# Quantitative analysis of biodiesel in diesel fuel by UV-Vis spectroscopy

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**Abstract**. A preliminary methodology for determination of biodiesel content in commercial diesel fuel by ultraviolet and visible absorption spectroscopy (UV-Vis) was developed seeking its potential application in optical sensors for monitoring the diesel/biodiesel mixtures in heavy vehicles. Absorbance of visible light between 400 nm and 500 nm showed a linear response of the optical signal as a function of the biodiesel content for the investigated volume concentration range of biodiesel varying from 0 % to 20 %. Multivariate analysis was used to validate the construction of different calibration curves, differentiated by feedstocks origins for the starting pure biodiesel and diesel components, and determine the optimal wavenumber to perform ordinary linear regression. A narrow range of the visible spectrum around 450 nm provided the best coefficient of correlation for all calibration curves. The effects of the supplier of base biodiesel and diesel components used to make the calibration curves on the predictions of the singlevariate model was also assessed.

## 1. Introduction

Given a wide variety of feedstocks for biodiesel production, Brazil has the natural tendency to produce biodiesels with different specifications, which are controlled by methods defined in legislation approved by the National Agency of Petroleum, Natural Gas and Biofuels (ANP) [1]. In order to address the specific characteristics of biodiesels produced in the country, technical-scientific research aimed at developing new control methods to guarantee the quality of biodiesel and its mixtures with diesel is essential. The identification of the oil-based diesel fuels obeys the following nomenclature: diesel BX denotes a blend of biodiesel with diesel oil, where X is the volume fraction (in %) of biodiesel in the mixture (blend level); and diesel A denotes the diesel oil with no biodiesel in its composition (B0). Currently, there are two types of commercial diesel sold in Brazil: BX S500 and BX S10, containing, nominally, 500 ppm and 10 ppm of sulfur, respectively. In order to distinguish the type of BX sold at gas stations, the ANP determines that S500 diesel oil must differ from S10 diesel by color with the addition of a dye. The specification for the BX mixture is regulated by ANP Resolution nº 50/2013[2].

In this work, we developed the methodology for determination of biodiesel content in diesel using a simple and accessible analytical technique such as ultraviolet-visible spectroscopy (UV-Vis). The main goal of this work was to evaluate the potentiality of the developed methodology for its application in optical sensors for online monitoring the diesel/biodiesel mixtures in heavy vehicles. In distinction to other similar studies [3,4], we investigated the absorbance properties of biodiesel in a visible segment

of the electromagnetic spectrum, between 400 nm and 500 nm. This spectral range for diesel fuel sensoring offers some advantages for the envisaged practical application, such as no need of dilution of the fuel, as in the case of UV region [5], and independence on varying amount of aromatic compounds in diesel fuels, as in the case of near infrared part of spectrum [6].

## 2. Experimental

### *2.1. Samples*

The construction of calibration curves used 60 blends of BX samples prepared by mixing of pure diesel and biodiesel components from specific suppliers. Among the base components of pure biodiesel one was the certified reference material (CRM), for water content, produced at National Institute of Metrology, Quality and Technology – Inmetro. Mixtures of pure diesel and of pure biodiesel (blends of respective pure samples from various sources) were also used as base components to construct the calibration curves.

The samples were prepared by adding biodiesel to diesel in volumetric percentages ranging from 2 % (B2) to 20 % (B20) with the nominal biodiesel concentration step of 2 % in the mixtures. The construction and implementation of the analytical curves for determining the biodiesel content in diesel through UV-Vis spectroscopy were guided by the European standard EN 14078 [7].

Table 1 summarizes the base components of pure diesel and pure biodiesel used in construction of calibration curves, and Table 2 identifies the constructed calibration curves by specifying the respective base components of pure diesel and biodiesel.

**Table 1.** Pure biodiesel and pure diesel samples used in the construction of calibration curves.

| Biodiesel | |
|---|---|
| B_1 | Biodiesel, CRM (Inmetro) |
| B_2 | Biodiesel, supplier 1 (undefined feedstock) |
| B_3 | Biodiesel, supplier 2 (blend of different feedstocks of biodiesel at supplier) |
| B_4 | Biodiesel, supplier 3 (soy feedstock) |
| B_5 | Biodiesel blend (equal parts mixture, by volume, of six samples of pure biodiesel: B_1, B_2, B_4, and 3 samples of B_3 collected at different times) |
| **Diesel A** | |
| D_1 | A S10, supplier 1 |
| D_2 | A S500, supplier 2 |
| D_3 | A S10, supplier 2 |
| D_4 | A S10 blend (equal parts mixture, by volume, of four samples of pure diesel: D1 and 3 samples of D_3 collected at different times) |
| D_5 | A S500 blend (equal parts mixture, by volume, of three samples of pure diesel: 3 samples of D_2 collected at different times) |

**Table 2.** Biodiesel and diesel components used for the construction of calibration curves.

| Nº of curve | Base components |
|---|---|
| Curve 1 | B_1 + D_1 |
| Curve 2 | B_2 + D_2 |
| Curve 3 | B_3 + D_3 |
| Curve 4 | B_4 + D_3 |
| Curve 5 | B_5 + D_4 |
| Curve 6 | B_5 + D_5 |

*2.2. Spectra acquisition*

The absorption spectra of biodiesel-diesel mixtures were obtained in the spectral range between 200 nm and 800 nm, with a resolution of 1 nm, using a Perkin Elmer Lambda 950 spectrophotometer equipped with a quartz cell with a 1 mm optical path length. Data collections comprised three replicates for each sample.

*2.3. Data Analysis*

Data processing was performed in MATLAB environment using both multivariate analysis with the partial least squares regression (PLSR) method, which took into account absorption data from a specific range of a spectrum, and ordinary least squares regression (OLSR), resulting in an absorbance versus biodiesel concentration calibration curve for a specific wavelength of a spectrum.

The PLSR method, although more accurate than OLSR, as it evaluates many more measurement points, is much difficult to be implemented in the practical construction of a sensor. The use of PLSR aimed at validating the samples used for the construction of calibration curves by evaluating the respective curves quality. The validation of the mixtures prepared for the construction of the calibration curves was performed using the leave one group out cross-validation (LOGOCV) method.

In this method, one generates the PLSR model based on all data points for concentrations except for one that is then used as a blind sample to estimate the concentration predicted by the model. This procedure is repeated leaving out one by one all available data points and estimates how far the predicted values are from the true values, assessing thus a quality of a calibration curve.

In the next step, a simple linear regression was performed between absorbance values and concentrations to obtain calibration curves for each wavelength in the respective range of interest. Once again, the validation protocol (LOGOCV) was applied to each of these calibration curves, and the curve, associated with a specific wavelength, which provided the smallest error between predicted and actual values of concentrations was selected for the final tests on the prediction of biodiesel concentrations in commercial diesel BX samples.

## 3. Results

*3.1. Analysis of commercial B diesel samples Samples*

Figure 1 shows the raw spectra of the seven commercial diesel B samples used to evaluate the obtained calibration curves. The most prominent differences in the diesel B spectra of the used samples appeared in the range between 400 nm and 600 nm. The absorbance of B S500 samples shows an increase in values below 580 nm that causes a systematic displacement of their spectra in comparison with the B S10 samples. This displacement can be attributed to the presence of a dye [7] added to diesel oil A S500 as a compulsory marker [8].

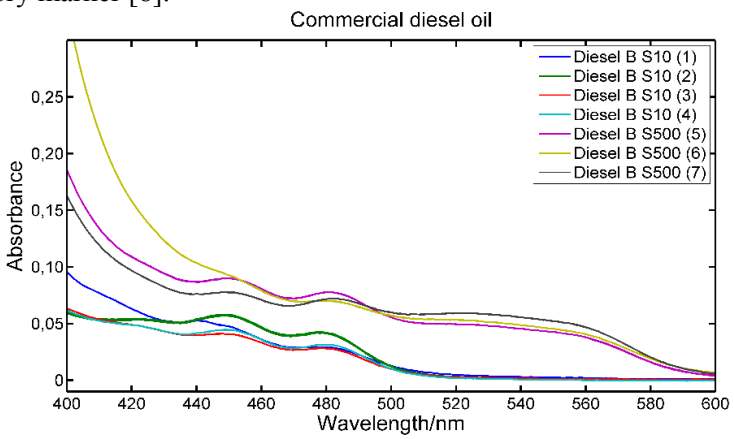


**Figure 1**. Spectra of commercial diesel B S10 and diesel B S500 samples.

Figure 2a shows the absorbance spectra of calibration samples and the validation results for calibration curve 1 (see Tables 1 and 2). A linear trend in band intensities variation has been observed in the absorbance graph as the concentration of biodiesel in the calibration mixtures increased from 0 % to 20 %. The validation process for the curve demonstrates the strong linear relationship between the predicted and actual concentration, with the correlation coefficient of 0.995 (Figure 2b).

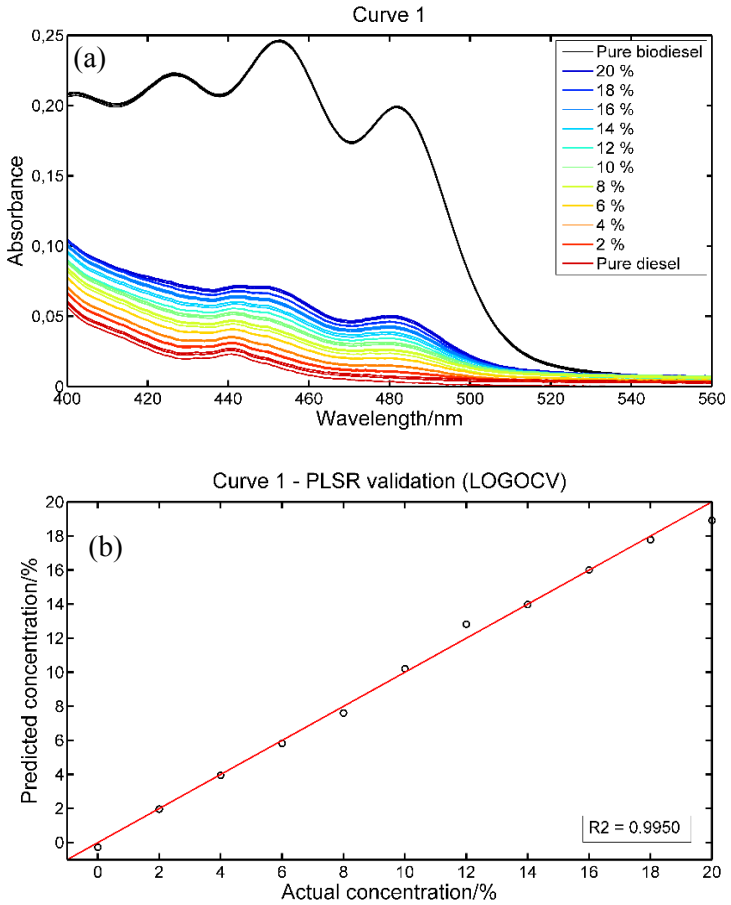


**Figure 2.** Absorbance spectra (a) and PLSR validation of calibration curve 1 (b).

Figure 3a shows the predicted concentration values as a function of wavelength for the different mixtures (colored lines), together with the respective reference values (black lines). The vertical line indicates the wavelength for which the error of the predictions is minimum, calculated as the sum of squares of the residuals of the respective regression model. The graph in the Figure 3b shows the correlation curve for the chosen wavelength.

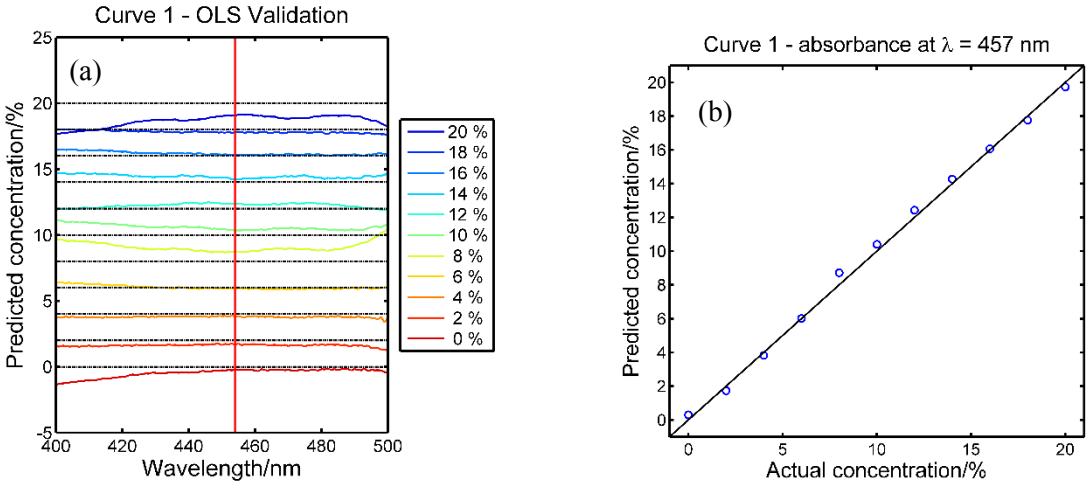


**Figure 3.** Graphical representation of wavelength selection using OLSR (a) for the calibration curve 1 with the best accuracy (b).

Finally, the prediction of biodiesel concentrations in the samples of commercial blends (diesel B) was made using the calibration curve for the wavelength selected in the previous step. In order to assess the accuracy of the constructed calibration curves, the predicted biodiesel concentrations were compared with the respective concentrations determined by other standardized methods from external certified laboratories. Figure 4a shows the prediction curves for the diesel B samples together with the prediction obtained at the specific wavelength of a spectral response (vertical red line in the figure) that results in the smallest overall error in the calculated concentrations of biodiesel in the tested samples (Figure 4b).

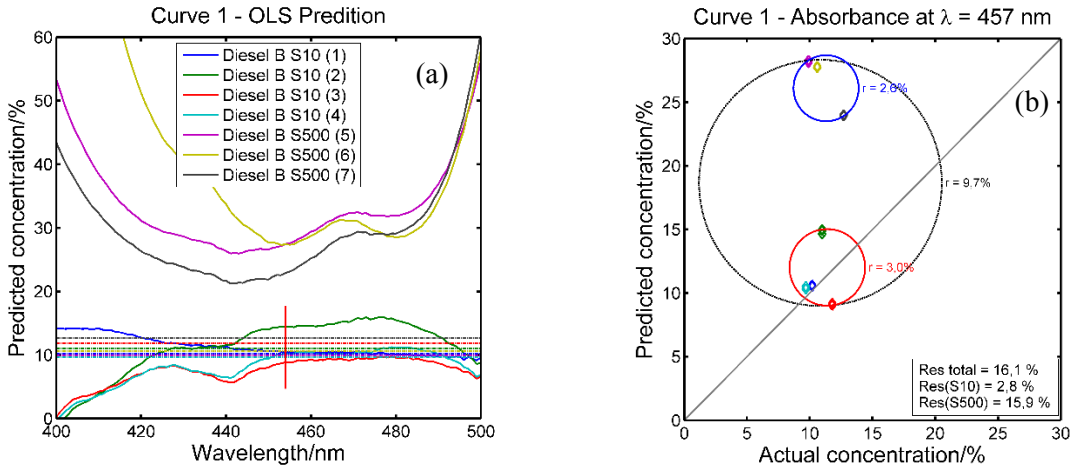


**Figure 4.** Prediction of concentrations for commercial diesel B samples in the overall wavelength range of interest (a) and for the specific wavelength using the calibration curve 1 (b). Consecutive numbers in the legend denote the samples feedstock. Radius of the circles and residual parameters are given in the figure (see the text for details).

The circles in the Figure 4b are a visual depiction for the expected accuracy of the developed measurement method. One can observe in Figure 4b that the predicted results for diesel samples of type S500 show a significant systematic shift to greater values of concentrations. This result was already expected, since the calibration curve 1 was constructed using S10 type of diesel in the reference samples, whereas the absorbance spectra of the B S500 diesel samples show a systematic shift to higher

absorbance values over the entire wavelength range of interest (see Figure 1). Nevertheless, the relative dispersions of predicted values of biodiesel concentrations for both B S10 and B S500 samples (red and blue circles, respectively) were nearly the same, of about 3 %. We attribute the effect of separation of B S10 and B S500 results to the presence of a dye in the B S500 samples. The quality of the calibration curve 1 can be assessed from the residual parameters shown in the Figure 4b (defined as a square root of residual sum of squares). The value of total residual of 16,1 % (all commercial diesel samples are considered) is mainly defined by the residual related to B S500 samples (15,9 %), whereas the residual corresponding to B S10 samples was significantly smaller (2,8 %). These residual parameters can be used to compare the calibration curves constructed using different suppliers for the base pure diesel and biodiesel components.

### *3.2. Effect of diesel and biodiesel supplier on the results of biodiesel concentration measurements by UV-Vis spectrometry*

Figure 5 shows the correlations between the predicted and the actual values of commercial diesel samples B obtained for all types of calibration curves constructed in this study (see Table 2). It is noteworthy that, in all cases, the wavelength that provides the best accuracy in the prediction is around 450 nm, which corresponds to the center of the absorption band of the conjugated double bond systems, characteristic, for example, of carotenoids [8] naturally present in biodiesel.

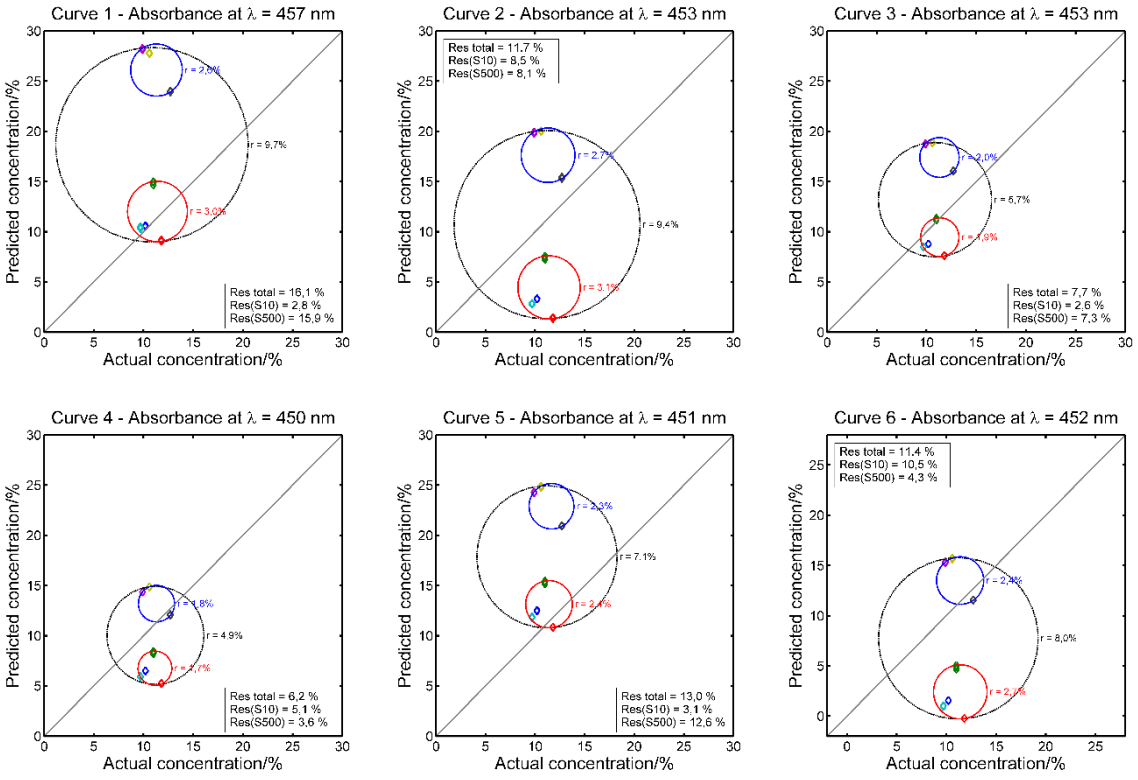


**Figure 5.** Effect of the calibration curve model on the predicted versus actual results.

As explained in 3.1, the circles in the prediction figures visualize the scale of relative scattering of the results upon the determination of biodiesel concentrations in commercial BX blends using the respective calibration curve. The black circles represent the relative accuracy scale expected when a specific calibration curve is used for measurements of both S10 and S500 types of diesels. Blue and red

circles outline the relative spread of measured concentrations for S500 and S10 type mixtures, respectively.

The results presented in the Figure 5 provide important insights about the application of the investigated method for the monitoring of biodiesel in the vehicles. A systematic difference in the absorbance properties, translated into systematic differences in the measured biodiesel concentrations, between S500 and S10 types of diesels, in the studied spectral segment, cannot be smeared by the type of calibration curve. The predicted versus actual concentrations of biodiesel in all graphs of Figure 5 are clearly divided in two respective groups of data. The use of A S10 diesel as a base component for calibration curves results in much lower residual parameters for B S10 diesels (see plots for calibration curves 1, 3 and 5). Whereas, the use of A S500 diesel provides lower residuals for B S500 diesels. These results point out that two calibration curves, for S10 and S500 types of diesel, can be provided in the eventual monitoring system and this may extend the respective capabilities to a distinguishing between S10 and S500 types of fuel.

The influence of pure biodiesel component, used for the construction of calibration curve, on the results of the measurements, one can rationalize by considering the parameters of calibration curves by themselves (Figure 6) together with the overall residual parameters (size of black circles in plots of Figure 5).

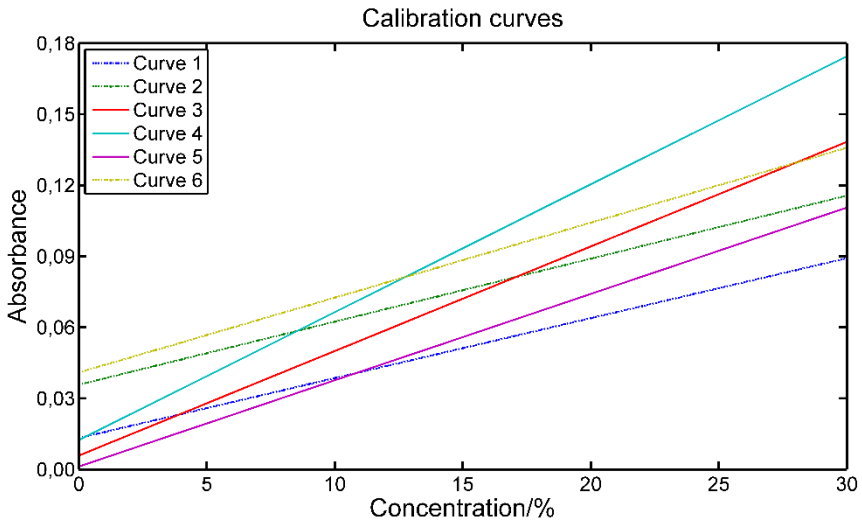


**Figure 6.** Calibration curves for the studied combinations of pure diesel and biodiesel components.

One can note that the calibration curves 4, 3 and 5 result in smaller overall residual parameters (r = 4,9 %; 5,7 % and 7,1 %, respectively), as compared to the respective parameters estimated in case of calibration curves 6, 2 and 1 (r = 8,0 %; 9,4 % and 9,7 %, respectively). Not only this grouping of calibration curves, but also their ranking according to the values of residuals, perfectly correlates with the sensitivities of the obtained calibration curves (see Figure 6). The highest sensitivity (slope of the line) of the calibration curve 4 results in the lowest residual parameter. The lowest sensitivity obtained for the calibration curves 2 and 1 produced the highest values for the respective residual parameters. As was already stated, the absorbance of a biodiesel at ~450 nm is defined by the amount of unsaturated bond systems with a certain number of double bonds in conjugation (11 in the case of β-carotene) [9] present in a biodiesel. The reduction of the amount of such systems can be an indicative of the overall degradation of oxidative resistance of biodiesel by transformation of unsaturated C=C bonds of esters in biodiesel as well [10]. The consequence of a reduced absorbance of a pure biodiesel used in the construction of calibration curves is a reduced sensitivity of the respective calibration curve.

## 4. Conclusions

UV-Vis spectroscopy study of diesel-biodiesel blends in the wavelength region between 400 nm and 500 nm showed that the quantification of biodiesel concentration in the blends, which is based on the absorbance at around 450 nm, strongly depends on the two main factors. The first one is related to a dye, which is compulsorily added to the S500 type of diesel, and is not present in the S10 type. The second factor is defined by the origin of the pure biodiesel used for the construction of a calibration curve.

The differences in the amount of systems with unsaturated bonds, such as polyenes, present in a pure biodiesel component used for the calibration curve definition, will affect the sensitivity of the quantification method and, as a consequence, will influence its accuracy. Nevertheless, a standardization of the amount of dye in diesel and of naturally or artificially present antioxidants, as carotenoids, in biodiesels may offer an important features to the method. Such a standardization may provide not only a better accuracy for quantification of biodiesel in diesel blends, but also will make the method to be selective to the type of diesel blend (S500 or S10), as well as, potentially, to be sensitive to oxidation stability of the diesel fuel.

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