RESEARCH ARTICLE

Fingerprinting diesel and petrol fuels for adulteration in Sri Lanka

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Abstract: Adulteration of petrol (gasoline) and diesel using petrochemical based products has often been reported in developing countries. This leads to the degradation of engine performances and fugitive emissions. Having similar chemical properties, the fuel and the adulterant cannot be distinguished easily leading to complications in identification and quantification of the adulterants.

In this investigation, a synchronous fluorimetric analysis method was modified targeting to obtain the fingerprints for these fuels based on their polycyclic aromatic hydrocarbon (PAH) content. In a synchronous fluorescence scan, both the excitation and emission wavelengths are scanned keeping the wavelength difference at a fixed value. PAHs are a group of compounds with fused benzene ring systems, which are naturally present and/or formed during fuel processing that exhibit significant differences in their synchronous fluorescence scans. Simulated adulterated samples of petrol or diesel with kerosene, diluted in hexane, were prepared from the fuels collected from the petroleum refinery. These simulated fuel samples showed linear variations of the synchronous emission intensity with the level of kerosene in the fuel at specific wavelengths. This relation was utilized to investigate the level of adulteration for petrol and diesel available at different petrol stations. Diesel adulteration was found to be in the range of 0 to 35 % while petrol adulteration was found to be in the range of 0 to 48 % in Colombo and its suburbs.

Keywords: Adulterations, auto fuels, kerosene, PAHs, synchronous fluorescence.

INTRODUCTION

Adulteration of petrol (gasoline) and diesel has become a flourishing business in developing countries due to the significant price differences between the motor vehicle fuels and the adulterants. The price differences of the fuel types through different taxes are meant for relaxing the economic burdens to the poor. However,

this situation has been exploited for financial gains causing numerous environmental and social problems (Ale, 2003; Lima *et al*., 2004).

The choice of the adulterant is based on the financial gains, easy blending ability, availability and the similarity of the chemical and physical properties of the fuel to the adulterant. Often petroleum-based adulterants satisfy these requirements for the adulteration of petrol and diesel. Among the common adulterants, kerosene seems to be the most popular while industrial solvents, used lubricants and mixtures of hydrocarbons are the other possible alternatives (Ale, 2003; Kalligeros *et al.*, 2003; Yadav *et al*., 2005; Wiedemann *et al*., 2005; Taksande & Hariharan, 2006; Takeshita *et al*., 2008).

Having similar chemical properties, the fuel and the adulterant cannot be distinguished easily leading to complications in identification and quantification of the adulterants. A number of analytical techniques are available ranging from simple density measurements to modern techniques such as gas chromatography/ mass spectroscopy for identification of adulterants. The common testing methods for the fuels are density measurements, rate of evaporation, ash content determinations and viscosity measurements (Kalligeros *et al*., 2003), optical sensors (Bahari *et al*., 1992; Roy, 1999), spectroscopic methods (Canizares & de Castro, 1996; Patra *et al*., 2000; Patra & Mishra, 2001a,b, 2002 a,b,c; Lima *et al*., 2004; Divya & Mishra, 2007; Al-Ghouti *et al*., 2008) and chromatographic (Pedroso *et al*., 2008) fingerprinting methods. Inclusion of different marker compounds such as dyes to the fuels can also be utilized for investigation of the levels of adulterants. Although chromatographic based methods are reliable and more sensitive than the classical methods, they are time

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consuming and costly for routine analysis. In addition, such facilities are limited in developing countries. Spectroscopic methods targeting the impurities or added markers in the fuels are more popular due to their convenience of handling and high analytical throughput than the chromatographic methods.

Establishment of a routine analysis methodology with minimum sample handling steps and absence of cumbersome sample preparation, and separation processes seems to be the most viable solution in monitoring and quantifying the fuel adulterants. In this respect, a selective spectroscopic based method would be the most sensitive and reliable analytical implement. Of all the spectroscopic techniques, spectrofluorimetry is well-suited to be used in combination with the analysis of multi-component samples, because there are only a few compounds with intrinsic fluorescence characteristics.

Among the compounds having intrinsic fluorescence, polycyclic aromatic hydrocarbons (PAHs) are particularly important due to their mutagenic and/or carcinogenic effects. From the analytical point of view, PAHs have good molecular fluorescence properties due to rigid π electron systems in the fused ring structures. Furthermore, high fluorescence sensitivity allows their determination at very low concentrations (Eiroa *et al*., 2000).

Almost every petroleum product contains PAHs however, the PAH profile vary with the boiling range of the fuel. Low boiling petrol contains PAHs with a lesser number of fused rings in a molecule, while the PAH fraction in diesel has a higher number of fused rings in a molecule. The PAH profile in kerosene is different from petrol and diesel. Hence, the fluorescence fingerprint corresponding to different fuel compositions is different from each other (Patra & Mishra, 2000, 2002 a, b, c). But the conventional fluorescence methods based on scanning of either the excitation or emission wavelength while the other is kept at a fixed value, may not be successful in the evaluation of fuel adulterants. The overlapping of broad spectral bands for individual fluorophore is the main difficulty of applying this technique for the mixtures having multi fluorophores.

A relatively simple and rapid approach for the simultaneous analysis of multi flurophores is the synchronous fluorescence spectroscopy (SFS) (Patra & Mishra, 2002 a, b, c). SFS consists of varying both the excitation and emission wavelengths simultaneously while keeping a constant difference among them. The advantages of SFS are narrowing spectral bands, simplification of the emission spectra, reduction of the spectral change for a given analyte, and easing compensation for Rayleigh and Raman scattering. Furthermore, this technique can be applied using any spectrofluorometer without further modifications (Patra *et al*., 2000; Patra & Mishra, 2000, 2001 a, b; 2002 a, b, c).

The main objective of this study is to establish a method to investigate diesel and petrol adulteration. The method is based on SFS investigation of PAH profiles present in different fuel types. First, emphasis was paid to establish optimum SFS parameters for petrol, diesel and kerosene separately. These optimum SFS conditions were utilized to develop fingerprints for different formulations of kerosene in petrol or diesel samples. Based on SFS fingerprint features, several analytical parameters were evaluated based on linear regressions to establish quantitative measures for the appraisal of adulterant levels. These linear regressions were exploited to assess the levels of adulteration for twenty commercial fuel samples purchased from Colombo and its suburbs.

METHODS AND MATERIALS

Diesel, petrol and kerosene samples obtained from the Ceylon Petroleum Cooperation distribution center at Sapugaskanda were used as references, and the synthetic mixtures were prepared by mixing them with appropriate proportions. Commercial samples were purchased from ten different petrol stations located in Colombo and its suburbs for assessing the level of adulteration. Distilled hexane with no fluorescence characteristics was used for diluting the synthetic mixtures and commercial samples. Shimadzu Hitachi RF 5000 spectrofluorometer equipped with a Xe lamp was used to obtain SFS, keeping the excitation and emission slit widths at 1.5 nm and 3.0 nm, respectively.

Optimum SFS conditions were established by scanning the SFS for pure samples from 200 - 700 nm region, keeping $\Delta\lambda$ ($\Delta\lambda = \lambda_{ex} - \lambda_{em}$) from 10 - 100 nm and the changes were made at 10 nm intervals. Near the optimum SFS conditions, $\Delta\lambda$ was changed by 1 nm intervals to sharpen the signals with maximum fluorescence intensity. Several analytical parameters including SFS intensity, bandwidth of the signal, shifting of the signals and the intensity ratios were evaluated against the level of kerosene added to the synthetic mixtures. The linear regressions with correlation coefficient, r^2, closer to 1 were selected as the analytical parameters for the assessment of adulteration of the commercial samples under identical conditions.

RESULTS AND DISCUSSION

The spectral bandwidths and the intensities varied with the changes of Δλ values as reported earlier, (Patra *et al*., 2000) for diesel, petrol and kerosene reference samples. Both the SFS emission intensity and the sharpness of the emission signal were used as criteria for evaluating the optimum parameters. In general, SFS has more features when Δλ is a lower value and a broad band with lesser intensity was common at higher Δλ values (Figure 1). Thus, both kerosene and diesel exhibited optimum Δλ at 30 nm, and the optimum Δλ for petrol was found to be at 25 nm.

The synthetic formulations of kerosene in both diesel and petrol for 0 to 100 % of kerosene v/v were prepared with 10 % increments. The SFS of the individual mixtures were investigated keeping Δλ at 30 nm and excitation and emission slit widths at 1.5 and 3.0 nm, respectively.

Primarily, SFS has two maxima for diesel and kerosene mixtures. The maximum towards the shorter wavelength has a strong red shift with increasing diesel composition of the mixture, while the maximum at higher wavelength virtually remain unchanged with the change of diesel composition as in Figure 2. The red shifting of the low wavelength maximum with increasing diesel composition indicates that the signal is predominantly due to the low molecular weight PAHs from kerosene (Patra & Mishra, 2000). The maximum at higher wavelength is dominated by the high molecular weight PAHs present in diesel. It was found that the intensity of the maximum at higher wavelength decreases with increasing kerosene content and it seemed that the emission intensity correlates with the levels of diesel in the mixture.

SFS for synthetic mixtures of petrol and kerosene exhibited a different pattern from diesel and kerosene mixtures (Figure 3). The clear differences of the SFS fingerprints facilitate the identification of the two different fuel types and it can be utilized for qualitative analysis of the fuel type. Basically there were four maxima in the SFS of petrol and kerosene mixture with some shoulders. As with the SFS of diesel and kerosene mixtures, the maximum towards the lower wavelength made a red shift and the three remaining maxima remained virtually unchanged with decreasing intensities as diesel composition decreases. This is consistent with the previous studies carried out by Patra and Mishra (2001 a, b). The red shift for the signal at the lower wavelength was less pronounced compared to diesel and kerosene mixtures. This is in agreement with the

molecular weight distributions of the PAHs in the three fuel types. The differences of the molecular weights for kerosene and diesel mixtures were greater than the molecular weight differences for kerosene and petrol.
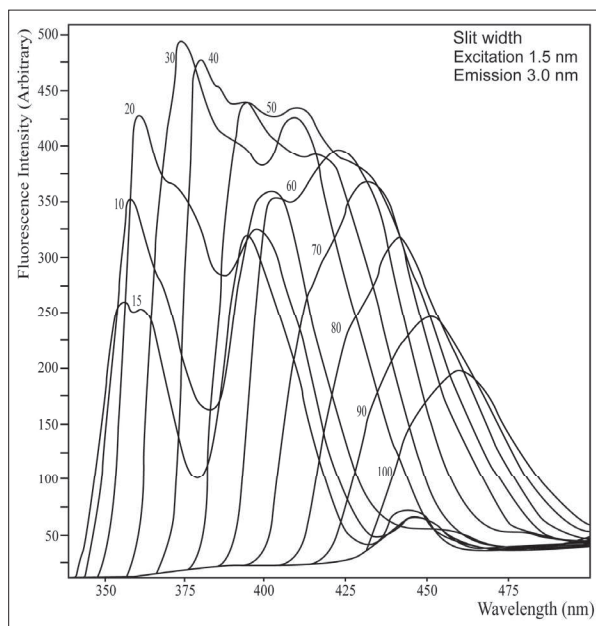

Figure 1: Synchronous fluorescence spectra of kerosene at different Δλ (λ_{ex}- λ_{em}) values
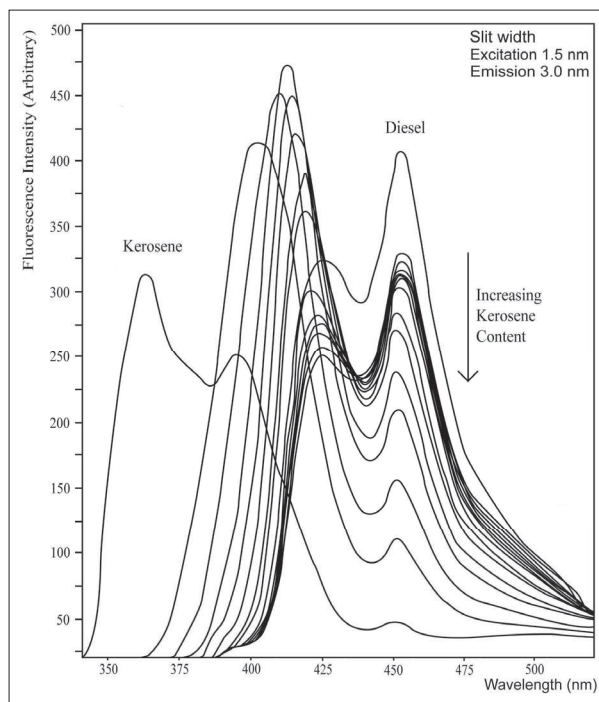

Figure 2: Synchronous fluorescence spectra of kerosene and diesel (0 to 100 %) mixtures
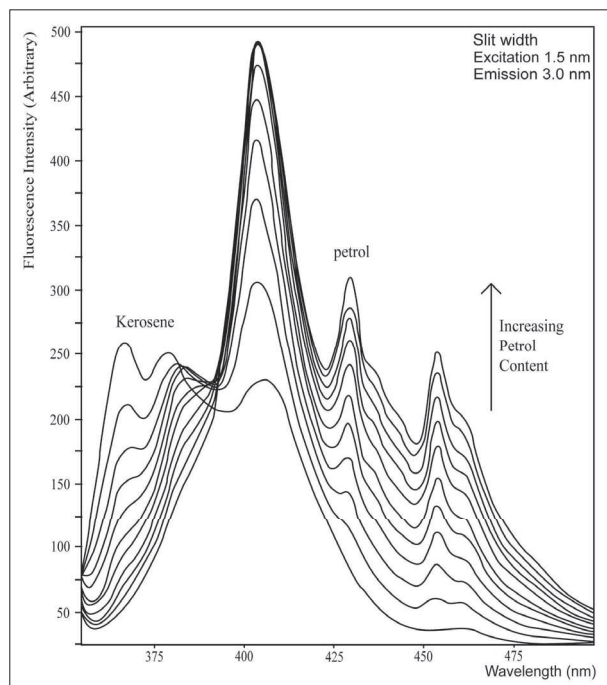
Figure 3: Synchronous fluorescence spectra of kerosene and petrol (0 to 100 %) mixtures

The maximum SFS intensities, which did not exhibit shifting due to adulteration, intensity ratios at selected wavelengths, widths of the SFS signals and the red shifts of the maxima were evaluated with petrol or diesel composition as the quantitative parameters for the adulteration. The regressions of fluorescence intensity with petrol or diesel composition exhibit better correlations than the red shifts promoting to investigate linear correlations for the quantification.

For synthetic mixtures with no dilutions, curves of SFS intensities were found to be concaving with the increase of petrol or diesel composition due to self-quenching of the signals dominated by the PAH profiles of petrol or diesel (Patra & Mishra, 2001 a, b; 2002 a, b, c). This postulate of self quenching was tested by diluting the mixtures in a non-fluorescence media of hexane and plotting the SFS intensities with the petrol or diesel composition. The 5 fold, 10 fold and 20 fold dilutions improved the linearity of the correlations and the correlation coefficients were found to be closer to unity for both fuel types with 10 and 20 fold dilutions implying the validity of the postulate. Hence, all the synthetic mixtures and the commercial samples were diluted 20 times in hexane prior to the SFS analysis.

The linear correlations for kerosene in both petrol and diesel synthetic mixtures were utilized to determine the level of adulteration in commercial samples purchased

from Colombo and its suburbs. In each case, the SFS intensities at three different wavelengths were utilized to estimate the fuel level and hence the level of adulteration. The corresponding SFS wavelengths and the estimated level of adulterants were tabulated with the average values in Tables 1 and 2 for commercial diesel and petrol samples, respectively.

Table 1: Estimated levels of kerosene in commercially available diesel samples

	Estimated level of the adulterant %			
Sample	at $\lambda = 410$ nm	at $\lambda = 429$ nm	at $\lambda = 466$ nm	Average
Diesel	2.8	0.0	0.0	0.9
A	10.0	5.6	8.2	7.9
B	28.8	21.0	22.4	24.1
C	31.0	36.8	46.8	38.2
D	12.8	14.8	16.5	14.7
E	5.5	2.2	4.4	4.0
F	16.6	10.2	11.6	12.8
G	5.6	1.6	3.2	3.5
H	2.8	0.0	0.0	0.9
I	5.6	1.6	3.2	3.5
J	8.6	9.2	4.4	7.4

Table 2: Estimated levels of kerosene in commercially available petrol samples

	Estimated level of the adulterant %			
Sample	at $\lambda = 431$ nm	at $\lambda = 456$ nm	at $\lambda = 464$ nm	Average
Petrol	1.2	0.0	0.0	0.4
A	43.6	49.6	49.1	47.4
B	28.7	25.5	28.1	27.4
C	3.8	0.7	0.8	1.8
D	4.4	1.7	3.0	3.0
E	17.9	16.7	17.2	17.3
F	14.1	15.6	14.0	14.6
G	30.6	29.2	31.0	30.3
H	30.6	29.2	30.8	30.2
I	29.5	27.6	28.9	28.7
J	29.8	27.9	29.6	29.1

Out of the ten diesel samples, six samples had the adulteration levels of less than 7 %, which is within the level of confidence for the analysis. Two other samples were found to have a level of adulteration of 12 % and 15 % while the other two had significantly higher levels of adulteration at 25 % and 38 % (Table 1). However for the petrol samples, circumstances were found to be inferior. Two stations had not adulterated their petrol and the levels estimated were less than 3 % and two other stations had adulteration levels of 15 % and 17 %. Five of the stations had higher levels of adulteration around 30 % and one other station had an adulteration level as high as 48 % (Table 2). These findings are comparable to the adulteration levels in the region where
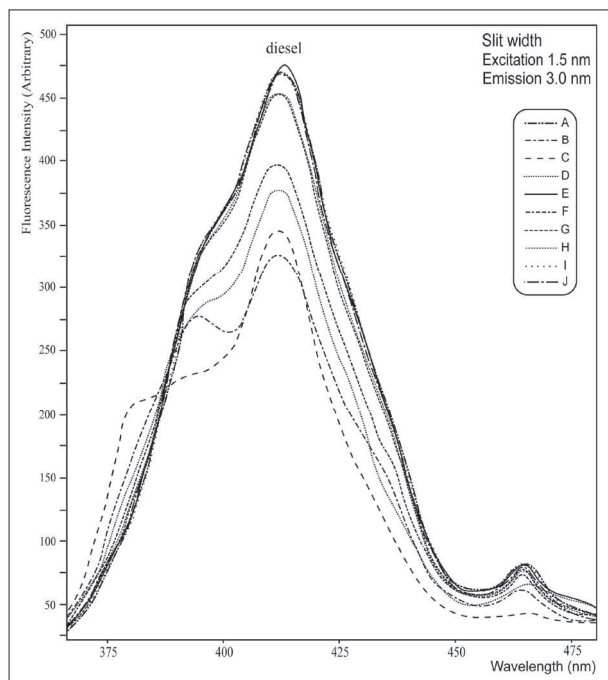
Figure 4: Synchronous fluorescence spectra of ten commercial diesel samples with the reference diesel sample (20 times diluted in hexane)

Figure 5: Synchronous fluorescence spectra of ten commercial petrol samples with the reference diesel sample (20 times diluted in hexane)

35 − 50 % of kerosene was found in both petrol and diesel samples sold in Katmandu City, Nepal (Yadav *et al*., 2005).

The SFS of commercial petrol and diesel samples have their characteristic fingerprints as the synthetic mixtures that have been formulated for this study (Figures 4 and 5). Interestingly, the worst petrol sample had a different fingerprint than the synthetic samples and other commercial samples. Presumably, some other adulterants have been added to this sample and the added adulterant might have quenched the PAH signals drastically indicating unusually higher level of adulteration. The observation that adulteration is higher for petrol than diesel probably reflects the price differences in petrol, diesel and kerosene.

CONCLUSION

It can be concluded that the adulteration of petrol and diesel can be assessed with a significant accuracy using the prescribed method. The method based on Patra and Mishara (2000, 2001 a, b, 2002 a, b, c), is sensitive, simple and quick, involving a single dilution step and scanning the SFS under the prescribed conditions. The dilution can be done using other solvents that are
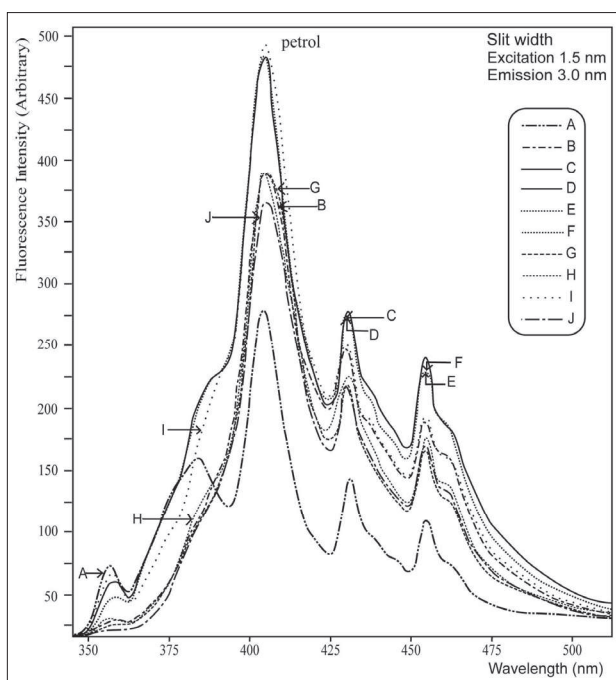
completely miscible with the fuel of interest and having no fluorescence characteristics. However, the calibration curves need to be plotted for different solvent systems because fluorescence intensity depends on the medium.

The fingerprinting pattern suggests that 19 out of the 20 samples tested in this analysis have resemblances to the fingerprints developed for the synthetic samples formulated by mixing kerosene and petrol or diesel. However, it cannot be concluded that kerosene is the only adulterant in the commercial samples. Any solvent having no fluorescence characteristics may have been used for adulteration. This is the major drawback of the method developed in this study. This problem arises because the quantifications were based on the intensities of the signals that are dominated by petrol or diesel. Hence, the method assesses the level of adulterantion but it does not identify the type of adulterant.

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