Simultaneous determination of quality parameters in biodiesel/diesel blends using synchronous fluorescence and multivariate analysis

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ABSTRACT

An analytical method was developed to determine four quality parameters (Biodiesel percentage, Cetane Number, Heat of Combustion Gross and Color) in biodiesel/diesel blends through a simple synchronous fluorescence spectrum of the samples.

For this purpose, chemometrics models based on fluorescence spectra and PetroSpect data obtained from mixtures of biodiesel/diesel were built. A variable selection by the successive projections algorithm (SPA) was used in order to obtain simple multiple linear regression (MLR) models based on a small subset of wavelengths. The SPA-MLR results were compared with a partial least squares (PLS) full spectrum regression. The best values found for the root mean square error of prediction using external validation were 0.37% (w/w) for the biodiesel in diesel, 0.5 for cetane number, 0.013 MJ/kg for heat of combustion and 0.1 for color.

1. Introduction

Over the past decade, the world trends are the use of renewable sources of energy to replace fossil fuels partially or totally. Among biofuels, biodiesel is one the best alternatives for fuel. It is obtained from vegetable oils, animal fats and recycled greases (also called cooking oil or yellow grease).

Argentina is now the first biodiesel exporting country. Most of Argentina's pure biodiesel (known as B100) is already exported to foreign markets, and production capacity is expected to increase 300% in the next 3 years. The biodiesel Argentine industry is mainly based on the use of soybean as feedstock. In the first 3 months of this year, the production of Argentinean biodiesel increased in 44%, to reach up 693.124 tons of this product [1].

The world production and consumption of pure biodiesel and its binary mixtures with diesel have increased substantially. In early 2010, the Argentine government allowed the commercial use of biodiesel blends. Today, the domestic market for transport fuels requires the addition of 7% (B7) of biodiesel, and in the next months is expected to increase to 10% (B10) [2].

Biodiesel/Diesel blend is a very complex mixture of thousands of individual compounds with carbon numbers between 9 and 23 (number of carbon atoms per hydrocarbon molecule). Most biodiesel compounds are esters, glycerides, pigments and antioxidants. The diesel compounds are paraffinic, naphthenic and aromatic in different proportions.

The determinations of biodiesel quality parameters are important for end-users, engine manufacturers and petroleum refining to ensure that the biodiesel can be used directly or blended with petroleum diesel. The addition of biodiesel to diesel produces several changes in parameters such as: cetane number, color, combustion heat and sulfur content, volatility, oxidation stability, lubricity, foaming, particles (total contamination), and turbidity [3,4].

There are several papers in the literature related to the use of infrared spectroscopy and multivariate calibration for monitoring the quality of pure biodiesel (B100) obtained [5–9]. Both, near and mid infrared spectroscopy (NIR, MIR) are used to determine quality parameters in mixtures of biodiesel/diesel [10–13]. In fuel laboratories and refineries there are currently compact equipments used to determine chemical and physical properties using this technique [14,15]. Flôres Ferrão worked with HATR-FTIR (Horizontal Attenuated Total Reflectance Infrared) to determine parameters in Biodiesel/diesel blend [16]. ^{1}HNMR (Hydrogen Nuclear Magnetic Resonance) is frequently used to follow the biodiesel synthesis [17–19], and its correlation with NIR was also described for the determination of soybean biodiesel in diesel [5,17].

Recent works predicts the content of biodiesel in biodiesel/diesel blends using fluorescence spectroscopy [20,21]. Owing to a higher selectivity and simplicity of synchronous fluorescence spectroscopy

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(SFS), this technique has been successfully applied in our previous work to discriminate biodiesel samples with respect to the base oil employed in their production [22].

The SFS was also used to determine residual oil in diesel/kerosene mixtures [23] and to determine PACs (Poly Aromatic Compounds) in crude petroleum products such as petrol and kerosene [24].

In our previous work, the application of chemometric techniques such as SPA-MLR (Successive Projection Algorithm–Multiple Linear Regression) was used utilizing the fluorescence spectral data [25,26].

The SPA–MLR algorithm works in three stages [27–30]. First, it builds ordered chains of variables by selecting variables with the least colinearity with previous ones. It is similar in nature to the approach pioneered by Jurs et al. [31] although the mechanics of the implementation may be different. Then, MLR models for each chain of variables are built and the best model that yields the lower root mean square error (RMSE) values is selected. Finally the algorithm removes the variables that do not contribute significantly to the model. A full cross-validation leave-one-out procedure has been currently used in the SPA algorithm [27].

PLS performs data decomposition into spectral score and loading matrices prior to model building with the aid of these new variables, using spectral and concentration data. MLR yields models are simpler and easier to interpret than PLS, since this calibration technique performs regression on latent variables, which do not have physical meaning. On the other hand, MLR calibration is more dependent on the spectral variables selection.

The aim of this work is to propose a fast method to determine four main parameters (fatty acid methyl ester (FAME), Cetane number (CN), Heat of combustion (HOC), and color); that establish the quality of a commercial biodiesel/diesel blend. For that purpose chemometrics models were built by using multivariate calibration and molecular fluorescence spectroscopy.

1.1. Quality parameters of biodiesel/diesel blends

1.1.1. Quantification of biodiesel

Infrared (IR) analysis is the most widely used measurement technology for measuring biodiesel in diesel. Both EN 14078 [32] and ASTM D7371 [33] methods use infrared as the analytical method and more specifically FTIR (Fourier Transform Infrared) spectroscopy. EN 14078 involves dilution in hexane followed by a transmission measurement and comparison of the carbonyl peak height measurement against a calibration curve. The ASTM D7371 specifies an attenuated total reflectance (ATR) measurement on the neat fuel blend and a chemometric partial-least-squares (PLS) model. In the biodiesel measurement, the fatty acid methyl ester (FAME) has a characteristic absorption at 1745 cm^{-1} (5.4 μm) due to the carbonyl group. Both EN and ASTM methods specify this wavelength for the biodiesel measurement.

1.1.2. Cetane number

It is one of the most studied parameters in literature. It is defined as the measure of a diesel fuel ignition quality in a compression-ignition engine. The CN is determined by a standard engine test (ASTM D613) [34], requiring a relatively large volume of fuel sample. Also, because of the time required to conduct the test, this method cannot be used on-line to control diesel blending. Fast and reliable methods were developed to monitor CN in the refinery [35,36].

Lower CN is obtained as higher percentage of biodiesel in the sample [37]. This parameter is influenced by structural features of fatty acid alkyl esters, such as chain length, degree of unsaturation and branching of the chain [38]. Usually, the CN increases with increasing chain length, and decreases with increase in unsaturation in global biodiesel/diesel composition [3].

1.1.3. Heat of combustion gross

The so-called gross heat of combustion or "higher heating value", also called gross calorific value, is the enthalpy of total combustion of a fuel, that means that, all carbon converted to carbon dioxide, and all hydrogen converted to water.

The precise determination of the HOC is of great interest for trading automotive diesel due to the fact that the HOC is the most important parameter for determining the price of the automotive diesel to be paid. Numerous empirical equations have been published to relate the fuel HOC to the hydrogen elemental composition of fuel as obtained by elemental analysis (ASTM D240) [39]. Another relationship could be made with chain length, instauration and molar weight [40].

1.1.4. Color

Determining the color of petroleum products is an important quality characteristic, since color serves as an indication of the degree of refinement of the material, contamination, degradation, or oxidation of diesel. This occurs when diesel is stored for long periods of time, when it is exposed to temperatures above room temperature or in the presence of moisture. Most diesel compounds, partially hydrogenated aromatic hydrocarbons, hydroxyaromatics, pyrroles, indoles, polycyclic aromatics, as well as olefins are susceptible to oxidation.

The diesel compounds associated to color measurement like indoles, cycloalkylindoles, and benzoindoles (predominantly carbazoles), are polycyclic aromatics.

The methodology recommended for determining the color of automotive diesel oil samples is the colorimetry analysis according to ASTM D1500, by which a sample is introduced into a glass cell and the color of the sample is compared with an optical filter color scale [41].

2. Experimental

2.1. Apparatus

FIA Laboratory (INQUISUR, UNS-CONICET):

Spectrofluorimeter Shimadzu RF-5301, with a xenon discharge light source (150 W), was used to obtain all the spectra. Synchronous fluorescence spectra were performed using a quartz cell, 0.2 cm × 1 cm × 3 cm = 0.6 mL. The wavelength interval (Δλ) utilized was 50 nm.

PETROBRAS Laboratory (Refinery Ricardo D. Eliçabe, Bahía Blanca):

PetroSpec fuel equipment (PAC) (TD PPA) is a near and mid infrared spectroscopic analyzer. PetroSpec TD PPA was used for determining FAME, CN, HOC and color.

This instrument lets the determination of above mentioned parameters with repeatability and reproducibility agree with those required by the standard ASTM Methods [14]. It has an internal library with a diverse matrix of over 600 fuels, developed globally by major fuel producers (Shell and Ethyl Corp). Table 1 shows the operational range parameters of the PetroSpec analyzer.

Table 1
PetroSpec: parameters range and performance.

	Range	Repeatability	Reproducibility
Biodiesel [% w/w]	0–15	0.1	0.3
Cetane number	30–70	0.3	0.8
Gross heat of combustion [MJ/kg]	44.100–48.800	–	–
Color	1–5[a]	–	–

[a] ASTM color.

The outlier samples are detected by this instrument through the Mahalanobis distances [42] from the calibration set.

2.2. Reagents

Isooctane (2, 2, 4-trimethylpentane), of 99.8% anhydrous (Sigma-Aldrich) was used as solvent of biodiesel/diesel samples.

2.3. Samples

A set of 30 diesel samples were acquired in different gas stations (from diverse refineries) in Bahía Blanca city, 15 with 5% of biodiesel (w/w), and the others 15 with 7% of biodiesel (w/w).

PETROBRAS supplied 5 samples of soybean biodiesel (B100) and 1 sample of pure diesel.

In addition to the 30 purchased biodiesel/diesel samples, 40 samples were prepared by using those samples supplied by PETROBRAS, mixing diesel and biodiesel in order to obtain percentage range to between of 1.5% to 12.0% biodiesel (w/w), in 1.5% (w/w) increments.

All samples were used for building the chemometrics models, for that purpose the spectra of diluted sample were registered. The dilution of samples was done in volumetric flask, 0.5 ml of sample is diluted to 10.0 ml with isooctane 99.8%. Samples without any dilution were used in the PetroSpec instrument.

2.4. Processing data

Data obtained from respective spectra and PetroSpec analyzer were preprocessing and PLS modeling with The Unscrambler 9.7 software. It was used full cross validation (CV) to determine the number of latent factors. The MLR variables (wavelength) were selected through the SPA. The model was obtained using CV to define the number of variables. The algorithm is a lab-made routine implemented in Matlab 7.6.

The overall set of 70 samples were divide into 40 samples for calibration and 30 for prediction set by applying the SPXY (Sample set Partitioning based on joint x–y distances) algorithm [43]. SPXY is an extended KS algorithm [44] by encompassing both x- and y-differences in the calculation of inter-sample distances in order to evaluate the prediction ability of the resulting model. The resultant prediction set is representative and ensures that the predictive ability of the model is evaluated in a fair manner along the entire calibration range.

The SPXY algorithm consists of augmenting the distance defined in Eq. (1) with a distance in the dependent variable (y) space for the parameter under consideration. Such a distance d$y(p, q)$ can be calculated for each pair of samples p and q as:

$$d_y(p,q) = \sqrt{\left(y_p - y_q\right)^2} = \left|y_p - y_q\right|; \quad p,q \in [1,N]$$

(1)

In order to assign equal importance to the distribution of the samples in the x and y spaces, distances d$x(p, q)$ and d$y(p, q)$ are divided by their maximum values in the data set. In this manner, a normalized xy distance is calculated as:

$$d_{xy}(p,q) = \frac{d_x(p,q)}{\max_{p,q \in [1,N]} d_x(p,q)} + \frac{dy(p,q)}{\max_{p,q \in [1,N]} dy(p,q)}; p,q \in [1,N]$$

(2)

A stepwise selection procedure similar to the KS algorithm can then be applied with d$xy(p, q)$ instead of d$x(p, q)$ alone.

The CV study was done in a single calibration set. The prediction set was employed to compare the performance of the resulting models according to the root mean square error of prediction (RMSEP) metric, which is defined by using an Eq. (3), where y_{pred} and y_{obs} are predicted and reference values, respectively, of 'i' sample set and 'n' is the number of samples used. It is worth noting that the prediction samples are not used in any phase of the variable selection or calibration procedures. The predictive ability of the models was evaluated by the RMSEP.

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{\text{pred}} - y_{\text{obs}}\right)^2}{n}}$$

(3)

3. Results and discussion

3.1. Synchronous fluorescence spectra acquisition

Biodiesel and diesel show native fluorescence [20,45], the overlapping spectra prevented the direct determination of the whole parameters [21]. So, synchronous fluorescence was used in order to reduce this overlapping and the SPA algorithm allowed the resolution of the four parameters in the mixtures. To avoid self-quenching all samples should be diluted [46]. When synchronous fluorescence technique is used, the selection of wavelength interval (Δλ) is one of the most important experimental parameters. This selection was made testing different Δλ and multivariate analysis. The scans were recorded from Δλ = 10 to 80 nm in 10 nm increments. The best SPA-MLR and PLS models were obtained with Δλ = 50 nm.

The fluorescent spectra of the samples were obtained in synchronous mode, within a range of 272–800 nm, keeping a fixed Δλ of 50 nm, with excitation and emission slits of 5 nm and a scan speed of 230 nm min^{-1}. These selected spectral regions have 529 wavelength values for each sample that were used in the multivariate analysis.

4. Chemometric models

The best results for preprocessing were obtained with a smoothing with Savitzky–Golay algorithm using first order polynomial and a 13 points window. The data were mean centered for PLS analysis. Multivariate calibration involves the development of a mathematical model that relates a property, in this case the fluorescence intensity of a set of known reference samples. It involves a calibration step in which the relationship between spectra and parameter values is estimated from a set of reference samples, and a prediction step in which the results of the calibration are used to estimate the parameter values from an unknown sample spectrum.

The algorithms use a calibration (X_{cal}) and a prediction (X_{pred}) set consisting of instrumental data and parameter values measured by the PetroSpec (y-values).

For PLS modeling were eliminated the noisy variables by the package tools given.

The essence of SPA consists of projection operations carried out on the calibration matrix. A detailed explanation of the projection operations is given elsewhere [27,28]. It is worth noting that prediction samples are not used in any phase of the variable selection or calibration procedures. Table 2 presents the results of both multivariate calibration methods and the number of latent variables (LV for PLS) and selected variables (NV for SPA-MLR) used in the models. Fig. 1 present de selected variables for each parameter in an average spectrum.

4.1. Quality of estimates and predictions

In order to obtain the quality of the estimates, prediction and bias can be used. Bias can be defined as the mean of the errors and can be written as:

$$Bias = \frac{\sum_{i=1}^{n} \left(y_{pred} - y_{ref}\right)}{n}$$

(4)

Table 2
Results from multivariate analysis.

		PLS	SPA-MLR
FAME (% biodiesel w/w)	LV/NV	6	14
	RMSECV	0.58	0.65
	RMSEP	0.37	0.58
	BIAS	− 0.03	0.09
	SEP	0.37	0.59
	r	0.9945	0.9846
Cetane number	LV/NV	7	9
	RMSECV	0.9	0.9
	RMSEP	0.7	0.5
	BIAS	0.01	− 0.15
	SEP	0.7	0.5
	r	0.9621	0.9693
Heat of combustion (MJ/kg)	LV/NV	7	11
	RMSECV	0.018	0.035
	RMSEP	0.013	0.026
	BIAS	0.00	0.01
	SEP	0.014	0.027
	r	0.9924	0.9677
Color	LV/NV	2	18
	RMSECV	0.2	0.2
	RMSEP	0.2	0.1
	BIAS	0.00	− 0.09
	SEP	0.2	0.2
	R	0.9470	0.8785

The standard error of prediction (SEP) measures the precision of a prediction [47]. The SEP is defined as:

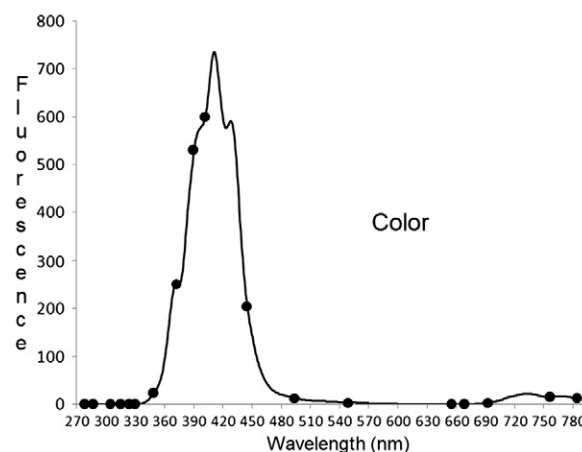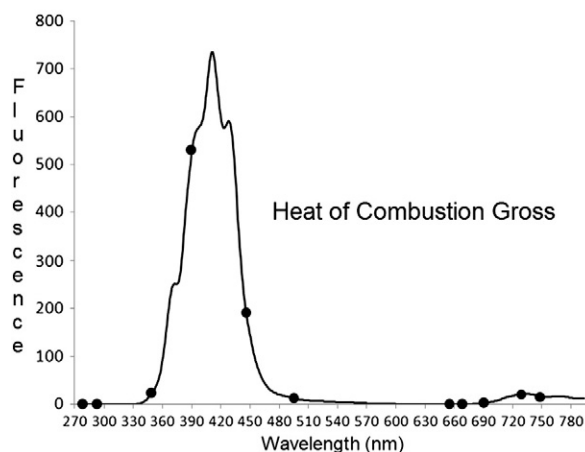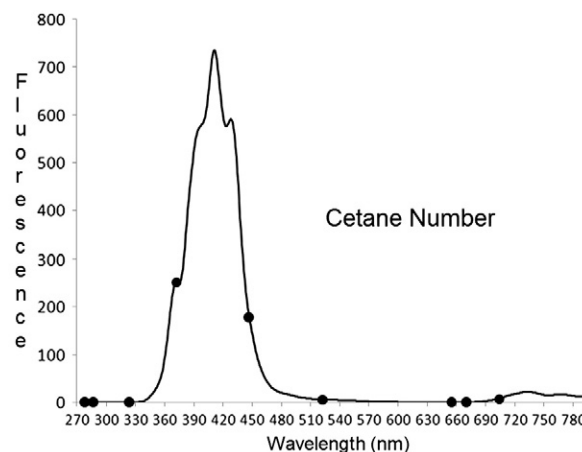$$SEP = \sqrt{\sum_{i=1}^{N_p} \frac{(\hat{y}_i - y_i - BIAS)^2}{(N_p - 1)}} \qquad (5)$$
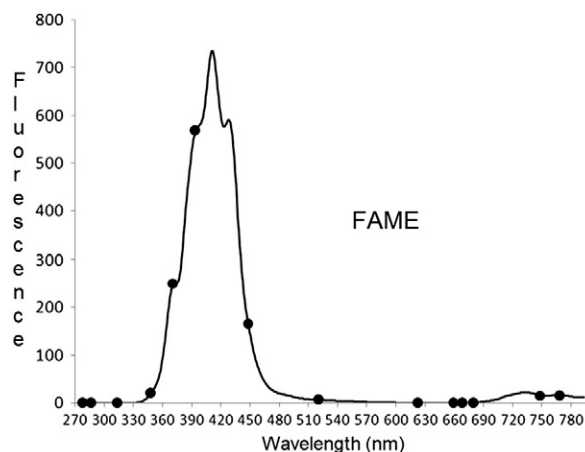
The full cross-validation leave-one-out procedure was applied, which consists of systematically removing one of the training samples in turn, and using only the remaining ones for the construction of the latent factors and regression models [48].

The best choice for measuring the calibration merits is root mean square error of the validation (RMSECV) and that explains the ruggedness of the model. The ability of a model to predict a new sample is expressed in terms of root mean square of prediction (RMSEP). This RMSEP obtained for each parameter shown in Table 2 are comparable to other techniques [11,41,49].

Table 3 shows the results of FAME, CN, HOC and Color determinations using ASTM methods and the proposed method with SPA-MLR modeling. As can be observed, for all analyzed samples, the obtained concentrations by proposed method were in close agreement with those obtained of ASTM methods.

5. Conclusions

A rapid, simple and inexpensive method for determining quality parameters (fatty acid methyl esters, cetane number, gross heat of combustion and color) of biodiesel/diesel commercial blends is proposed. The parameters were determined from the synchronous fluorescence spectra data of real samples by using the chemometric models.

Based on the results obtained in this proposal, we would suggest using this methodology to build a compact piece of equipment to be used in commercial samples, with a simple on-line dilution and specific light sources and sensors for each wavelength selected by the SPA.

Fig. 1. Selected variables for each parameter in an average spectrum.

Table 3
Determination of FAME, CN, HOC and color in biodiesel/diesel commercial blends.

Sample	ASTM				Proposed method			
	FAME (ASTM D7371)	CN (ASTM D613)	HOC (ASTM D240)	Color (ASTM D1500)	FAME	CN	HOC	Color
1	5.39 (0.02)	30.8 (0.3)	45.635 (0.010)	1.7 (0.1)	5.25 (0.37)	31.0 (0.4)	45.645 (0.025)	1.7 (0.1)
2	7.87 (0.03)	37.8 (0.2)	45.756 (0.009)	2.3 (0.0)	7.86 (0.21)	37.8 (0.2)	45.739 (0.010)	2.4 (0.0)
3	6.56 (0.02)	39.3 (0.3)	45.540 (0.005)	2.2 (0.0)	6.70 (0.43)	39.1 (0.5)	45.542 (0.021)	2.2 (0.0)
4	4.98 (0.04)	33.1 (0.1)	45.661 (0.008)	1.6 (0.0)	5.09 (0.15)	33.4 (0.4)	45.669 (0.008)	1.7 (0.1)
5	5.12 (0.01)	33.2 (0.1)	45.653 (0.008)	1.1 (0.0)	4.95 (0.36)	33.3 (0.3)	45.645 (0.014)	1.1 (0.1)

The samples were analyzed in triplicate ($n = 3$). Standard deviations are indicated in brackets.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.microc.2012.12.007.

References

[1] Quarterly Report from Argentinean National Statistics Institute (INDEC), http://www.indec.gov.ar/, (May of 2012).
[2] Press report from Fernando Peláez president of the "Cámara Argentina de biocombustibles (CARBIO), http://www.carbio.com.ar/es/, (May of 2012).
[3] R.A. Candeia, M.C.D. Silva, J.R. Carvalho Filho, M.G.A. Brasilino, T.C. Bicudo, I.M.G. Santos, A.G. Souza, Influence of soybean biodiesel content on basic properties of biodiesel–diesel blends, Fuel 88 (2009) 738–743.
[4] W. Zhang, W. Yuan, X. Zhang, M. Coronado, Predicting the dynamic and kinematic viscosities of biodiesel-diesel blends using mid- and near-infrared spectroscopy, Applied Energy 98 (2012) 122–127.
[5] G. Knothe, Determining the blend level of mixtures of biodiesel with conventional diesel fuel by fiber-optic near-infrared spectroscopy and 1H nuclear magnetic resonance spectroscopy, J. Am. Oil Chem. Soc. 78 (2001) 1025–1028.
[6] I.P. Soares, T.F. Rezende, R.C. Silva, E.V.R. Castro, I.C.P. Fortes, Multivariate calibration by variable selection for blends of raw soybean oil/biodiesel from different sources using Fourier transform infrared spectroscopy (FTIR) spectra data, Energy Fuel 22 (2008) 2079–2083.
[7] F.L.B. Lira, M.S. Albuquerque, J.G.A. Pacheco, T.M. Fonseca, E.H.S. Cavalcanti, L. Stragevitch, M.F. Pimentel, Infrared spectroscopy and multivariate calibration to monitor stability quality parameters of biodiesel, Microchem. J. 96 (2010) 126–131.
[8] P. Baptista, P. Felizardo, J.C. Menezes, M.J.N. Correia, Multivariate near infrared spectroscopy models for predicting the methyl esters content in biodiesel, Anal. Chim. Acta 607 (2008) 153–159.
[9] P. Baptista, P. Felizardo, J.C. Menezes, M.J.N. Correia, Multivariate near infrared spectroscopy models for predicting the iodine value, CFPP, kinematic viscosity at 40 °C and density at 15 °C of biodiesel, Talanta 77 (2008) 144–151.
[10] J.S. Oliveira, R. Montalvão, L. Daher, P. Suarez, J.C. Rubim, Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies, Talanta 69 (2006) 1278–1284.
[11] M.F. Pimentel, G.M.G.S. Ribeiro, R.S. Cruz, L. Stragevitch, J.G.A.P. Filho, L.S.G. Teixeira, Determination of biodiesel content when blended with mineral diesel fuel using infrared spectroscopy and multivariate calibration, Microchem. J. 82 (2006) 201–206.
[12] L.F.B. Lira, F.V.C. Vasconcelos, C.F. Pereira, A.P.S. Paim, L. Stragevitch, M.F. Pimentel, Prediction of properties of diesel/biodiesel blends by infrared spectroscopy and multivariate calibration, Fuel 89 (2010) 405–409.
[13] V. Gaydou, J. Kister, N. Dupuy, Evaluation of multiblock NIR/MIR PLS predictive models to detect adulteration of diesel/biodiesel blends by vegetal oil, Chemom. Intell. Lab. Syst. 106 (2011) 190–197.
[14] PAC [Internet], Advance Analytical Instrumentation for Lab and Process Application, http://www.paclp.com/.
[15] Eralytics [Internet], Analytical Instrumentation, http://www.eralytics.com/.
[16] M.F. Ferrão, M.S. Viera, R.E. Panta Pazos, D. Fachini, A. Engel Gerbase, Marder, Simultaneous determination of quality parameters of biodiesel/diesel blends using HATR-FTIR spectra and PLS, iPLS or siPLS regressions, Fuel 90 (2011) 701–706.
[17] M. Morgenstern, J. Cline, S. Meyer, S. Cataldo, Determination of the kinetics of biodiesel production using proton nuclear magnetic resonance spectroscopy (1H NMR), Energy Fuel 20 (2006) 1350–1353.
[18] G.F. Ghesti, J.L. Macedo, I.S. Resck, J.A. Dias, S.C.L. Dias, FT-Raman spectroscopy quantification of biodiesel in a progressive soybean oil transesterification reaction and its correlation with 1H NMR spectroscopy methods, Energy Fuel 21 (2007) 2475–2480.
[19] F. Jin, K. Kawasaki, H. Kishida, K. Tohji, T. Moriya, H. Enomoto, NMR spectroscopic study on methanolysis reaction of vegetable oil, Fuel 86 (2007) 1201–1207.
[20] M.D. Scherer, S.L. Oliveira, S.M. Lima, H.C. Andrade, A.R.L. Caires, Determination of the biodiesel content in diesel/biodiesel blends: a method based on fluorescence spectroscopy, J. Fluoresc. 21 (2011) 1027–1031.
[21] A.R.L. Caires, V.S. Lima, S.L. Oliveira, Quantification of biodiesel content in diesel/biodiesel blends by fluorescence spectroscopy: evaluation of the dependence on biodiesel feedstock, Renew. Energy 46 (2012) 137–140.
[22] M. Insausti, A.A. Gomes, F.V. Cruz, M.F. Pistonesi, M.C.U. Araujo, R.K.H. Galvão, C.F. Pereira, B.S.F. Band, Screening analysis of biodiesel feedstock using UV–vis, NIR and synchronous fluorescence spectrometries and the successive projections algorithm, Talanta 97 (2012) 579–583.
[23] O. Divya, A.K. Mishra, Multivariate methods on the excitation emission matrix fluorescence spectroscopic data of diesel–kerosene mixtures: a comparative study, Anal. Chim. Acta 592 (2007) 82–89.
[24] D. Patra, A.K. Mishra, Recent developments in multi-component synchronous fluorescence scan analysis, Trends Anal. Chem. 21 (2002) 787–798.
[25] M.F. Pistonesi, M.S. Di Nezio, M.E. Centurión, A.G. Lista, W.D. Fragoso, J.C. Pontes, M.C.U. Araújo, B.S. Fernández Band, Simultaneous determination of hydroquinone, resorcinol, phenol, m-cresol and p-cresol in untreated air samples using spectrofluorimetry and a custom multiple linear regression-successive projection algorithm, Talanta 83 (2010) 320–323.
[26] M.F. Pistonesi, M.S. Di Nezio, M.E. Centurión, M.E. Palomeque, A.G. Lista, B.S. Fernández Band, Determination of phenol, resorcinol and hydroquinone in air samples by synchronous fluorescence using partial least-squares (PLS), Talanta 69 (2006) 1265–1268.
[27] R.K.H. Galvao, M.C.U. Araujo, E.C. Silva, G.E. Jose, S.F.C. Soares, H.M. Paiva, Cross-validation for the selection of spectral variables using the successive projections algorithm, J. Braz. Chem. Soc. 18 (2007) 1580–1584.
[28] R.K.H. Galvão, W.D. Fragoso, M.C.U. Araujo, S. Soares, H. Paiva, A variable elimination method to improve the parsimony of MLR models using the successive projections algorithm, Chemom. Intell. Lab. Syst. 92 (2008) 83–91.
[29] R.L.S. Otero, R.K.H. Galvão, M.C.U. Araújo, E.T.G. Cavalheiro, Thermogravimetric determination of l-ascorbic acid in non-effervescent formulations using multiple linear regression with temperature selection by the successive projections algorithm, Termochim. Acta 526 (2011) 200–204.
[30] S.F.C. Soares, R.K.H. Galvão, M.C.U. Araújo, E.C. Silva, C.F. Pereira, S.I.E. Andrade, F.C. Leite, A modification of the successive projections algorithm for spectral variable selection in the presence of unknown interferents, Anal. Chim. Acta 689 (2011) 22–28.
[31] J.S. Dixon, J.M. Sutter, P.C. Jurs, Automated descriptor selection for quantitative structure–activity relationships using generalized simulated annealing, J. Chem. Inf. Comput. Sci. 35 (1995) 77–84.
[32] European Standard EN 14078: Liquid petroleum products - Determination of fatty acid methyl esters (FAME) in middle distillates - Infrared spectroscopy method, 2008.
[33] ASTM International D7371: Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FT-IR-ATR-PLS Method), 2007.
[34] ASTM D613 Standard Test Method for Cetane Number of Diesel Fuel Oil. Book of Standards vol. 05.05, 2010.
[35] F.B. Gonzaga, C. Pasquini, A low cost short wave near infrared spectrophotometer: application for determination of quality parameters of diesel fuel, Anal. Chim. Acta 670 (2010) 92–97.
[36] N. Ladommatos, J. Goacher, Equations for predicting the cetane number of diesel fuels from their physical properties, Fuel 74 (1995) 1083–1093.
[37] YPF [Internet] Impacto de porcentajes crecientes de Biodiesel en las propiedades de las mezclas con Gas Oil, http://www.ypf.com.
[38] G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Proc. Tech. 86 (2005) 1059–1070.
[39] ASTM D240-02, Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter, Book of standards volume: 05.01, 2007.
[40] K. Cheenkachorn, Predicting properties of biodiesels using statistical models and artificial neural networks, As. J. Energy Env. 7 (2006) 299–306.
[41] ASTM D1500 Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale). Book of Standards vol. 05.01, 2007.
[42] P.C. Mahalanobis, On the generalized distance in statistics, Proc. Natl. Inst. Sci. India 12 (1936) 49–55.
[43] R.K.H. Galvão, M.C.U. Araújo, G.E. José, M.J.C. Pontes, E.C. Silva, T.C.B. Saldanha, A method for calibration and validation subset partitioning, Talanta 67 (2005) 736–740.

[44] R.W. Kennard, L.A. Stone, Computer aided design of experiments, Technometrics 11 (1969) 137–148.

[45] C.N.C. Corgozinho, V.M.D. Pasa, P.J.S. Barbeira, Determination of residual oil in diesel oil by spectrofluorimetric and chemometric analysis, Talanta 76 (2008) 479–484.

[46] D. Patra, A.K. Mishra, Concentration dependent red shift: qualitative and quantitative investigation of motor oils by synchronous fluorescence scan, Talanta 53 (2001) 783–790.

[47] T. Naes, T. Isaksson, T. Fearn, T. Davies, A User-Friendly Guide to Multivariate Calibration and Classification, NIR Publications, Chichester, UK, 2002.

[48] D.M. Haaland, E.V. Thomas, Partial least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information, Anal. Chem. 60 (1988) 1193–1202.

[49] D.W.E.A. Santana, M.P. Sepulveda, P.J.S. Barbeira, Spectrophotometric determination of the ASTM color of diesel oil, Fuel 86 (2007) 911–914.