method.

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