

Determination of Adulterants in Diesel by Multivariate Calibration Associated With LED Spectrofluorimetry

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Abstract

In this paper, multivariate calibration models have been developed for determination of common adulterants (kerosene, turpentine and residual oil from fried foods) added to diesel. The samples were analyzed by LED spectrofluorimetry and the multivariate calibration models were developed by Partial Least Squares (PLS). The proposal is suggested as an analytical methodology of low-cost, fast and non-destructive able to quantify the presence of contaminants in the diesel. The results showed that adulterants concentrations were adequately reproduced by the fluorescence spectral data.

Keywords: adulteration, diesel, PLS, spectrofluorimetry

1. Introduction

The intentional addition of adulterants to diesel has a negative effect on fuel properties and on the engine performance, such as fuel consumption, engine start-up control and engine heating. In addition, adulteration of fuel increases the emission of exhaust gases, hydrocarbons and particulate material (Corgozinho, Pasa, & Barbeira, 2008).

Several analytical methodologies have been developed for identification or quantification of adulterants in diesel and biodiesel-diesel blends in recent years. Patra and Mishra developed a method for detected contamination in diesel by excitation-emission matrix spectral subtraction fluorescence (Patra & Mishra, 2002). Corgozinho et al. related a method for quantifying of residual vegetable oil in diesel oil using synchronous spectrofluorimetry and PLS (Corgozinho, Pasa, & Barbeira, 2008). Oliveira et al. reported a method to determine adulteration of diesel/biodiesel blends by vegetable oil using Fourier transform (FT) near infrared spectrometry and FT-Raman spectroscopy (Oliveira, Brandão, Ramalho, Costa, Suarez, & Rubim, 2007). Vasconcelos et al. using near-infrared overtone regions determined biodiesel content and adulteration of diesel/biodiesel blends with vegetable oils (Vasconcelos, Souza Jr., Pimentel, Pontes, & Pereira, 2012). Pontes et al. detected adulteration in diesel/biodiesel blends using a method based near infrared spectrometry and multivariate classification (Pontes, Pereira, Pimentel, Vasconcelos, & Silva, 2011). Gaydou et al. detected vegetable oil as an adulterant in diesel/biodiesel blends associating NIR/MIR PLS (Gaydou, Kister, & Dupuy, 2011). Roy developed a fiber-optic sensor for determining kerosene as an adulterant in petrol and diesel (Roy, 1999). Souza et al. determined adulteration of Brazilian S-10 diesel by lubricant oil using MIR spectroscopy and PLS (Souza, Mitsutake, Gontijo, & Borges Neto, 2014). Brandão et al. used high performance liquid chromatography and multivariate methods to determine adulteration of diesel by vegetable oils and fats (Brandão, Braga, & Suarez, 2012).

In a previous work, our team developed a method and a sensor for monitoring quality in processes for obtaining fuels using spectrofluorimetry and Principal Component Analysis (PCA) (Quintella, Guimarães, & Musse, 2009). Also we reported a method for identification of the adulteration to diesel by the addition of residual cooking oil using spectrofluorimetry total 3D and PCA (Meira et al., 2011) and a spectrofluorimeter was patented (Quintella et al., 2011). This present study focuses on the quantification of adulterants added to diesel (kerosene, turpentine and residual oil from fried foods) by high-power light-emitting diode (LED) spectrofluorimetry and partial least squares (PLS) regression. LEDs have the following advantages as alternatives sources of excitation in

spectrofluorimetry: They are near monochromatic, have low cost, produce very little heat, have no coherence problems, have extended life, are small and can easily be modulated (Young, Garini, Dietrich, van Oel, & Liqui Lung, 2004).

2. Materials and Methods

Standard of diesel was supplied by Petrobras-Brazil and the mixtures of diesel with adulterants (kerosene, turpentine and residual oil from fried foods) were prepared at concentrations of 0 to 100%. Diesel neat and mixtures were analyzed in a LED Fluorescence Spectrometer of Quimis Q-798FIL. These standards were analyzed in duplicate without any prior treatment being used the natural fluorescence of fluids, with quartz cuvettes of 1 cm. The standards were excited with violet LED and emission was detected from 335-1000 nm at intervals of 0.38 nm in LED spectrofluorimeter.

To assess the applicability of the fluorescence method for quantifying the adulterants content multivariate calibration models were developed by Partial Least Squares (PLS) using the software Unscrambler X 10.0.1. Through the PLS models fluorescence spectra are correlated with the corresponding values of the concentration of each adulterant. Each PLS was developed using mean centered fluorescence spectra as independent variables and the concentration values as dependent variables. In calibration step of each PLS, the relationship between spectra and concentration values was estimated from a set of reference samples, and in the validation step the results of the calibration were used to estimate the concentrations from samples that were not used in the calibration step. In this case, mixtures of diesel with adulterant (kerosene, turpentine or residual oil from fried foods).

3. Results and Discussion

3.1 Calibration of the PLS models

Table 1 shows the mixtures of each adulterant added to diesel (kerosene, turpentine and residual oil from fried foods) analyzed by LED spectroluorimetry and used in the construction of the multivariate calibration models that were developed by partial least squares (PLS) regression using the entire spectral and the entire calibration set described in Table 1. The PLS models were built using the whole fluorescent spectra as independent variables and the values of the concentrations of each adulterant in diesel as dependent variables (Table 1).

Table 1. Concentration of adulterant added to diesel used in the construction of the PLS models

Kerosene (%)	Turpentine (%)	Residual oil from fried foods (%)
0	0	0
2	2	2
4	4	4
6	6	6
8	8	8
10	10	10
20	20	20
30	30	30
40	40	40
50	50	50
60	60	60
70	70	70
80	80	80
90	90	90
100	100	100

Figures 1 and 2 present respectively fluorescence spectra and PLS for the mixtures of kerosene in diesel. The

coefficient of correlation of the curve presented near to 1 (0.9969) and R^2 of 0.99818 indicate the strength of the association between the two variables and the efficiency of the PLS to carry out the predictions. Figure 3 presents that two latent variables predicted 100% of the total variance (almost 100% for the first latent variable). Therefore, the model was proved useful to predict changes in concentration of turpentine added to diesel based on the fluorescence spectral variance.

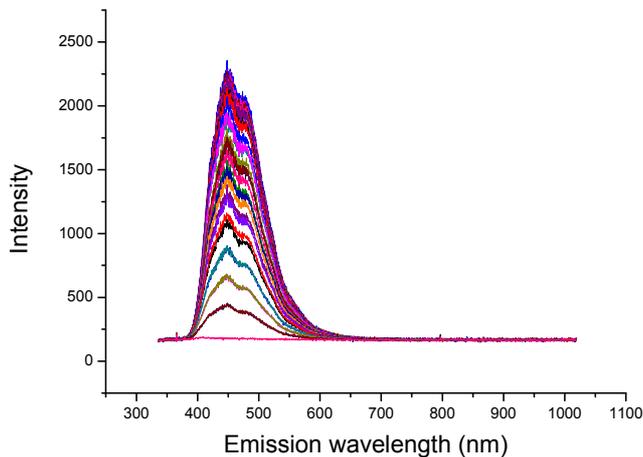


Figure 1. Fluorescence spectra of mixtures of kerosene in diesel (0-100%)

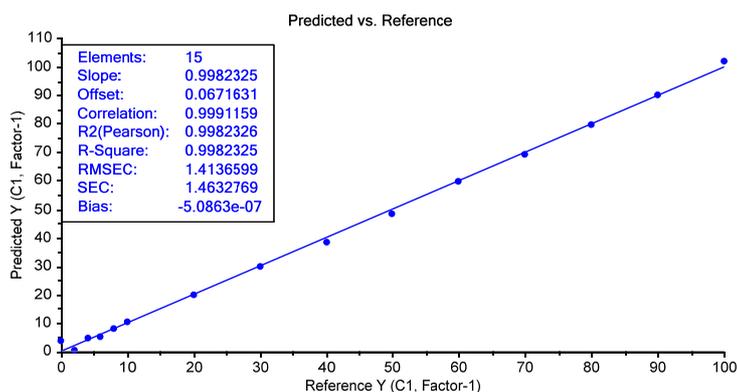


Figure 2. PLS model de mixtures of kerosene added to diesel

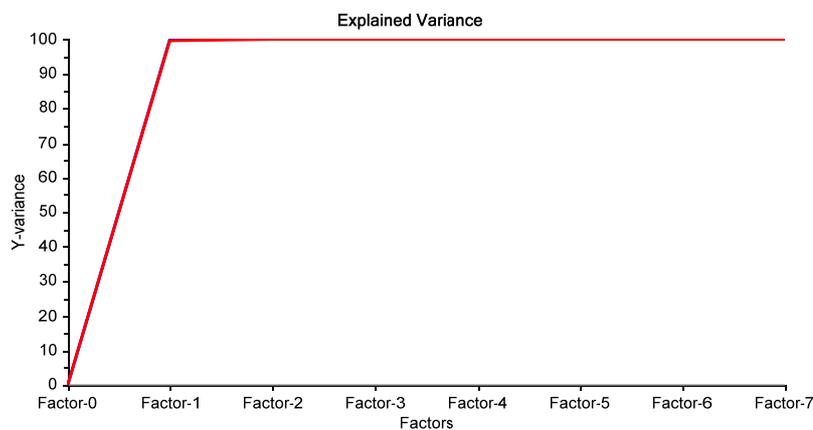


Figure 3. Explained variance of the PLS model de mixtures of kerosene added to diesel

Figures 4 and 5 present respectively fluorescence spectra and PLS for the mixtures of turpentine in diesel. The coefficient of correlation of the curve presented near to 1 (0.9991) and R^2 of 0.9982 indicate the strength of the association of the two variables and the efficiency of the PLS to carry out the predictions. Only two latent variables predicted almost 100% of the total variance (Figure 6).

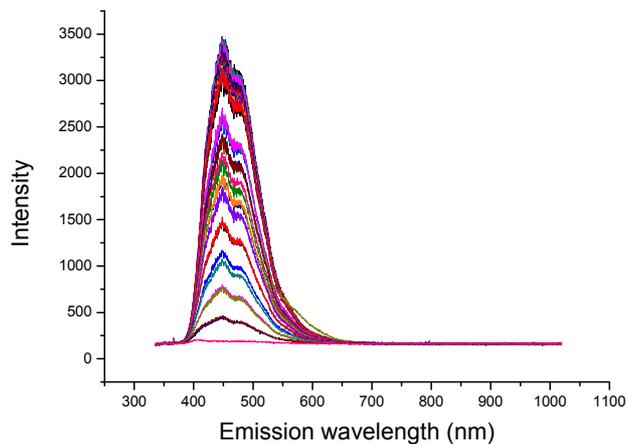


Figure 4. Fluorescence spectra for mixture of turpentine in diesel (0-100%)

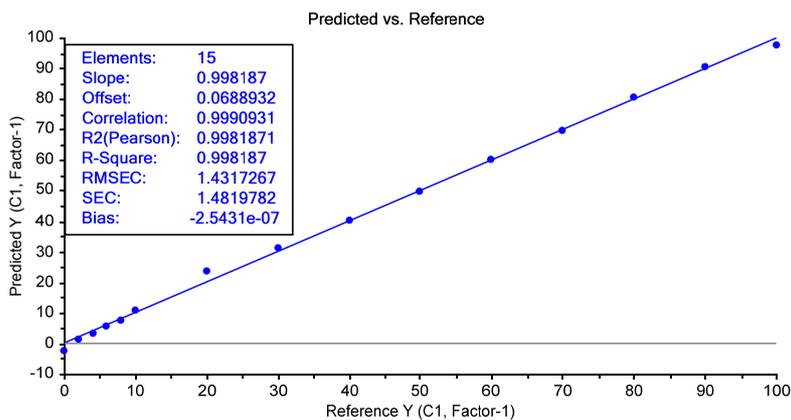


Figure 5. PLS model de mixtures of turpentine added to diesel

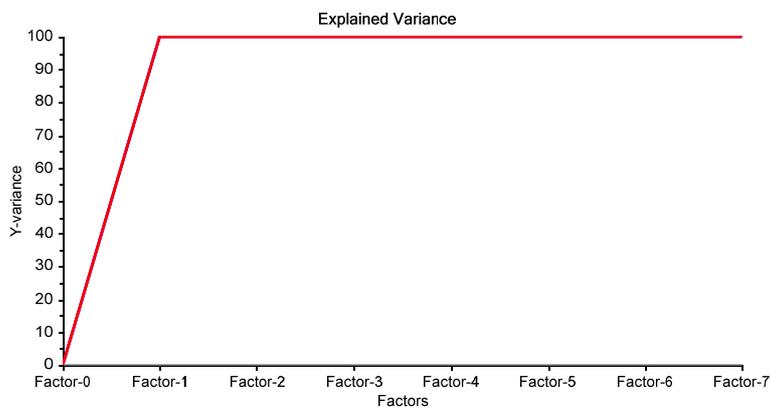


Figure 6. Explained variance of the PLS model de mixtures of turpentine added to diesel

Figures 7 and 8 present respectively fluorescence spectra and PLS for the mixtures of residual oil from fried foods in diesel. The coefficient of correlation of the curve presented near to 1 (0.9991) and R^2 of 0.9938 indicated the strength of the association of the two variables and the efficiency of the PLS to carry out the predictions. For mixtures of residual oil from fried foods added to diesel only two latent variables were shown to predict almost 100% of the total variance, 86% for the first and 13% for the second latent variable) (Figure 9). Therefore, the model was proved useful to predict changes in concentration of residual oil from fried foods added to diesel based on the fluorescence spectral variance.

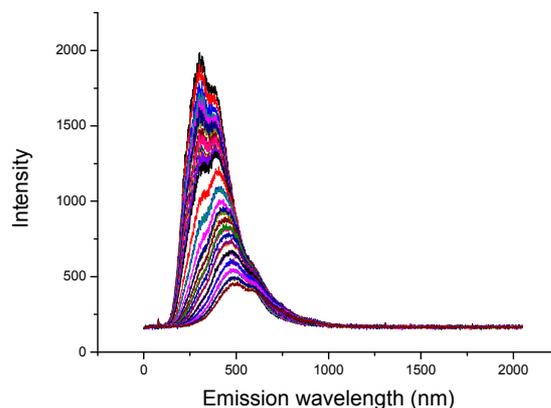


Figure 7. Fluorescence spectra for mixture of residual oil from fried foods in diesel (0-100%)

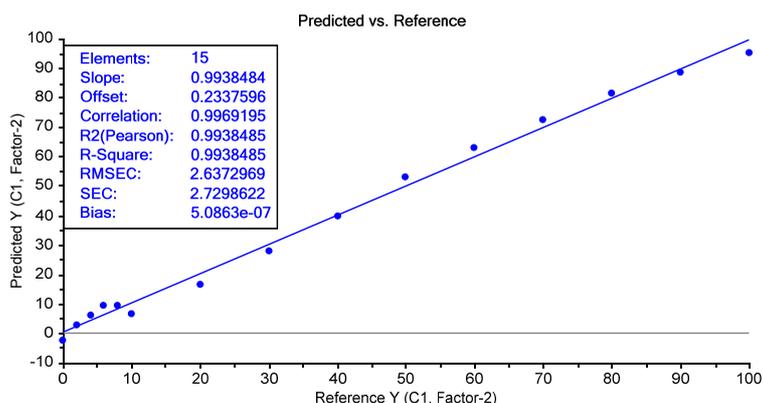


Figure 8. PLS model de mixtures of residual oil from fried foods added to diesel

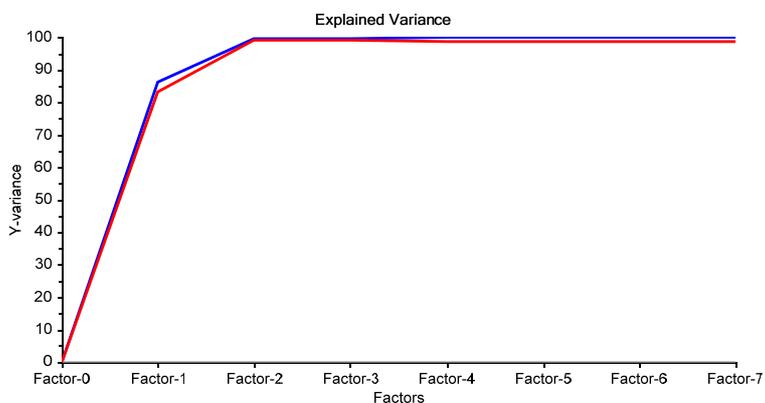


Figure 9. Explained variance of the PLS model de mixtures of residual oil from fried foods added to diesel

3.2 Validation of the PLS Models

The results of the calibration were used to estimate the concentrations from samples that were not used in the PLS models. The concentration values of the mixtures of diesel with adulterant (kerosene, turpentine or residual oil from fried foods) used in this validation procedure are shown in Table 2. The mixtures of each adulterant added to diesel were analyzed by LED values. Table 2 also shows the values of the concentrations predicted by the PLS models. For mixtures of turpentine in diesel and residual oil in diesel some anomalous samples determined by the software Unscrambler were excluded of the data set of validation.

Table 2. Concentration values of the mixtures of diesel with adulterant (kerosene, turpentine or residual oil from fried foods) used in validation procedure

Kerosene		Turpentine		Residual oil from fried foods	
Reference concentration (%)	Predicted concentration (%)	Reference concentration (%)	Predicted concentration (%)	Reference concentration (%)	Predicted concentration (%)
4	4.447487	4	2.275425	4	4.882298
6	7.13217	6	6.629976	8	7.487326
7	6.610565	7	6.524025	9	8.7575
8	6.716967	8	8.505703	20	16.39527
9	10.24765	9	10.05119	25	22.19561
10	11.11698	10	8.880089	35	32.90361
15	15.35029	20	23.57909	40	38.77464
20	19.18914	30	31.68184	45	45.54182
25	26.73995	35	37.47498	50	52.12151
30	29.39688	45	44.97174	60	62.11739
35	33.88729	50	49.81948	70	72.27793
40	40.12534	60	59.53387	80	80.72224
45	43.4324	70	72.39371	90	88.56984
50	50.78994	80	81.3277		
60	56.99543	90	90.1039		
70	69.38918				
80	79.42979				
90	90.06597				

4. Conclusion

The association of spectrofluorimetry and PLS was suitable for predict the concentration of adulterants (kerosene, turpentine or residual oil from fried foods) added to diesel

The advantages of the fluorescence spectroscopy inducted by LED, such as simplicity, quickness, low-cost suggest this method as a analytical procedure for the evaluation of the concentration of adulterants previously identified qualitatively in diesel.

The R^2 near to 1 for mixtures of diesel with kerosene, turpentine and residual oil from fried foods indicated the accuracy of the models to predict concentrations values of this adulterants added to diesel.

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