Spectrophotometric Methodology to Quantify Antioxidants in Biodiesel by Multivariate Calibration

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Abstract

The aim of this work was to quantify three different antioxidants in biodiesel: Santoflex, Baynox and Tocopherol using Infrared spectroscopy and chemometrics. For the construction of the models, 28 samples containing antioxidant in the range of 0.1 mg/Kg to 500 mg/Kg in biodiesel were used. Were developed three models based on PLS 1 multivariate calibration method to quantify each of the three antioxidants separately and a model based on PLS 2 method to quantify simultaneously all the antioxidants. All models were compared to the values of root mean square error of calibration (RMSEC) and validation (RMSEP). The methodology described here is fast, non-destructive and can be used for quality control of antioxidants present in biodiesel.

Introduction

Biodiesel [1] a renewable fuel, is described as long chain mono alkyl ester derived of fatty acid, obtained through chemical reaction, transesterification of lipids, oils and fats. Biodiesel can be obtained from different sources as vegetable oils, animal fat or algae that react with alcohol and a catalyst. In recent years has become an important biofuel, because it represents a real environmental policy and a new class of renewable energy source. Biodiesel, an environmentally friendly compound is used mixed with diesel; this one causes a lower emission of carbon dioxide and sulfur, produce less smoke and particulate emissions. Decreasing the pollution level, contributes to the maintenance of historical monuments. Biodiesel derived of oilseed in general degrades faster due to its composition, the presence of unsaturated compounds. An useful alternative to diminish the rate of decomposition is the use of antioxidants.

In this study where used three different commercial antioxidants, Baynox, Santoflex and Tocopherol. In order to verify the effectiveness of antioxidants, a technique of green chemistry, was used, spectroscopy methods, due to its low cost, small amount of sample, accuracy and reliability when associated to chemometrics methods. Multivariate methods can help the analysts to extract the relevant qualitative or quantitative information from spectra, and these methods can even help when it is necessary rapid quality control evaluation. In this paper were compared different PLS chemometric methods for the quantification of three different antioxidants, in biodiesel based on (MIR) mid-infrared spectroscopy. The goal in this study is to show the possibility of simultaneous determination of all antioxidants in biodiesel quickly, accurately and the possibility of using intact samples presented directly to the instrument without any pre-treatment.

Materials & Methods

Biodiesel from sunflower was obtained by basic homogeneous catalysis. The parameters used for the transesterification reaction were: oil molar ratio of methanol /catalyst: 7.1 / 0.3. The products were obtained after 30 min of reaction at 45 °C. Three different antioxidants types were used: Baynox^{R} (Lanxes inc.), Santoflex^{R} (Solutia) and Tocopherol (Merck). Infrared spectra were obtained from a Nexus 470 Nicolet IR spectrometer. The spectra were obtained in a NaCl sealed cell of 0.027 mm using an average of 64 scans. The background was obtained using clean sealed cell with an average of 64 scans. After recording each spectrum, the NaCl sealed cell was cleaned with n-hexane. The developed methodology used the absorbance spectra. It was studied the use of antioxidant

concentrations in blends (biodiesel/antioxidant) between 0.1 to 500 mg/Kg in sunflower biodiesel. The Matlab version 6.5 and PLS Toolbox from Eigenvector Research version 4.21 computer programs were used to build the PLS model for the MIR results of biodiesel/antioxidant blends [2].

Results

Table 1: Results summary for the PLS calibration models developed

PLS calibrations	SEC (ppm)	SECV (ppm)	R^2	SEP (ppm)	Latent variables
PLS-1 (Santoflex)	18.8	34.8	0.99	21.1	4
PLS-1 (Baynox)	37.2	83.2	0.96	26.7	4
PLS-1 (Tocopherol)	9.0	12.9	0.99	68.6	4
PLS-2 (Santoflex)	1.1	1.4	0.99	4.2	2
PLS-2 (Baynox)	7.3	9.2	0.99	28.4	2
PLS-2 (Tocopherol)	7.7	9.8	0.99	29.9	2

Some statistical parameters[3] were calculated to compare PLS 1 and PLS 2 models (Table 1), root mean square error of calibration (RMSEC), root mean square error of the cross validation (RMSECV), root mean square error of prediction (RMSEP) and correlation coefficient (*r*) between the real concentration and the concentration predicted during the calibration. As shown in Table I, the RMSEC, RMSECV and RMSEP values related to the PLS 2 model were smaller than values of PLS 1 models for all antioxidants, except for the Baynox antioxidant. Therefore, it can be concluded that the PLS 2 model offers the best performance for most of the antioxidants. The degree of freedom in the F-test was 8 for both models. The F-test obtained results were 5.26, 1.13, and 25.24 for Tocopherol, Baynox, and Santoflex, respectively. The F values calculated to PLS 1 and PLS 2, models Tocopherol and Santoflex were greater than 3.44, which is the critical F-value (with confidence level of 95 %). Thus, these results demonstrate that there is a difference between the PLS 1 and PLS 2. For the F-test, the following expression was used: $F = (RMSEP_i)^2/(RMSEP_j)^2$ where RMSEP is the root mean square error of prediction (validation), and the subscripts *i* and *j* represent the models that have the largest and lowest RMSEP values, respectively.

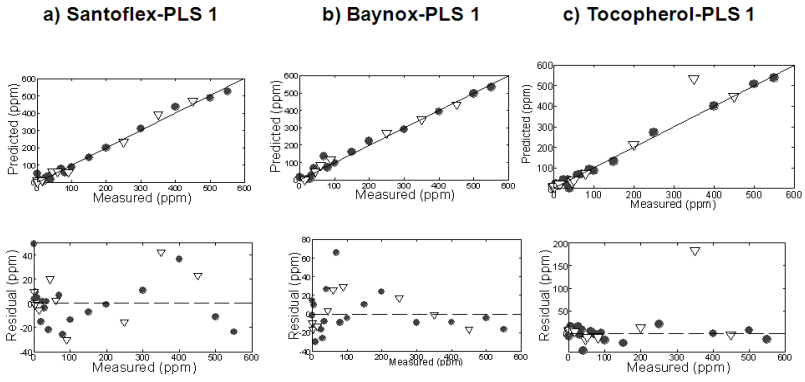

Fig 1; Plot of predicted versus reference values for Santoflex (left), Baynox (center) and Tocopherol (right)antioxidants by PLS 1. Calibration (●) and validation (∇).

Conclusions

In this work it was presented a rapid and non-destructive method to determine all the content of antioxidants in biodiesel simultaneously and separately employing (FT-IR) Fourier Transform Infrared spectroscopy and Chemometrics methodology. The results obtained demonstrated that it is possible to determine the antioxidant content in blends with biodiesel employing both PLS 1 and PLS 2 models. Through the F-test it was possible to conclude that there is no significant difference in errors for the determination of the antioxidant Baynox, present in biodiesel given by the two models (PLS 1 and PLS 2) within 95% of confidence level. This technique is in concern with the actual green chemistry; especially because don't generate waste, toxic residues.

References

1) F.C. Silva, K.S.B. Cavalcante, H.C. Louzeiro, K.R.M. Moura, A.P. Maciel, L.E.B. Soledade, A.G. Souza, Production of biodiesel from babassu oil using methanol-ethanol blends, *Ecl. Quím.*, 35(1), (2010), 47-54.
2) R.W. Kennard, L.A. Stone, Computer aided design of experiments, *Technometrics*, 11(1), (1969), 137-148.
3) Y. Wang, M. Yang, G. Wei, R. Hu, Z. Luo, G. Li, Improved PLS regression based on SVM classification for rapid analysis of coal properties by near-infrared reflectance spectroscopy, *Sens. Actuator B-Chem.*, 193, (2014), 723-729.