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ORIGINAL PAPER

Quantification of Ethanol in Ethanol-Petrol and Biodiesel in Biodiesel-Diesel Blends Using Fluorescence Spectroscopy and Multivariate Methods

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Abstract Ethanol blended petrol and biodiesel blended diesel are being introduced in many countries to meet the increasing demand of hydrocarbon fuels. However, technological limitations of current vehicle engine do not allow ethanol and biodiesel percentages in the blended fuel to be increased beyond a certain level. As a result quantification of ethanol in blended petrol and biodiesel in blended diesel becomes an important issue. In this work, calibration models for the quantification of ethanol in the ethanol-petrol and biodiesel in the biodiesel-diesel blends of a particular batch were made using the combination of synchronous fluorescence spectroscopy (SFS) with principal component regression (PCR) and partial least square (PLS) and excitation emission matrix fluorescence (EEMF) with N-way Partial least square (N-PLS) and unfolded-PLS. The PCR, PLS, N-PLS and unfolded-PLS calibration models were evaluated through measures like root mean square error of cross-validation (RMSECV), root mean square error of calibration (RMSEC) and square of the correlation coefficient (R^2). The prediction abilities of the models were tested using a testing set of ethanol-petrol and biodiesel-diesel blends of known ethanol and biodiesel concentrations, error in the predictions made by the models were found to be less than 2%. The obtained calibration models are highly robust and capable of estimating low as well as high concentrations of ethanol and biodiesel.

Keywords Ethanol · Petrol · Diesel · Biodiesel · Blend · SFS · EEMF · Multivariate methods

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Introduction

In order to meet the increasing demand of hydrocarbon based fuels such as petrol and diesel, ethanol blended petrol and biodiesel blended diesel are being introduced in many countries with a certain permissible limit of ethanol and biodiesel. Both ethanol and biodiesel are non-fossil fuels. Ethanol can be fermented and extracted from natural products, whereas biodiesel is mainly comprised of mono-alkyl esters of saturated and unsaturated long-chain fatty acids, derived from the transesterification reaction of vegetable oils or animal fats and alcohols. As a fuel, both ethanol-petrol and diesel-biodiesel blends are found to have better anti-knock properties [1–5]. Ethanol blended petrol and biodiesel blended diesel are found to have higher octane and cetane numbers compare to unblended petrol and diesel, respectively. Use of blended fuel also leads to significant reduction in carbon monoxide (CO), and unburned hydrocarbon (UHC) emissions [1–5]. In spite of these advantages, due to technological limitations, percentage of ethanol in ethanol-petrol and biodiesel in biodiesel-diesel blends can not be increased beyond a certain level. Some of the problems associated with the use of ethanol blended petrol and biodiesel blended diesel as fuels are the following. (i) It causes corrosion of metallic components of the engine [6–8]. (ii) It causes the blockage of fuel pipes, valves and filters of vehicles engine [6, 9, 10]. (iii) Ethanol forms a low boiling azeotrope with hydrocarbons, which may increase the vapour pressure of blended fuel above the permissible limit for the safe handling of fuel [11]. (iv) Low energy content of ethanol and biodiesel as compared to ethanol and diesel increases the consumption of fuel. Thus, quantification of ethanol and biodiesel in ethanol-petrol and biodiesel-diesel blends becomes an important issue to

ensure the fuel quality of the blend. In literature, methods based on gas and liquid chromatographic techniques [12–14], infrared (IR) [15, 16], nuclear magnetic resonance (NMR) [17, 18] are reported for the quantification of ethanol and biodiesel in the ethanol-petrol and biodiesel-diesel mixtures. Some of these methods are either too elaborate requiring sample preparation steps, or limited in their ability to quantify ethanol and biodiesel in a particular range. Hence, in view of this, development of an analytical method which is simple and capable of estimating ethanol in ethanol blended petrol blend and biodiesel in biodiesel blended diesel of any composition is relevant.

Petroleum products like diesel, petrol etc. contain number of polycyclic aromatic hydrocarbons (i.e. naphthalene, anthracenes, phenanthrenes, benzophenanthrenes, and fluorene etc.) [19], porphyrins [20] and other compounds of natural origin which are strongly fluorescent. Biodiesel being derived from vegetable oils and animal fats are also expected to contain fluorescent pigments and molecules, which could act as intrinsic fluorescent markers for a particular type of biodiesel. An analytical technique based on the intrinsic fluorescence of petrol, diesel and biodiesel is an attractive proposition because fluorescence spectroscopy is a simple, sensitive and non-destructive technique. However the presence of multiple fluorophores at unknown concentration with overlapping absorption and emission spectra make the systems complex multifluorophoric. It is known that conventional fluorescence spectroscopy can not be used for analysis of such systems [21, 22]. Synchronous fluorescence spectroscopy (SFS) [23] and excitation emission matrix fluorescence (EEMF) [24] are the two widely used fluorescence techniques for the analysis of multifluorophoric systems such as petroleum products [25–29] and humic acids [22, 30, 31]. In SFS both the excitation and emission monochromators are scanned simultaneously by keeping a constant wavelength offset ($\Delta\lambda$) between them. By using the optimum wavelength offset the synchronous fluorescence reduces the spectral overlap by narrowing the spectral bands and simplifies the spectra. The EEMF produces the fluorescence spectra of a sample at various excitation wavelengths and provides a "fingerprint" consisting of a three dimensional diagram of emission, excitation and fluorescence intensity.

The combination of fluorescence spectroscopy and multivariate methods has not been used so far for the analysis of ethanol-petrol and biodiesel-diesel blends. The objective of the present work is to explore whether synchronous fluorescence spectroscopy (SFS) and excitation emission matrix fluorescence (EEMF) spectroscopy along with multivariate methods like principal component regression (PCR), partial least square (PLS), N-way partial least square (N-PLS) and unfolded-PLS can be used for the quantification of ethanol in the ethanol- petrol blend and biodiesel in biodiesel-diesel blends.

Material and Methods

Materials and Sample Preparation

Ethanol, petrol, biodiesel (karanja) and diesel were procured from the local sources in Chennai. The ethanol sample was found to show some fluorescence which could be due to some contamination. Since ethanol is fermented and extracted from natural plant sources, the presence of trace amounts of plant pigments cannot be ruled out. In the context of blending ethanol with petrol for fuel applications, we preferred to use the commercial grade ethanol instead of using ultrapure non-fluorescent ethanol for creating chemometric calibration models. A calibration set of 21 samples were made for both ethanol-petrol and biodiesel-diesel blends by mixing ethanol and biodiesel with petrol and diesel, respectively. Amount of ethanol in ethanol-petrol blends and biodiesel in biodiesel-diesel blends are given in the Table 1.

Instrument and Data Acquisition

Fluoromax 4 (Horiba Jobin Yvon) spectrofluorometer, with a 150 W xenon lamp as excitation source, was used for the fluorescence measurement. Band pass for excitation and emission monochromator were kept at 4 nm. Synchronous fluorescence spectra were collected in the excitation wavelength range of 250–600 and 250–750 nm with an interval of 1 nm for the ethanol-petrol and biodiesel-diesel blends, respectively. EEMF spectra were collected in the excitation wavelength range of 250–570 and 250–750 nm with an interval of 5 nm and in emission wavelength range of 260–580 and 260–760 nm with an interval of 5 nm for ethanol-petrol and biodiesel-diesel blends, respectively.

Principal Component Regression (PCR)

PCR is one of the most widely used multivariate calibration method in chemometrics [32–35]. Its algorithm is described as a two step procedure of principal component analysis (PCA) followed by multi-linear regression. In the first step, PCA decomposes the data set, D, of independent variables as

$$\mathbf{D} = \mathbf{A}\mathbf{P}^{\mathbf{T}} + \mathbf{R}_1 \quad (1)$$

where A is the score matrix and P is the loading matrix while R_1 is the residual matrix containing the unexplained variance of D. The linear regression model of dependent

Table 1 Amount of ethanol in ethanol-petrol and biodiesel in biodiesel-diesel calibration sets

	Ethanol-Petrol Calibration set			Biodiesel-Diesel Calibration set		
Sample	Ethanol (ml)	Petrol (ml)	Ethanol (%)	Biodiesel (ml)	Diesel (ml)	Biodiesel (%)
1	0.00	5.00	0.00	0.00	5.00	0.00
2	0.25	4.75	5.00	0.25	4.75	5.00
3	0.50	4.50	10.00	0.50	4.50	10.00
4	0.75	4.25	15.00	0.75	4.25	15.00
5	1.00	4.00	20.00	1.00	4.00	20.00
6	1.25	3.75	25.00	1.25	3.75	25.00
7	1.50	3.50	30.00	1.50	3.50	30.00
8	1.75	3.25	35.00	1.75	3.25	35.00
9	2.00	3.00	40.00	2.00	3.00	40.00
10	2.25	2.75	45.00	2.25	2.75	45.00
11	2.50	2.50	50.00	2.50	2.50	50.00
12	2.75	2.25	55.00	2.75	2.25	55.00
13	3.00	2.00	60.00	3.00	2.00	60.00
14	3.25	1.75	65.00	3.25	1.75	65.00
15	3.50	1.50	70.00	3.50	1.50	70.00
16	3.75	1.25	75.00	3.75	1.25	75.00
17	4.00	1.00	80.00	4.00	1.00	80.00
18	4.25	0.75	85.00	4.25	0.75	85.00
19	4.50	0.50	90.00	4.50	0.50	90.00
20	4.75	0.25	95.00	4.75	0.25	95.00
21	5.00	0.00	100.00	5.00	0.00	100.00

variables C and the score matrix A, whose columns are orthogonal to each other, is given by the equation,

$$\mathbf{C} = \mathbf{AB}_1 + \mathbf{R}_2 \tag{2}$$

where B_1 is the PCR regression coefficient matrix and R_2 is the residual matrix

Partial Least Square Regression (PLS)

PLS is another widely used method for making calibration models [32, 35, 36] PLS algorithm searches for a set of components which explains the maximum covariance between the independent and dependent variables. It is achieved by the simultaneous decomposition of both D (independent variables) and C (dependent variables) data set, followed by a regression model relating the two decomposition models.

$$\mathbf{D} = \mathbf{ES}^{\mathbf{T}} + \mathbf{R}_3 \tag{3}$$

$$\mathbf{C} = \mathbf{VZ}^{\mathbf{T}} + \mathbf{R}_4 \tag{4}$$

where E and V are the score matrices, S and Z are the loading matrices of the D and C block data set, respectively. R_3 and R_4 are the residual matrices containing the unexplained variances of D and C, respectively. The inner relationship between the score matrices E and V is given by the equation,

$$\mathbf{V} = \mathbf{EB}_2 + \mathbf{R}_5 \tag{5}$$

where B_2 is the PLS regression coefficient matrix and R_5 is the residual matrix.

N-Way Partial Least Square Analysis (N-PLS)

N-PLS is a generalization of PLS to work with the multi way data sets [32, 37]. In three way PLS, three way array, X (I×J×K), of independent and Y (I×M×N), of dependent variables are decomposed simultaneously as,

$$\mathbf{X} = \mathbf{T}\,\mathbf{G}_{\mathbf{x}}\left(\mathbf{W}^{\mathbf{K}} \otimes \mathbf{W}^{\mathbf{J}}\right)^{\mathbf{T}} + \mathbf{E}_{\underline{\mathbf{x}}} \tag{6}$$

$$\mathbf{Y} = \mathbf{U}\,\mathbf{G}_{\mathbf{Y}}\left(\mathbf{Q}^{\mathbf{N}} \otimes \mathbf{Q}^{\mathbf{M}}\right)^{\mathbf{T}} + \mathbf{F}_{\underline{\mathbf{Y}}} \tag{7}$$

where X and Y are unfolded matrices of size (I×JK) and (I×MN) respectively. T and U are the first mode score matrices, W^J and Q^M are the second mode weight matrices, W^K and Q^N are the third mode weight matrices,

$E_{\underline{X}}$ and $F_{\underline{Y}}$ are the residual matrices of $\underline{X}$ and $\underline{Y}$ respectively. The symbol ⊗ denotes the Kronecker product. Gx is the unfolded matricized array of dimensions F × FF where F is the number of retained latent variables. A regression model connecting the two decomposition models is given as

$$\mathbf{U} = \mathbf{TB}_3 + \mathbf{R}_6 \tag{8}$$

where B_3 is the regression matrix and R_6 is the residual matrix.

Unfolded-PLS

In the unfolded-PLS method [37] three-way array is unfolded along the first mode and usual PLS regression algorithm is applied to make the calibration model.

Measures of Calibration Model

The root mean square of calibration (RMSEC) [32, 35] a measure of goodness of model's fit to the data set, is defined as,

$$RMSEC = \sqrt{\frac{\sum_{i=1}^{n}\left(y_{pred} - y_{ref}\right)^2}{n}} \tag{9}$$

where y_{pred} and y_{ref} are the predicted and the reference value of the i^{th} sample in calibration set, respectively and n is the number of samples used. The root mean square error of cross-validation (RMSECV) [32, 35] is a measure of model's ability to predict new samples. It is defined as,

$$RMSECV = \sqrt{\frac{PRESS}{n}} \tag{10}$$

where PRESS (sum of squares of prediction error) [35] is given as,

$$PRESS_k = \sum_{i=1}^{n}\left(y_{pred} - y_{ref}\right)^2 \tag{11}$$

The square of correlation coefficient (R^2) a measure of goodness of fit [38], is calculated as,

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left(y_{ref} - y_{pred}\right)^2}{\sum_{i=1}^{n}\left(y_{ref} - y_m\right)^2} \tag{12}$$

In Eq. 9, 11, and 12 y_{pred} and y_{ref} are the predicted and the reference value of the i^{th} sample and y_m is the average of the reference values.

Software Used

PCR, PLS, N-PLS and unfolded-PLS analysis were carried out using PLS_Toolbox 5.0.3 written in MATLAB language.

Results and Discussion

Synchronous Fluorescence Spectroscopy (SFS) and Excitation Emission Matrix Fluorescence (EEMF) of Ethanol-Petrol and Diesel-Biodiesel Blends

SFS were recorded for all the samples of ethanol-petrol and biodiesel-diesel calibration sets with various wavelength offset values, the optimized Δλ value was found to be of 40 nm. It is in accordance of the earlier report which showed that Δλ of 40 nm is appropriate for the analysis of diesel [25] and petrol [29] samples. The synchronous fluorescence spectra of ethanol-petrol and biodiesel-diesel mixtures recorded with Δλ of 40 nm are shown in Fig. 1. From the spectra (Fig. 1a) of ethanol-petrol mixture, it is seen that, (i) the peak positions are blue shifted and (ii) the SFS intensity values at 332, 346, 365, 383, 426 and 436 nm decreases, with the increase in ethanol percentage. From the

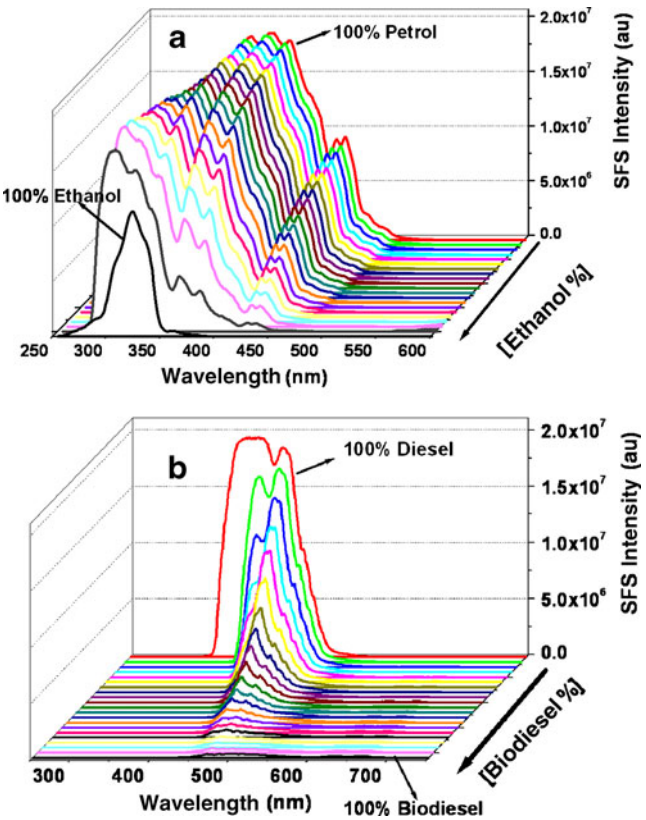

Fig. 1 Synchronous fluorescence spectra of **a** ethanol-petrol and **b** biodiesel-diesel blends at Δλ of 40 nm

SFS plot (Fig. 1b) of biodiesel-diesel mixture it is seen that the fluorescence intensity values at 420 nm and 444 nm decreases with the increase in biodiesel concentration. For both ethanol-petrol and biodiesel-diesel calibration set, intensity value at any of the wavelength did not change linearly over the entire range of ethanol and biodiesel concentration. As a result intensity based univariate methods could not be used for making the calibration models.

EEMF spectra were recorded for all the samples of ethanol-petrol and biodiesel-diesel calibration set, contour plots of ethanol, petrol, biodiesel and diesel are shown in Fig. 2 Unblended petrol showed highest fluorescence intensity around excitation wavelength of 380 nm and emission wavelength of 405 nm. With the increase in ethanol concentration the contour maxima was found to be blue shifted. For the pure diesel sample the maximum fluorescence intensity was observed at the excitation wavelength of 400 nm and emission wavelength of 430 nm. The maximum fluorescence intensity for the pure biodiesel sample, which was found to be 10 times lesser than that of diesel, was seen at the excitation wavelength of 670 nm and emission wavelength of 680 nm. From the Fig. 2 it is clearly seen that the diesel and biodiesel samples contains different fluorescent active components.

Data Arrangement

The SFS spectra with offset $\Delta\lambda$ 40 nm for the 21 samples of ethanol-petrol calibration set were collected in the excitation range of 250–600 nm with an interval of 1 nm which gives 351 data points. The data were arranged in a two way array (sample×excitation), of dimension 21×351. The SFS spectra of biodiesel-diesel set were collected in the excitation range of 250–750 nm with an interval of 1 nm which gives 501 data points which were arranged in two way array of dimension 21×501.

EEMF spectra of ethanol-petrol calibration set were collected in the excitation range of 250–570 and emission range of 260–580 with an interval of 5 nm, which gives 65 data points each along the excitation and emission wavelength axes. EEMF spectra of biodiesel-diesel set were collected in the excitation range of 250–750 and emission range of 260–760 with an interval of 5 nm, which gives 101 data points each along the excitation and

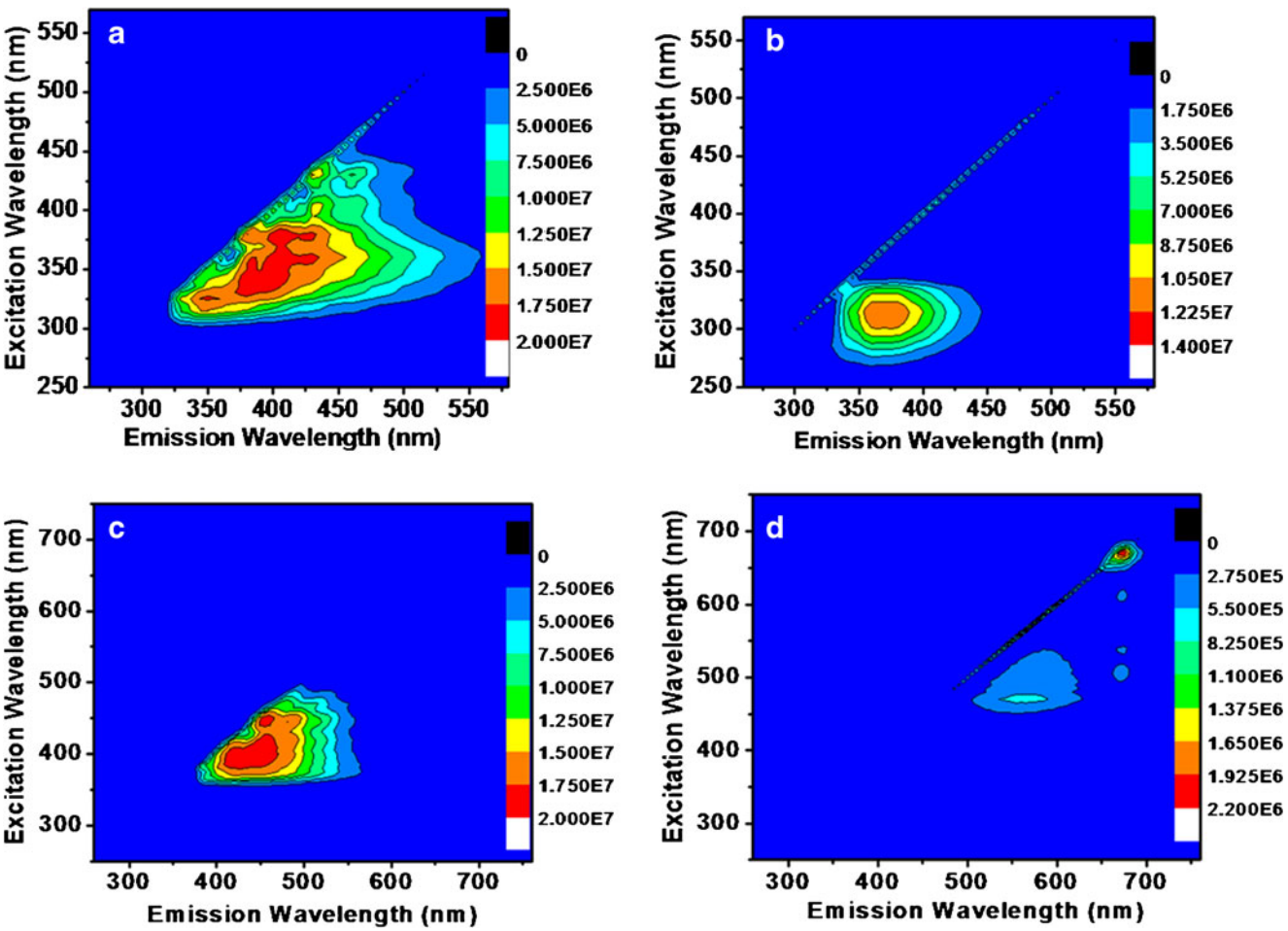

Fig. 2 EEMF contour plots of **a** Petrol, **b** Ethanol, **c** Diesel and **d** Biodiesel

emission wavelength axes. These EEMF data were arranged in a three way array (sample x emission x excitation), of dimension 21×65×65 and 21×101×101 for ethanol-petrol and biodiesel-diesel set, respectively. The data sets for biodiesel-diesel calibration were larger than those for ethanol-petrol because diesel and biodiesel fluorescence appear in two separate regions of the spectrum, showing maximum intensity at 430 nm for diesel and 680 nm for biodiesel. The SFS data were used for PCR and PLS analysis and EEMF data were used for N-PLS and unfolded-PLS analysis.

Cross-Validation

Leave one out cross-validation [35] was used to find the optimum number of factors. In this approach, a calibration model is made using all the samples of calibration set except for one and the model is used to predict the concentration of the left out sample. This procedure is repeated, so that every sample of the calibration set is left out and predicted once. The predicted sum of squares (PRESS) and root mean square error of cross validation (RMSECV) values are calculated and plotted against the number of factors (i.e. principal components or latent variables). The number of factors giving minimum RMSECV value is used to build the model.

Ethanol-petrol as well as biodiesel-diesel blends are essentially two-component mixtures. If each of the component components were a single fluorescent molecular species the optimum number of factor that would be required for the PCR, PLS, N-PLS and unfolded-PLS analysis of each system would be two. However since each of these components are complex multifluorophoric systems, the optimum number of factors required to fit the data set and to have minimum RMSECV values is expected to be more than two.

PCR and PLS Analysis

SFS data of ethanol-petrol and biodiesel-diesel blends were mean-centered before the PCR and PLS analysis. From the PRESS plots, given in Fig. 3a and b the optimum number of factors were found to be 6 for the PCR and 5 for the PLS analysis of ethanol-petrol and biodiesel-diesel blends In order to verify the minimum number of factors required to

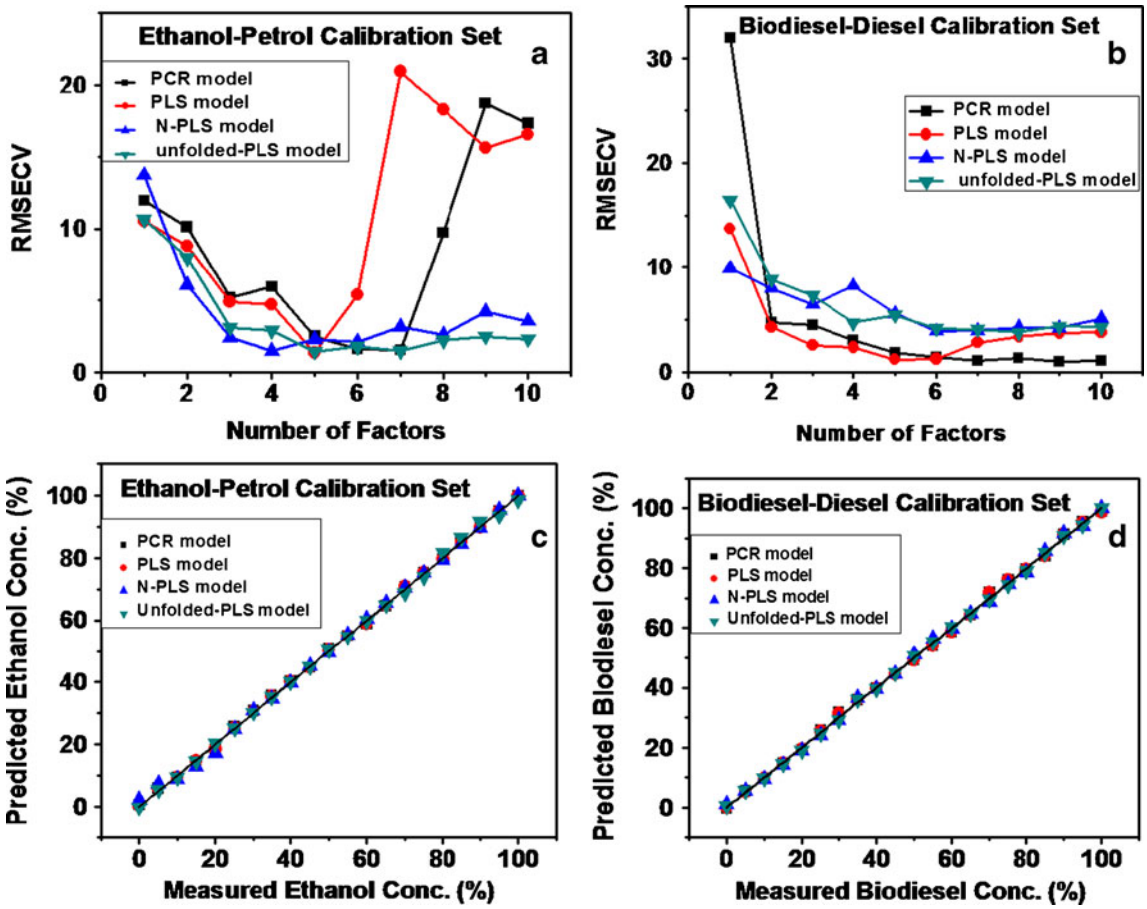

Fig. 3 **a**, **b** RMSECV versus number of factors, measured versus predicted **c** ethanol and **d** biodiesel concentration plots of PCR, PLS, N-PLS and unfolded-PLS model for ethanol-petrol and biodiesel-diesel calibration set

explain the variation in the data set, PCR and PLS models were also cross-validated with other methods such as venetian blind and contiguous cross validation approach, the optimum number of factors in all the cases were found to be 6 and 5 for PCR and PLS models, respectively. Hence, PCR model of 6 factors and PLS model of 5 factors were made for the ethanol-petrol and biodiesel-diesel mixtures. The PCR and PLS models were found to explain more than 99.9% variance of the spectral and concentration data of both the calibration set. The predicted ethanol and biodiesel concentrations of PCR and PLS models were plotted against the measured concentrations of ethanol and biodiesel and are shown in Fig. 3c and d, respectively. Various measures of the PCR and PLS model for ethanol-petrol and biodiesel-diesel sets are summarized in the Tables 2 and 3 respectively. The low RMSECV, RMSEC and R^2 value close to one indicates the obtained PCR and PLS models are highly robust.

N-PLS Analysis

Mean centered EEMF data of ethanol-petrol (21×65×65) and biodiesel-diesel (21×101×101) blends were used to make the N-PLS model. From the RMSECV and number of factor plots, shown in Fig. 3a and b, the optimum numbers of factors were found to be 4 and 6 for the ethanol-petrol and biodiesel-diesel blends, respectively. The 4 factor N-PLS model for the ethanol-petrol set was found to explain 90.7% and 99.9% variance of EEMF and concentration data, respectively. The N-PLS model of 6 factors for the biodiesel-diesel blends were found to capture 91.3% of spectral data and 99.9% variance of concentration data. In order to see the robustness of the model, predicted concentration of ethanol and biodiesel were plotted against the measured ethanol and biodiesel concentrations and are shown in Fig. 3c and d, respectively. The low RMSECV and RMSEC values and R^2 value close to one indicates the obtained N-PLS models are robust. Various measures of the N-PLS model ethanol-petrol and biodiesel-diesel blends are given in Tables 2 and 3, respectively. N-PLS calibration models were also made with the EEMF data for emission region between first and second order Rayleigh scattering. For this purpose, the EEMF spectral region outside the region of interest was set to zero intensity value. This effectively removes the Rayleigh scattering for the data set to be analyzed. The RMSECV values were 1.5 and 3.8 and RMSEC values were 1.1 and 0.8 for the N-PLS models made with scattering free EEMF data set of ethanol-petrol and biodiesel-diesel blends, respectively, which shows that the removal of scattering did not improve the model's robustness.

Table 2 Measures of PCR, PLS, N-PLS and unfolded-PLS models for the ethanol-petrol calibration set

	PCR	PLS	N-PLS	Unfolded-PLS
R^2	0.999	0.999	0.999	0.999
RMSECV	1.60	1.37	1.48	1.45
RMSEC	0.65	0.79	1.13	0.88
RMSEP	0.56	0.52	1.48	0.69

Table 3 Measures of PCR, PLS, N-PLS and unfolded-PLS models for biodiesel-diesel calibration set

	PCR	PLS	N-PLS	Unfolded-PLS
R^2	0.999	0.999	0.999	0.999
RMSECV	1.42	1.18	3.89	4.15
RMSEC	0.91	0.90	0.95	0.54
RMSEP	0.86	0.86	0.55	0.52

Unfolded-PLS Analysis

Two dimensional data sets of sizes 21×4225 and 21×10201 were obtained by unfolding the three way EEMF data of ethanol-petrol (21×65×65) and biodiesel-diesel (21×101×101) blends along the first mode, respectively. The optimum number of factors from the RMSECV and number of factors plot, given in Fig. 3a and b was found to be 5 for the ethanol-petrol and 6 for the biodiesel-diesel mixtures. The unfolded-PLS model for both sets of blended fuel explained 99.9% variance of both spectral and concentration data. The predicted and measured concentrations of ethanol and biodiesel were plotted and are shown in Fig. 3c and d. The various measures of the model for ethanol-petrol and biodiesel-diesel blends, summarized in Tables 2 and 3, shows that the obtained unfolded-PLS models are robust.

Prediction Ability of PCR, PLS, N-PLS and Unfolded-PLS Models

In order to see the prediction ability of developed PCR, PLS, N-PLS and unfolded-PLS calibration models, a testing set of 8 samples containing 2, 7, 12, 18, 33, 54, 77 and 92% of ethanol and biodiesel in blended petrol and diesel, respectively were used. The concentration predictions made by the calibration models for the ethanol and biodiesel are given in Tables 4 and 5, respectively. The root mean square error of prediction (RMSEP) values for the calibration models made for ethanol-petrol and biodiesel-diesel blends are given in Tables 2 and 3, respectively. The low RMSEP values indicate the obtained models are capable of estimating the unknown ethanol and biodiesel concentrations of blended fuels with a very small error in the estimation.

Table 4 Measured and the predicted ethanol concentration of the ethanol-petrol testing set

Measured ethanol concentration (%)	Predicted ethanol concentration (%)			
	PCR	PLS	N-PLS	Unfolded-PLS
2	2.55	2.23	4.32	1.88
7	7.87	8.00	9.31	7.46
12	11.44	11.42	10.78	11.51
18	17.48	17.71	15.95	17.51
33	33.74	33.64	33.92	33.23
54	54.46	54.44	53.63	54.34
77	77.28	77.32	77.21	76.99
92	91.82	91.82	91.62	93.72

By taking the representative samples of ethanol, petrol, biodiesel and diesel available in the market and by using SFS and EEMF with multivariate methods, calibration models were made for the quantification of ethanol in ethanol-petrol and biodiesel in biodiesel-diesel blends. Ethanol, petrol, biodiesel and diesel samples are of natural origin, the composition of fluorescent active components in these samples are expected to vary from batch to batch. However a library of calibration plots can be created by taking various combinations of, ethanol and petrol, diesel and biodiesel which could make it possible to estimate the ethanol in ethanol-petrol and biodiesel in biodiesel-diesel blends. In addition, unlike chromatographic methods which involve time consuming sample preparation steps or the NMR based methods where the cost associated with NMR instrument and its application is high, the combination of fluorescence spectroscopy and multivariate analysis gives a simple, fast and cost effective way of finding the ethanol and biodiesel content in ethanol-petrol and biodiesel-diesel blends without presaparation. However, chromatographic, NMR or IR based analytical methods are also precise in estimating ethanol and biodiesel in blended fuel [12–18].

Conclusions

In the present work, quantification of ethanol and biodiesel concentrations in the ethanol-petrol and biodiesel-diesel blends for a particular batch of fuel were achieved by the combination of synchronous fluorescence spectroscopy and excitation emission matrix fluorescence with multivariate methods like PCR, PLS, N-PLS and unfolded-PLS. The square of the correlation coefficient (R^2) values were found to be close to one for all the four models for both the fuel blends which shows that the measured and predicted ethanol and biodiesel concentrations are in close correspondence. The RMSEC and RMSEP values were less than 2% which indicates that all the four calibration models fitted the calibration data accurately and predicted the concentrations of the unknown samples with a small error of predictions. Additionally, the present work has advantages such as it is easier to use, cost-effective; do not involve ethanol and biodiesel separation from the fuel blends. In summary, all the four calibration models are highly robust, however, PCR and PLS models made using the SFS data of $\Delta\lambda$ 40 nm has advantage over the EEMF based N-PLS and unfolded-PLS model, because acquisi-

Table 5 Measured and the predicted biodiesel concentration of the biodiesel-diesel testing set

Measured biodiesel concentration (%)	Predicted biodiesel concentration (%)			
	PCR	PLS	N-PLS	Unfolded-PLS
2	1.97	2.00	3.15	2.57
7	7.36	7.09	7.51	7.59
12	11.51	11.75	11.58	11.85
18	17.69	17.91	17.37	17.71
33	34.57	34.45	33.30	32.21
54	53.22	53.15	54.21	54.64
77	78.07	78.18	76.67	76.41
92	90.90	90.75	92.10	92.05

tion of EEMF spectra is time consuming. The combination of SFS and EEMF with multivariate methods makes a viable method for the estimation of ethanol and biodiesel in blended fuels.

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