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Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies

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Abstract

Partial last square regression (PLS) and artificial neural network (ANN) combined to FTIR-ATR and FTNIR spectroscopies have been used to design calibration models for the determination of methyl ester content (%, w/w) in biodiesel blends (methyl ester + diesel). Methyl esters were obtained by the methanolysis of soybean, babassu, dende, and soybean fried oils. Two sets of samples have been used: Group I, binary mixtures (diesel + one kind of methyl ester), corresponding to 96 biodiesel blends (0–100%, w/w), and Group II, quaternary mixtures (diesel + three types of methyl esters), corresponding to 60 biodiesel blends (0–100%, w/w). The PLS results have shown that the FTNIR model for Group I is more precise and accurate (±0.02 and ±0.06%, w/w). In the case of Group II the PLS models (FTIR-ATR and FTNIR) have shown the same accuracies, while the ANN/FTNIR models has presented better performance than the ANN/FTIR-ATR models. The best accuracy was achieved by the ANN/FTNIR model for diesel determination (0.14%, w/w) while the worthiest was that of dende ANN/FTIR-ATR model (0.6%, w/w). Precisions in Group II analysis ranged from 0.06 to 0.53% (w/w) and coefficients of variation were better than 3% indicating that these models are suitable for the determination of diesel–biodiesel blends composed of methyl esters derived from different vegetable oils.

Keywords: Biodiesel; FTIR-ATR; FTNIR; PLS; Neural network

1. Introduction

In the last 20 years it became very import to find renewable fuel sources that could be used in Diesel motors [1]. In this sense, methyl esters, which are produced by a catalytic transesterification reaction of vegetable oils with short-chain alcohols, have been pointed out as an alternative fuel for these engines [1,2]. Indeed, methyl esters are interesting alternatives because they show a decrease in CO_2, SO_x, and unburned hydrocarbons emissions during the combustion process when compared with fossil fuels [2,3]. However, the methyl esters present higher viscosities, densities, flash points, and lower cold-filter plugging point as compared to conventional diesel [1]. Conventional diesel engines can run using blends of diesel and methyl esters up to 20%, as B20 for instance [4]. The use of pure methyl esters is possible if some modifications are introduced in the diesel engine.

The literature is very scarce in relation to the use of spectroscopic methods coupled to multivariate analysis as an analytical tool to evaluate biodiesel characteristics. Knothe has used near infrared (NIR) spectroscopy and partial least squares regression (PLS) [5] and ^{1}H NMR [6] to monitor the completion of the transesterification reaction and NIR and principal component analysis (PCA) as well as ^{1}H NMR to determine the blend level of biodiesel in conventional diesel fuel [4]. Recently, an analytical procedure was developed to monitor the ethanolysis of degummed soybean oil using Fourier-transform infrared spectroscopy (FTIR) and methods of multivariate analysis such as PCA and PLS [7].

The aim of this work is to develop calibration models based on FTNIR (transflectance-fiber optics) and FTIR-ATR combined to PLS and artificial neural network (ANN) analysis to determine the methyl ester contents in biodiesel blends (methyl ester + diesel). The methyl esters used were obtained by transesterification of soybean oil, soybean fried oil, and two kinds of oils extracted from palm trees largely commercialized in Brazil, one native (babassu, *Orbignia* sp.) and another not native known as dende (*Elaeis* sp.).

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The choice of the vegetable oils mentioned above is justified by the fact that the regulation of biodiesel production in Brazil [8] does not restrict the use of vegetable oils. Further, the Brazilian laws also provides taxes benefits for those that produce biodiesel using vegetable oils produced by familiar agriculture (babassu, for instance). In this sense it is important to have fast, precise, and accurate analytical methods that can detect methyl esters from different sources in the biodiesel blends in order to avoid fiscal frauds.

2. Experimental

2.1. Chemicals

Analytical grade reagents as methanol (MeOH), potassium hydroxide (KOH), sodium chloride (NaCl), and phosphoric acid (H_3PO_4) were obtained from commercial sources (VETEC, Rio de Janeiro, RJ, Brazil) and used without further purification. Refined soybean oil (Bunge, Gaspar, SC, Brazil) and refined babassu oil (Gecosa, São Luiz, MA, Brazil) were obtained from commercial sources and used as received. Refined dende oil was obtained from Embrapa Amazônia Occidental (Rio Urubu, AM, Brazil) and used without further purification. Fried soybean oil was obtained in a fast-food restaurant at the university campus and filtered before the alcoholysis reaction. The certified petroleum diesel (density 863.2 kg/m^3 at 20 °C, ASTM D1298 and D4052, and Flash Point 48, ASTM D93) was obtained from BR-Distribuidora (Brasília, DF, Brazil) and used as received.

2.2. Biodiesel synthesis

Potassium hydroxide was completely dissolved in MeOH under stirring in a glass batch reactor equipped with mechanic stirrer. Then the vegetable oil was added into the reactor and the reaction mixture was maintained under stirring at 5000 rpm for 2 h at room temperature (23 ± 1 °C). For the dende oil the mixture was stirred during 4 h due to its higher viscosity. Table 1 displays the reaction conditions for the transesterification reactions, considering the mass ratio of 100:33:1 (vegetable oil:MeOH:KOH). After 2 h (4 h for dende oil) for the reaction completion the mixture was allowed to stand and the two phases (one rich in glycerin and the other one in methyl ester) were separated. The excess of methanol in the methyl ester phase was removed by rotary evaporation at 70 °C. The methyl ester was then washed twice with a phosphoric acid water solution (5%, v/v) and with brine until a clear phase (methyl ester) was obtained. The methyl esters were analyzed by GC on a Shimadzu GC-17A chromatograph with flame ionization detector, equipped with a polydimethylsiloxane column (CBPI PRONA-M50-042) 50 m, 0.15 mm i.d. and film thickness of 0.2 μm, working between 60 and 110 °C, at a heating rate of 10 °C min^{-1}, standing at the final temperature for 5 min. The injector and detector temperatures were 250 °C. The methyl esters content in the reaction product was determined using dibutyl phthalate as internal standard. The reaction was repeated two or three times until purity of more than 99 mass% in methyl esters were detected by CG. It is worth mentioning that for the consecutive reactions a similar procedure was followed, using the reaction product instead of vegetable oil as reagent and the same amounts of methanol and KOH. The methyl esters were finally stored in amber flasks in a refrigerator at 6 °C.

Table 1
Masses of reagents and methyl esters (ME) and yields in the transesterification reactions

Vegetable oil source	Masses (g)				Yield (%)
	Vegetable oil	MeOH	KOH	ME	
Soybean	2742	902	29	2558	93
Dende	2444	791	25	1899	78
Babassu	666	253	8	607	91
Fried	2443	791	25	2212	91

2.3. Sample preparation

The biodiesel blends (mixtures of diesel and methyl esters) were prepared at room temperature using an analytical balance (Mettler, ±0.0001 g).

The samples were divided into two groups. The first group (Group I) corresponds to binary mixtures of diesel and one type of methyl ester. Group I is then composed of 96 blends with methyl ester contents of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 6.0, 8.0, 10, 12, 14, 16, 18, 20, 25, 30, 40, 50, 60, 70, 80, 90, and 100% (w/w); each sample has a final mass of 20 g. It is worth to mention that in this case it is impossible to avoid co-linearity. In the second group (Group II), 60 samples of biodiesel blends were prepared using a mixture of three different methyl esters and diesel. The relative amount of methyl esters and diesel varied in a random way to avoid co-linearity. The methyl esters and diesel contents for each sample are displayed in Table 2.

2.4. Instrumentation and software

The FTNIR and FTIR-ATR spectra were obtained on an Equinox 55 Fourier transform instrument from Bruker. The FTNIR spectra were recorded using an immersion transflectance accessory coupled to a Ge detector (not cooled) by an optical fiber. The optical path was 1 mm. The nominal spectral resolution was set to 8 cm^{-1} and each spectrum corresponds to the average of 16 scans, using air as reference. The FTIR-ATR spectra were recorded using a horizontal ATR cell, 7 cm long (10 reflections), from Pike Technologies, covering the 650–4000 cm^{-1} spectral range, using a DTGS detector. Each FTIR-ATR spectrum is the average of 32 scans, using air as reference, at 4 cm^{-1} nominal spectral resolution. All spectra were collected at 21 ± 1 °C.

The PLS calibration models were obtained by the Quant2 (PLS1) applicative included in the OPUS$^{\text{TM}}$ software. From the 96 samples of Group I, 48 samples were used in the PLS calibration (FTIR and FTNIR) and the other 48 samples were separated for validation. In the Group II, 30 samples (from 60) were used in the calibration (FTIR and FTNIR) and the other 30 were separated for validation.

Table 2
Diesel and methyl ester contents (%, w/w) for the 60 biodiesel blends samples of Group II

Sample name	Diesel content (%, w/w)	Methyl ester content (%, w/w)		
		Soybean	Dende	Babassu
MistM01	33.7681	29.0147	29.7486	7.4686
MistM02	13.7807	46.0256	17.4022	22.7916
MistM03	29.6258	6.4337	36.0705	27.87
MistM04	18.3701	32.1739	36.0853	13.3707
MistM05	3.9056	37.4703	36.3421	22.282
MistM06	17.1546	39.0944	30.9626	12.7884
MistM07	28.5638	20.0211	26.7138	24.7013
MistM08	11.4331	19.4445	47.3106	21.8118
MistM09	27.5219	26.7041	20.8044	24.9695
MistM10	24.0743	29.7165	21.9118	24.2973
MistM11	18.7566	41.3041	24.0747	15.8646
MistM12	18.3498	13.4501	11.5461	56.654
MistM13	25.1361	40.7101	19.7825	14.3713
MistM14	21.2178	17.9262	16.2997	44.5563
MistM15	28.1431	18.7107	21.5502	31.596
MistM16	6.6925	37.1161	17.1536	39.0379
MistM17	18.4581	33.0408	11.9968	36.5042
MistM18	35.2744	34.1005	13.4186	17.2065
MistM19	28.738	11.7392	4.0182	55.5046
MistM20	2.9736	33.9704	54.4549	8.601
MistM21	35.389	33.1569	15.0522	16.4018
MistM22	35.2794	23.0071	18.0485	23.6651
MistM23	36.9707	15.239	34.4054	13.3848
MistM24	32.6372	29.0216	27.3204	11.0208
MistM25	12.535	34.0409	21.1759	32.2482
MistM26	32.34	31.9715	21.9769	13.7115
MistM27	36.0987	21.2194	38.836	3.8458
MistM28	6.6505	33.8312	54.7924	4.7259
MistM29	27.643	24.6812	27.6111	20.0647
MistM30	30.494	32.4922	23.3285	13.6854
MistM31	17.7434	16.4952	28.0382	37.7232
MistM32	27.0962	25.4773	32.1656	15.2609
MistM33	41.4251	9.0289	37.5956	11.9504
MistM34	46.3224	38.3462	9.3662	5.9651
MistM35	58.0966	3.9025	26.8805	11.1204
MistM36	16.4998	22.1394	32.7948	28.566
MistM37	26.5452	20.3053	15.1822	37.9673
MistM38	13.5736	38.514	17.1731	30.7392
MistM39	10.5746	14.8851	64.5582	9.9821
MistM40	43.2368	1.6115	15.5591	39.5926
MistM41	79.3539	7.7415	5.7354	7.1691
MistM42	79.5907	6.4005	3.0848	10.9241
MistM43	79.7063	9.0905	8.3161	2.8871
MistM44	79.8144	7.7082	11.5351	0.9422
MistM45	88.9579	1.4749	5.3778	4.1894
MistM46	90.0313	2.2073	2.82	4.9414
MistM47	89.8531	1.0956	4.385	4.6663
MistM48	88.7638	0.5514	2.4304	8.2544
MistM49	91.774	2.4956	0.3185	5.412
MistM50	90.501	5.1022	1.6565	2.7403
MistM51	90.8388	2.3533	1.0954	5.7125
MistM52	91.8285	5.2089	2.5389	0.4237
MistM53	93.6866	2.3866	1.3186	2.6083
MistM54	94.5543	0.1524	2.1329	3.1604
MistM55	94.9924	2.3124	1.0046	1.6906
MistM56	95.9542	1.6787	2.237	0.1301
MistM57	97.5656	0.17	1.0944	1.1701
MistM58	98.351	0.1487	0.7414	0.7589
MistM59	97.8645	0.438	0.7536	0.9439
MistM60	97.7373	0.8328	0.5097	0.9201

The ANN calibration models were obtained using the Neurosolutions 4.0 from NeuroSolutions using a modular feedforward network (MFN) architecture. Details of this kind of neural network architecture were given elsewhere [9]. In the ANN analysis of Group I 58 samples were used in the training set and 38 were separated for validation. In the case of Group II 36 samples were used in the network training and 24 samples were separated for validation. It is worth to mention that we have also designed PLS calibration models using the same set of samples used in the ANN calibration. However, the results of validation, using the 30 samples of the ANN validation, were poorer than those obtained with the PLS model using 30 samples for calibration and 30 for validation.

3. Results and discussion

3.1. Characterization of the vegetable oils and methyl esters

The fatty acid compositions for the different vegetable oils used in this work, which are shown in Table 3, were determined in a previous study [3]. It is clear that the nature of the fatty acid present does not vary significantly, except for babassu oil that shows the highest concentration of short chain fatty acids. On the other hand, great variations in their proportions and unsaturation degrees are noted.

The chromatographic profiles obtained for the different biodiesel prepared in this work were similar to those obtained during the fatty acid composition determination. It is worth mentioning that the peak referent to methanol was not observed.

3.2. Biodiesel blends analysis

In order to build the PLS and ANN calibration models, FTNIR and FTIR-ATR spectra from all blends (Groups I and II) were recorded. Figs. 1 and 2 display the FTNIR and FTIR-ATR spectra of the diesel, and pure methyl esters.

The major differences in the FTNIR spectra of methyl esters (Fig. 1) are observed at 4670–4700 cm^{-1} (aliphatic CH stretching + C=O stretching combination modes), 5550–6100 cm^{-1} (first overtone of CH stretchings), 6900–7400 cm^{-1} (CH bending + CH stretching combination modes), and 8000–9000 cm^{-1} (second overtone of CH stretchings). In the infrared (Fig. 2), the

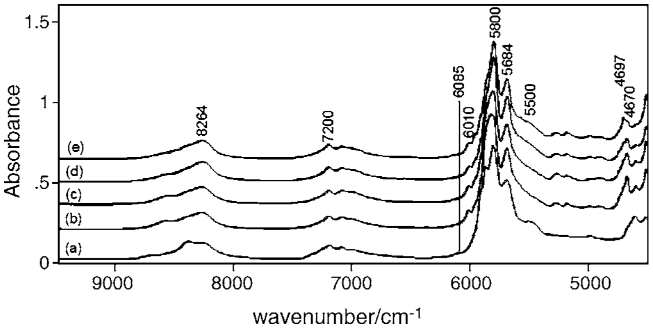

Fig. 1. FTNIR spectra of diesel (a) and pure methyl esters of soybean (b), fried (c), dende (d), and babassu (e) oils.

Table 3
Fatty acid composition of the vegetable oils used in the transesterification reactions

Vegetable oil	Fatty acid (%, w/w)[a]							Unsaturated fatty acid (%)
	C12	C14	C16	C18	C18:1(n9)	C18:2(n9,12)	Others	
Babassu	48	16	10	2	14	5	5	19
Dende	–	–	35	7	44	14	–	58
Soybean	–	–	14	4	24	52	6	76

[a] Ref. [3].

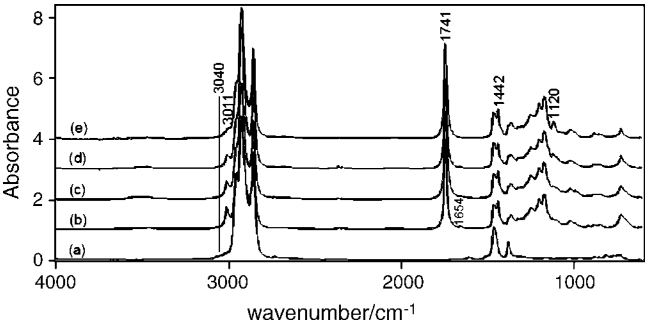

Fig. 2. FTIR-ATR spectra of diesel (a) and pure methyl esters of soybean (b), fried (c), dende (d), and babassu (e) oils.

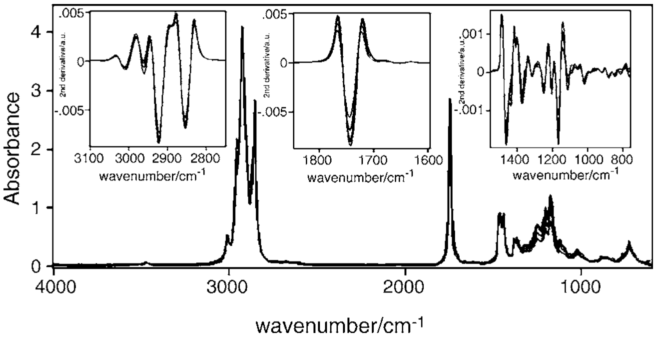

Fig. 3. FTIR-ATR spectra from five mixtures of the diesel and methyl esters (Group II) used in the calibration. The insets are the second derivative spectra (25 points smoothed) in the spectral regions chosen for PLS modeling.

major changes are observed mainly at ca. 3011 and 1654 cm^{-1}. These absorptions are assigned to ν(CH) and ν(C=C) stretching modes characteristic of olefins. Note that the FTIR spectrum of the soybean oil methyl ester presents the higher intensities at these spectral regions. Indeed the data displayed in Table 3 show that the soybean oil presents the largest content of unsaturated carbon atoms. Remarkable differences are also observed in the finger print region (1100–1500 cm^{-1}).

The spectral regions and pre-processing conditions selected to obtain the PLS calibration model for Group I are displayed in Table 4. The corresponding PLS parameters obtained with the 48 samples used in the validation are displayed in Table 5. The spectral regions that give the best PLS results were selected as indicated by the spectral distribution of the relative standard deviation in concentration ($s_c/c\%$) which is equivalent to the relative standard deviation in the absorbance, $\sigma_A/A\%$ [10,11]. In this method we calculate the $\sigma_A/A\%$ (see ref. [11] and page 131 of ref. [12] for its definition) at each wavenumber and choose the spectral regions that present the lowest values of $\sigma_A/A\%$.

In the following we have also designed PLS calibration models based on FTNIR and FTIR-ATR data from biodiesel blends of Group II. In this case, all blends have different contents of each of the four components: diesel and soybean, babassu, and dende methyl esters. Fig. 3 show the FTIR-ATR spectra of five samples (from 30) used to build the calibration models. The inset of Fig. 3 shows the spectral regions that presented the largest variations on the pre-processed spectra. The corresponding FTNIR spectra are presented in Fig. 1S (Supplementary material).

The method used to select the spectral region was similar to that used in the previous case (Group I). Using the $\sigma_A/A\%$ method we have obtained three spectral regions in the FTIR, 785–1841, 2769–3099, and 3261–3714 cm^{-1}. These regions were selected to determine the four components in the mixtures. After that we have also obtained the spectral distribution of the standard deviation in the absorbance, $\sigma_A^*\%$, for the 30 spectra corresponding to the 30 samples used in the validation. From these results we have selected the spectral regions that present the largest variation in the $\sigma_A^*\%$. As a consequence, the spectral region 3261–3714 cm^{-1} was deselected. Indeed we have observed that the RMSEP values were not dependent on this spectral region. The spectral regions used in the PLS models

Table 4
Spectral regions and pre-processing procedures used to design PLS calibration models

Method	Spectral region (cm^{-1})			Spectral pre-processing	
	Group I	Group II		Group I	Group II
		Diesel	Methyl ester		
FTIR-ATR	925–1841 and 2974–3699	1055–1543 and 2763–3105	785–1841 and 2769–3099	1st der.[a]	2nd der.[b]
FTNIR	7927–8930, 6685–7479, and 4463–6137	4528–8953	4528–8953	1st der.[b]	1st der.[b] + vector normalization

[a] Smoothed using a 9 points window.
[b] Smoothed using a 25 points window.

Table 5
PLS validation results for the analysis of biodiesel blends of Groups I and II

Group	Component	Method									
		FTIR-ATR					FTNIR				
		R^2	RMSEP	CV (%)	BIAS	PC	R^2	RMSEP	CV (%)	BIAS	PC
I	Methyl ester	99.99	0.202	0.80	0.004	10	100	0.061	0.24	−0.017	10
II	Diesel	100	0.200	0.41	−0.038	9	100	0.194	0.40	−0.033	6
	Soybean	99.94	0.273	1.20	−0.026	9	99.94	0.325	2.00	0.034	5
	Babassu	99.96	0.257	0.95	−0.210	10	99.94	0.333	2.04	−0.221	6
	Dende	99.92	0.362	1.33	0.028	9	99.95	0.357	1.88	0.016	10

R^2, determination coefficient; RMSEP, root mean square error of prediction; CV, coefficient of variation; BIAS, linear coefficient of the predicted vs. real values curve; PC, number of principal components.

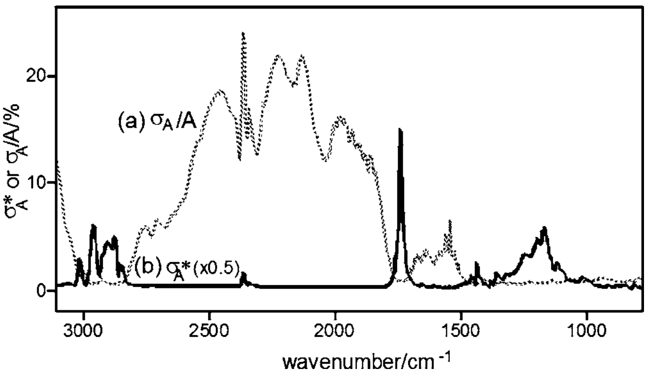

Fig. 4. FTIR-ATR spectral distribution of the relative standard deviation in the absorbance (a, · · ·) and standard deviation in absorbance (b, —).

for Group II and the respective PLS results are displayed in Tables 4 and 5, respectively. The spectral distributions of $\sigma_A/A\%$ and $\sigma^*_A\%$ for the FTIR-ATR and FTNIR data are displayed in Figs. 4 and 5, respectively.

In the ANN analysis it is very important to work with a reduced number of input neurons (intensities corresponding to the selected wavenumbers) to avoid memorizing effects. In this sense it was necessary to reduce the number of data in each spectrum. In order to reduce the number of input data we have used the same spectral pre-processing adopted in the PLS analysis. After that, the spectral distribution of the standard deviation of the pre-processed spectra was evaluated and the wavenumber selected were those that were above a established threshold. As an example, Fig. 6 illustrates the case of the FTIR-ATR spectra of the 60 samples of Group II. The wavenumber indicated in the spectrum are those whose intensities (first derivative) were used as input data in the ANN analysis. It is worth to mention that not all displayed wavenumbers in the FTIR were used to model diesel and methyl ester contents. Some wavenumbers were selected only for diesel, for instance. Table 1S of the Supplementary material shows the wavenumbers selected in each case (TIR-ATR and FTNIR). Note that all selected wavenumbers fall in the spectral range selected in the PLS analysis. The ANN validation results for Groups I and II are displayed in Table 5.

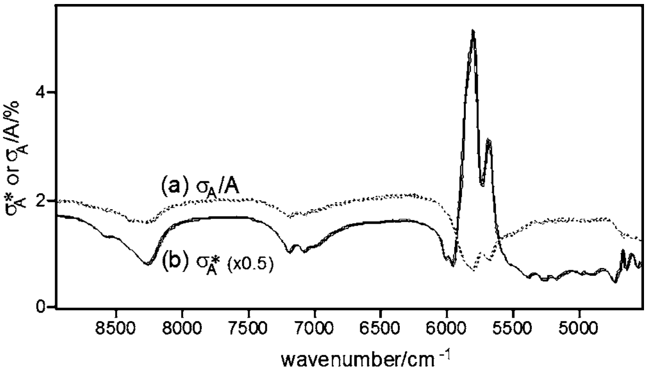

Fig. 5. FTNIR spectral distribution of the relative standard deviation in the absorbance (a, · · ·) and standard deviation in absorbance (b, —).

According to the results for Group I presented in Table 5, the PLS model based on near infrared data is more accurate than the one based on FTIR, since the F-test applied to the RMSEP values returns a value that is much larger than that expected for 47 degrees of freedom (48 samples) at 95% of confidence level. However, the coefficient of variation (CV) values for both

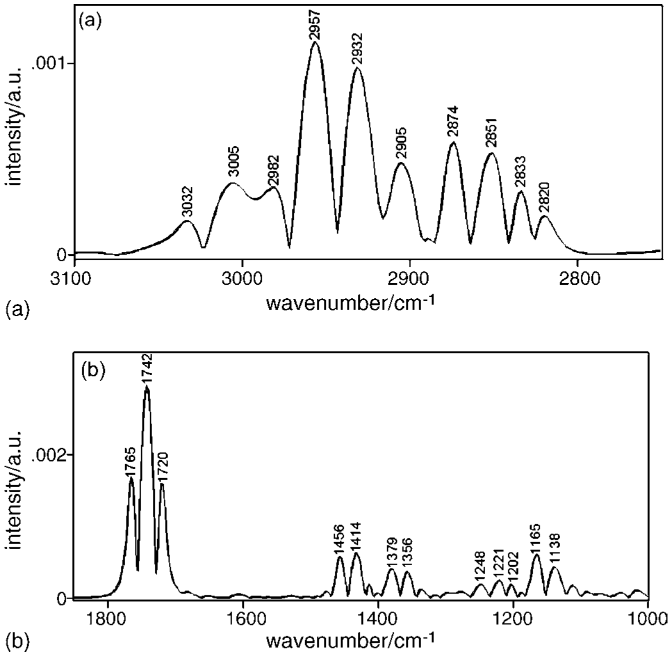

Fig. 6. Standard deviation spectra of the 60 FTIR-ATR first derivative spectra corresponding to the 60 samples of Group II (see text for details).

Table 6
ANN validation results for the analysis of biodiesel blends of Groups I and II

Group	Component	Method							
		FTIR-ATR				FTNIR			
		R^2	RMSEP	CV (%)	BIAS	R^2	RMSEP	CV (%)	BIAS
I	Methyl ester	100	0.213	0.757	−0.062	100	0.212	0.753	0.035
II	Diesel	100	0.188	0.433	−0.079	100	0.14	0.32	0.097
	Soybean	99.95	0.324	1.679	0.027	99.95	0.341	1.797	−0.108
	Babassu	99.94	0.373	2.313	0.237	99.96	0.325	2.017	0.049
	Dende	99.88	0.600	2.833	0.205	99.91	0.544	2.541	0.357

methods are equal to or better than 2% which means that both models could be used to determine the methyl ester content on biodiesel blends. The ANN models do not present the same differences in accuracy, since the RMSEP values are quite similar, 0.213 and 0.212, for FTIR and FTNIR, respectively. However, comparing both methods, PLS and ANN, the FTNIR/PLS model for single component (methyl ester) determination is statistically more accurate than the corresponding ANN model.

In the case of Group II (a four component system) the results in Table 5 show that the RMSEP values obtained with the PLS models (FTIR-ATR and NIR) are equivalent for diesel and dende-methyl ester while for the other components the PLS/FTIR-ATR models present better accuracies. In the ANN analysis of Group II samples, the results displayed in Table 6 show that both FTIR-ATR and FTNIR models present almost the same accuracy, i.e., RMSEP values very close to each other.

It is interesting now to compare the performance of the PLS and ANN models in the analysis of Group II samples. The results presented in Tables 5 and 6 show that the PLS/FTIR-ATR models are better than the respective ANN models, while the FTNIR models are in general quite similar.

As mentioned above in the case of Group I, the results in Table 5 show that the PLS calibration model based on FTNIR data is more accurate (smaller RMSEP values) than the model based on FTIR. We believe that the better performance of the PLS/FTNIR model in predicting only a single component, as the methyl ester content in Group I, is explained by the better signal-to-noise ratio presented by the FTNIR method in relation to the FTIR method.

In order to support this hypothesis we have calculated the relative standard deviation in the absorbance ($\sigma_{\mathrm{A}}/A\%$) in the spectral regions covered by the instrument for both techniques, using a set of 20 spectra of only one sample. These results are displayed in Figs. 4a and 5a, for FTNIR and FTIR, respectively. Note that the spectral regions we have selected are those that present the smallest values of $\sigma_{\mathrm{A}}/A\%$. This means that at these regions the relative errors in the determination of absorbance are smaller, since at these regions the signal-to-noise ratios are the higher. As the results show, at the instrumental conditions used, the FTNIR presents the lower values for the relative standard deviation in absorbance as compared to FTIR, and consequently should give better results in the PLS analysis.

The above considerations can well explain the better performance of the PLS/FTNIR model in the Group I analysis but fails to explain the results obtained for Group II. To explain the results of Group II we need to consider that in this case we are dealing with a multi-component analysis. So, we call the attention to the results of Figs. 4b and 5b. These spectra correspond to the spectral distribution of the standard deviation in the absorbance considering a group of 30 samples used in the validation, $\sigma^*_{\mathrm{A}}\%$. Note that the largest variations in $\sigma^*_{\mathrm{A}}\%$ are observed for the FTIR results (Fig. 5b). The $\sigma^*_{\mathrm{A}}\%$ values at the spectral regions considered for PLS analysis are at least three times larger in the FTIR than those observed in the FTNIR results (Fig. 4b). This means that the FTIR spectra are more sensitive to the variation in the composition of the biodiesel blends. Indeed, as we have observed before, the FTIR spectra of Fig. 2 are well correlated to the % of unsaturated fatty acid content of the vegetable oils. These results are in accordance to the finds of Cooper et al. [13]. They have designed FTIR and FTNIR PLS calibration models for the determination of BTEX, which involves the evaluation of the contents of benzene, toluene, ethyl benzene and *m*-, *o*-, and *p*-xylene in gasoline. They have observed that in this kind of multi-component analysis, the FTIR/PLS models present better results than FTNIR/PLS models.

In order to evaluate the repeatability of the calibration models we have performed the following experiments: (i) Group I—five spectra (FTNIR or FTIR) from four biodiesel blends were recorded along 5 days. Each spectrum was evaluated with the corresponding PLS (or ANN) model providing a recovered value in methyl ester content (%, w/w). The repeatability, or precision of the method was evaluated from the mean standard deviation of 100 measurements (25 spectra of 4 samples) and are displayed in Table 7. (ii) Group II—Four samples were used and the four components were evaluated along 5 days. In this case Table 7 displays the standard deviation obtained for each component, i.e., they represent the mean standard deviation of 100 (5 measurements per sample along 5 days).

The repeatability results for Group I and Group II samples are in accordance to the discussion above, relative to the signal-to-noise ratio, which are better for FTNIR than for FTIR. This means that the PLS/FTNIR model is more precise in the determination of the methyl ester content of binary mixtures as well as of quaternary mixtures, involving more than one kind of methyl ester. This is not valid for the ANN models, since they present the same repeatability. This result is in accordance to the discussion above regarding to the RMSEP values that are also equivalent for the FTIR-ATR and FTNIR methods.

Table 7
Repeatabilities of the PLS and ANN methods in the determination of methyl ester content in biodiesel blends

	PLS		ANN	
	FTIR-ATR	FTNIR	FTIR-ATR	FTNIR
Group I				
Sample 1	0.10	0.08	0.14	0.15
Sample 2	0.32	0.05	0.18	0.16
Sample 3	0.12	0.09	0.15	0.19
Sample 4	0.18	0.12	0.15	0.10
Mean	0.16	0.08	0.15	0.15
Group II				
Diesel	0.13	0.09	0.33	0.17
Soybean	0.20	0.10	0.14	0.36
Babassu	0.09	0.06	0.23	0.10
Dende	0.30	0.22	0.53	0.47

4. Conclusions

The results presented in this work have shown that the FTIR-ATR and FTNIR spectroscopies combined to PLS or ANN methods can be used to determine the content (%, w/w) of methyl esters in biodiesel blends. In the single component analysis, that is, in the determination of the methyl ester content, independently of the vegetable oil source (Group I), the FTNIR/PLS method has proved to be more precise and accurate (±0.02 and ±0.06%, w/w, respectively) than the FTIR-ATR/PLS method. On the other hand the FTIR and FTNIR ANN models for Group I present similar precisions and accuracies, close to 0.2% (w/w). These methods are not suitable for the determination of methyl ester contents considering different sources of vegetable oils, i.e., it cannot be used to determine mixtures of methyl esters. The calibration models based on Group II samples have shown to be more appropriate to this goal. In this case, both PLS methods (FTIR-ATR and FTNIR) have similar accuracies, ranging from 0.2 to 0.4% while the precision of the PLS FTNIR models are better, as in the case of Group I. The ANN models for Group II present almost equivalent precisions and accuracies. In general these are not better than the respective PLS models.

It is worth mentioning that the four calibration models for Group II (PLS and ANN) have coefficients of variation smaller than 5% (see Tables 5 and 6) for R^2 values equal or very close to 100. Besides suitable precision and accuracy, these methods are faster than the chromatographic ones and sample integrity is preserved. Therefore, they could be used to determine different methyl ester contents in the biodiesel being commercialized in countries like Brazil, where different vegetable oils can be used for biodiesel blends formulation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2006.01.002.

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