Quantitative Determination of Epoxidized Soybean Oil Using Near-Infrared Spectroscopy and Multivariate Calibration

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The quality of epoxidized soybean oil (ESO), industrially used as a plasticizer and heat stabilizer for PVC films, is given by the degree of epoxidation (EI), the number of double bonds expressed as the iodine index (II), and the water percentage in the final product. In this work, near-infrared (NIR) spectra recorded off line at the chemical industry during the epoxidation process, combined with the multivariate regression method partial least squares (PLS), was used for the quantification of EI, II, and water percentage in the ESO. The water levels were determined by the Karl Fischer titration. The content of iodine was determined by iodometry. The epoxide index was obtained by the hydrogen bromide reaction with the epoxide ring. On average, 50 samples were used to model each analyte and 10 were used for external validation. The results, expressed in terms of the statistical parameters RPD (ratio of standard deviation of experimental concentrations to the standard deviation of the residuals) and RER (ratio error range), were excellent for the EI (26.02 and 80.70, respectively). For the water % and II, the obtained results were fairly good. Good correlations between predicted and real concentrations were attained (0.984, 0.966 and 0.974 for water %, II, and EI, respectively). It is shown in this work that the use of NIRS combined with chemometric methods are of great importance, especially for industrial purposes.

Index Headings: **Soybean oil; Near-infrared spectroscopy; NIRS; Poly(vinyl chloride); PVC; Chemometrics; Partial least squares; PLS.**

INTRODUCTION

Soybean oil is a triglyceride that typically contains 14% stearic, 23% oleic, 55% linoleic, and 8% linolenic acid. Three of these are unsaturated acids: oleic (18:1), linoleic (18:2), and linolenic (18:3) (Scheme I).[1]

Chemical modification of commercially available soybean oil, such as epoxidation, can enhance its properties (reactivity) for certain industrial applications. In a fully epoxidized soybean oil, the linolenic acid with three double bonds (positions 9, 12, and 15), is more reactive than linoleic, which contains two double bonds per molecule.

Epoxidation of fatty acids is a reaction of a carbon–carbon double bond with an active oxygen, usually from a peroxide or a peracid, which results in the addition of an oxygen atom, converting the original –C=C– bond into a three-membered epoxide (oxirane) ring.[2] The epoxidized soybean oil (ESO) is extensively used in the plastic industry as a plasticizer to increase flexibility in poly(vinyl chloride) (PVC) products and as a stabilizer to minimize their decomposition. Materials such as PVC and polystyrene frequently contain epoxidized oil at levels ranging from 0.1 to 27%.[3]

It is known that PVC undergoes decomposition with increasing temperature (dehydrochlorination). During the thermal decomposition, hydrogen chloride is eliminated from PVC, conjugated double bonds are formed, and the process is followed by a change in the polymer's coloration, which goes from yellow to orange, red, brown, and finally black (Scheme IIa).[4]

The epoxide ring from ESO reacts with hydrogen chloride generated by polymer degradation and restores the labile chlorine atoms back into the polymer's chains. (Scheme IIb).[4] This prevents PVC from further dehydrochlorination and preserves its color.

In order to follow the soybean oil epoxidation process, it is necessary to quantify three analytes related to the product's quality and process efficiency. The epoxide index (EI) is directly related to the stabilizer feature of the product: the higher the epoxide index, the more efficient will be the additive as a thermal stabilizer. The iodine index (II) is an indicator of the amount of unsaturation present in the epoxidized soybean oil, which is unknown *a priori.* The unsaturated bonds are halogenated and the reagent excess is quantified by iodometry. The water percentage resulting from washing of the final product in the industrial process is another important analyte. Its concentration must be minimal, since water causes degradation of the epoxide group (Scheme III).[2]

Near-infrared spectroscopy (NIRS) has been successfully used during the last decade in a wide range of analyses for quantification purposes in industry.[5–10] Spectral features in this region are due to molecular absorptions of overtones and combinations of fundamental vibrational bands in the mid-IR region. Band assignments are not easy to interpret due to the fact that in this region one single band results, in general, from a combination of severely overlapped vibrations. The combination bands have been far more commonly misassigned than the overtones.[11] The low molar absorptivity (weak absorption bands) and broad band absorbance peaks are other shortcomings of the method. Although this wavelength region is only of limited value for detailed qualitative structure interpretation (as opposed to mid-infrared), it has been extensively used recently for the quantitative analyses of compounds containing OH–, NH–, and CH– functionalities.[12] Several qualities of NIR spectroscopy have made it an appealing alternative to many traditional chemical methods since it needs little or no sample preparation,

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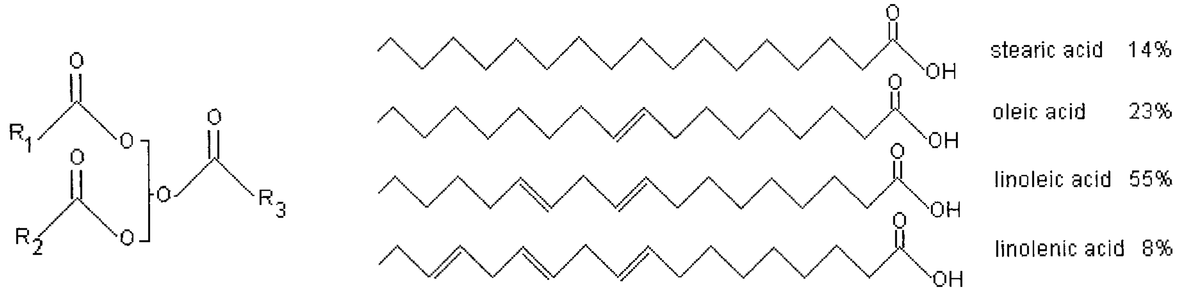


SCHEME I. Soybean oil structure and its substituted fatty acids.

has low cost, is not time consuming, and allows multiple analyses from one spectrum.[13] On the other hand, NIR spectroscopy wouldn't have become so popular without the availability of powerful computers and chemometric software for data analysis.

The spectral data used in this work were recorded off line at the chemical industry during the soybean epoxidation process. Calibration models were obtained for the three analytes (epoxide index, EI, iodine index, II, and water), and partial least squares (PLS) was the multivariate regression method[14–16] selected for the modeling.

MATERIALS AND METHODS

Karl Fischer titration, using a Methrom Karl Fischer Automat E547 and a Multi Dosimat E415, was the method used for measurement of low levels of water in the oils. In this method, water is converted stoichiometrically by the addition of iodine in the presence of sulfur dioxide, methanol, and a suitable base (pyridine) in excess. Sulfur dioxide is oxidized by iodine in the presence of water. In methanol solution, Karl Fischer reagent acts in a two-step reaction where, for each incoming water molecule, one iodine molecule is consumed (Scheme IV). The results are expressed in terms of water percentage, and for ESO the acceptable levels are below 0.3%.[17]

The content of iodine was determined by halogenation (with 0.2 M bromine solution) of the ESO double bonds. Mercury(II) acetate was added as a catalyst to reduce the reaction time (Scheme V), and the excess of bromine solution was determined by iodometry. The result is given in terms of grams of iodine per 100 g of the product (ESO), and it is a measure of the quantity of unconverted –C=C– double bonds. The maximum level acceptable for industrial purposes is 4.0 g iodine/100 g sample.[2]

There is no practical way to separate the epoxidized esters in ESO from esters with double bonds or from other fatty by-products, particularly because epoxidized groups, double bonds, and other (by-product) groups may be present in the same fatty triglyceride molecule. Hence, the efforts to improve the quality of ESOs and other fatty epoxide products have been focused on processes that optimize the conversion of the –C=C– double bonds into epoxide groups while minimizing the formation of by-products.[2] The determination of epoxide index in this work is based on the hydrogen bromide synthesis, by reaction of tetraethylammonium bromide with 0.1 M perchloric acid. Hydrogen bromide opens the epoxide ring by bromination and a hydroxyl group is formed (Scheme VI). The end point of the reaction is signaled by the color change of the indicator used, caused by the presence of free hydrogen bromide (produced by the excess of perchloric acid) after all epoxide groups have been consumed. This method measures the content of epoxide groups and thus the conversion to the desired product. The percentage of epoxide must be higher than 6.3%.[2]

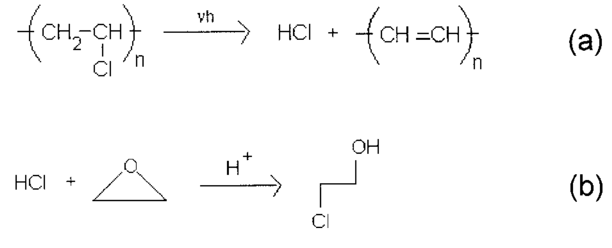
Near-infrared absorbance spectra were recorded from 9500 to 4500 cm^{-1} with a 2 cm^{-1} increment, using a Bomem MB160 FTIR spectrophotometer. The number of samples differs for each analyte. Figure 1 shows a generic recorded spectrum.

Calibration models were constructed using the PLS method.[14–16] In this method, the regression model is built relating the **X** block of independent variables, given by the spectra, to the **y** vector given by the analyte concentrations. PLS is a projection method, which uses the projection of the matrix **X** onto a lower dimensional orthogonal basis, or at least, a linear independent set, i.e., $\mathbf{XW} = \mathbf{T}$, where **W** and **T** are the projection and score matrices, respectively. **W** is determined such that **T** has the property of maximum covariance with **y**.

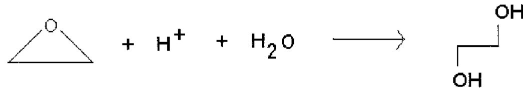
The PLS models were validated through the leave-one-out cross-validation procedure and also by using external data sets in order to verify the ability of the models in future predictions. For internal validation, the goodness of the model can be assessed by the standard error of cross-validation (SECV) parameter defined in Eq. 1.

$$\mathrm{SECV} = \left[\frac{\sum (y_{i,\mathrm{exp}} - y_{i,\mathrm{pred}})^2}{n}\right]^{1/2} = \left[\frac{\mathrm{PRESS}}{n}\right]^{1/2} \qquad (1)$$

where n is the number of samples used in the calibration



SCHEME II. (**a**) PVC degradation caused by sunlight, eliminating HCl; (**b**) reaction of oxirane ring with HCl inhibiting the degradation process.



SCHEME III. Degradation of epoxide group by water.

$$H_2O + I_2 + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N.HI + C_5H_5N.SO_3,$$

$$C_5H_5N.SO_3 + R - OH \rightarrow C_5H_5N.HSO_4R$$

SCHEME IV. Reactions involved in the water percentage determination.

set, $y_{i,\mathrm{exp}}$ is the known concentration for the ith sample, and $y_{i,\mathrm{pred}}$ is the predicted concentration by the model built without sample i.

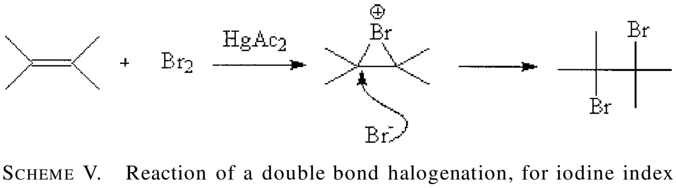
External data sets were also used to evaluate the performance of the models for prediction. The ratio of standard deviation of experimental concentrations to the standard deviation of the residuals, RPD, and the ratio error range, RER,[18] given by Eqs. 2 and 3, respectively, were used for this purpose. Both of these terms compare the range of variation of the analyte of interest in the external validation set to the standard error of prediction.

$$\mathrm{RPD} = \frac{\mathrm{std}(c_{\mathrm{exp}})}{\mathrm{std}(c_{\mathrm{exp}} - c_{\mathrm{pred}})} \tag{2}$$

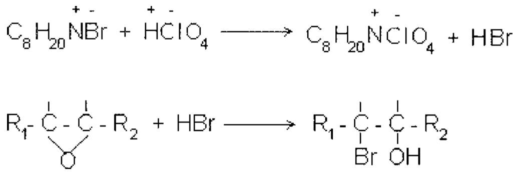
$$\mathrm{RER} = \frac{\mathrm{range}(c_{\mathrm{exp}})}{\mathrm{std}(c_{\mathrm{exp}} - c_{\mathrm{pred}})} \tag{3}$$

Here, std is the standard deviation, c_{exp} are the experimental concentrations of samples from the external validation set, c_{pred} are the corresponding values estimated by the calibration model, and range(c_{exp}) represents the range of experimental concentrations.

In order to reduce the size of the data set, a boxcar averaging[19] was applied to the raw data. In this method, one group of wavenumbers is replaced by its median and the respective intensity is represented by the average intensity of the group. The window size for the boxcar averaging was chosen to be 15 cm^{-1}. The PLS method was applied to this new data set, using mean centering as a preprocessing method. Variable selection was performed in two different ways. In the first (Selection A), the loadings and regression vector plots were simultaneously analyzed. The loadings express the relationship between the spectral variables and the principal component axes, which are used to build the PLS model. The regression vector contains the coefficients of the model, indicating which variables contribute to the prediction. Those variables with near zero values in both regression vector and loadings can be excluded since they will not contribute significantly to the modeling and prediction. In the second method (Selection B), the variables were selected by subtracting the spectrum of the sample with the highest analyte concentration from the spectrum of the sample with the lowest concentration of the same analyte. Only the spectral regions where the differences could be observed were included in the PLS model. For the method with smaller standard error of cross-validation (Selection A/B), the correlogram was applied. The correlogram is a plot of the wavenumber variables against their correlation coefficients with respect to the analyte concentration.[20] The selected variables correspond to those wavenumbers that show a correlation coefficient higher than a given cutoff value. Pirouette (Infometrix, Woodinville, WA) and PLS_Toobox 2.0 (Eigenvector Technologies, West Richland, WA) for MATLAB™ (The MathWorks, Nattick, MA) were the software used to carry out the data analysis.



SCHEME V. Reaction of a double bond halogenation, for iodine index determination.



SCHEME VI. Reactions involved in the epoxide index determination.

RESULTS AND DISCUSSION

Water. A set of 61 samples was used for this analyte, 51 of them in the calibration set and the other 10 in the external validation set. After boxcar averaging, the raw data (2400 variables) were reduced to 160 variables. The water percentage in this data set (in the range 0.02–0.45%) is characterized by samples distributed in three groups. The main group has a large number of samples with low analyte concentration (0.02–0.1%). The other group consists of 4 samples with water % in the range of 0.1–0.2%, and the last one has 2 samples with water % above 0.4%, which is higher than the acceptable level (0.3%). These last samples represent situations that are not very common, but could be reached in industry, and consequently, they cannot be considered outliers. The results for the PLS model using 160 variables are shown in Table I.

The variable selection followed the procedure described previously in the methodology. The loading and regression vectors for Selection A are shown in Figs. 2a and 2b. For Selection B, which uses the spectral difference, those variables where the differences can be observed were selected (see Fig. 2c). The model obtained from variable Selection B had the highest correlation coefficient (0.990) and was chosen for further analysis.

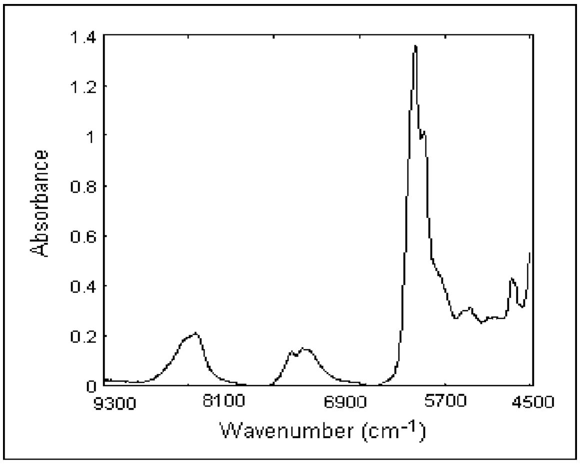


FIG. 1. Generic recorded spectrum of epoxidized soy bean oil (ESO).

TABLE I. PLS results for water.

Method	# Variables	Latent var.	SECV	PRESS	*R*
Boxcar averaging	160	4	0.013	0.008	0.986
Selection A	65	3	0.012	0.008	0.987
Selection B	22	3	0.012	0.009	0.990
Correlogram[a]	**3**	**2**	**0.016**	**0.014**	**0.984**
External val.[b]	3	2	0.018[c]	0.003	

[a] Variable selection by the correlogram applied to Selection B for cutoff = 0.95.

[b] External validation using PLS model with variables selected from the correlogram and 2 LVs.

[c] SEP (standard error of prediction).

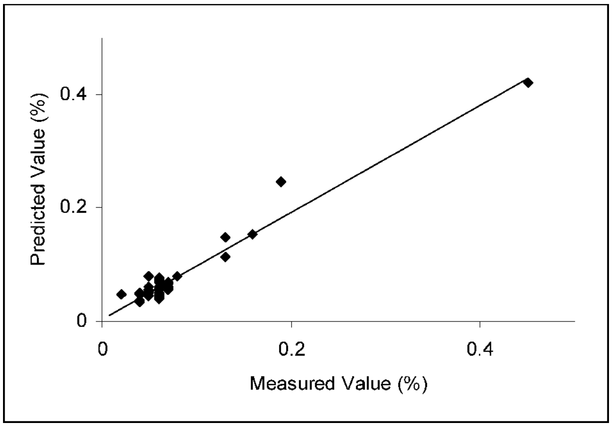
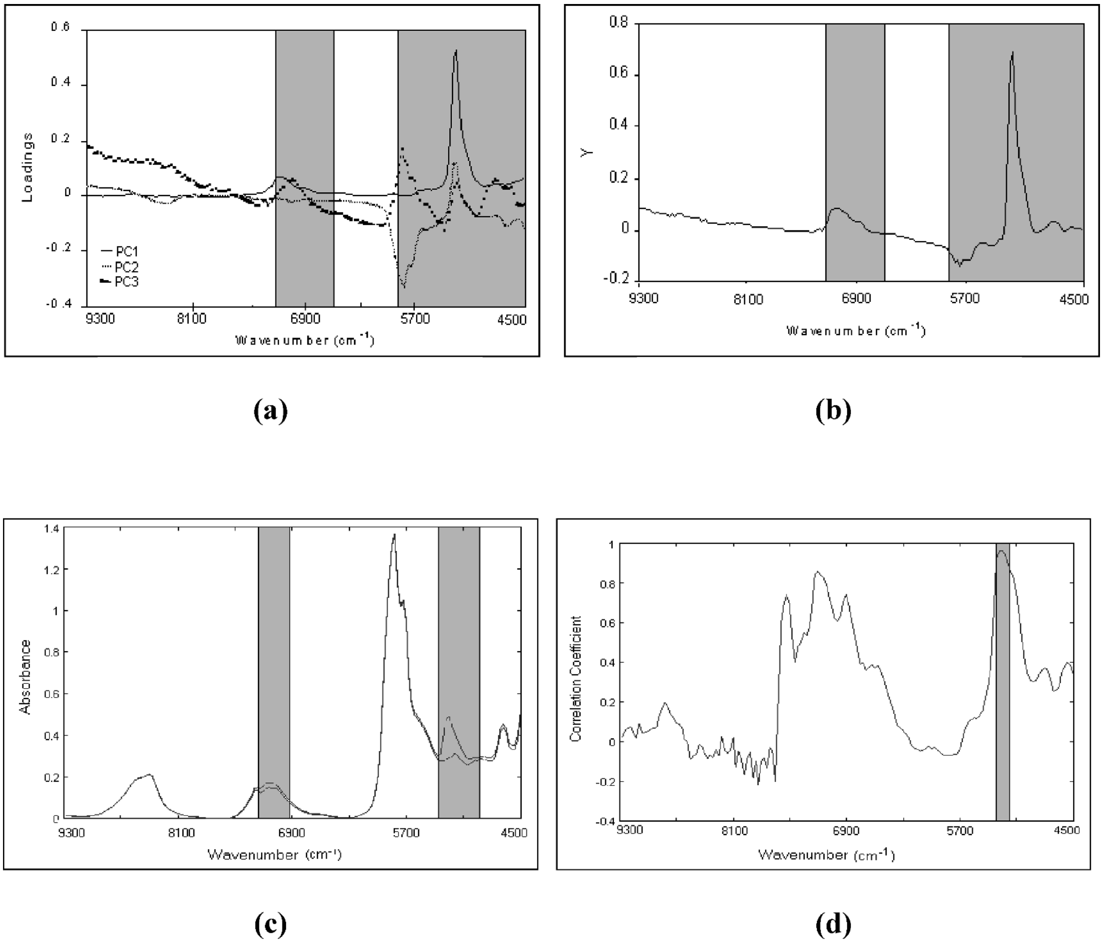


FIG. 3. Measured water % vs. the values predicted by leave-one-out cross-validation for a PLS model with 2 LVs.

The correlogram was then applied to the data from Selection B and only those variables with correlation coefficients greater than 0.95 (cutoff value = 0.95) were kept (see correlogram in Fig. 2d). The number of variables, latent variables, (LVs), and statistical parameters of the models are shown in Table I.

It can be seen from Table I how it was possible to construct a parsimonious calibration model with almost the same residual level, using only 3 variables and 2 latent variables, instead of the 160 used initially. The plot of measured vs. predicted water % by cross-validation using 2 LVs can be seen in Fig. 3. Lastly, 10 new samples were used to test the model. The water percentage of these samples was predicted under the conditions previously optimized, and the results obtained are also in Table I. In Table II, the experimental water %, the respective predicted values, and the statistical parameters showing the predictive ability of the model are shown. The standard deviation of the residuals, 0.019, is lower than the standard deviation of the experimental values, 0.056, giving an RPD (see Eq. 2) of 2.94, which seems not so good since the instrument is predicting the experimental values



(a) (b)

(c) (d)

FIG. 2. Percentage of water in ESO. (**a**) Loading vectors. (**b**) Regression vector for a PLS model with 3 LVs. (**c**) Spectra showing two samples, one with high and the other with low water percentage. (**d**) Correlogram for the full spectra. The selected wavenumbers are illuminated.

TABLE II. Experimental, estimated, and residual values for water % in the external validation set.

Sample	Experimental values	Predicted values	Residuals
9	0.06	0.048	−0.012
15	0.07	0.059	−0.01
19	0.05	0.053	0.003
27	0.08	0.079	−0.001
40	0.13	0.147	0.017
43	0.16	0.157	−0.003
44	0.19	0.238	0.048
50	0.13	0.114	0.017
56	0.06	0.051	0.008
60	0.008	−0.002	0.008
Mean	0.094	0.094	0.0006
Std.	0.056	0.070	0.019
Range	0.182		
RPD[a] 2.94		RER[b] 9.49	

[a] RPD = std(exp.)/std(residuals).

[b] RER = range(exp.)/std(residuals).

TABLE III. Results of PLS models for iodine.

Method	# Variables	Latent var.	SECV	PRESS	*R*
Boxcar averaging	160	5	0.272	4.454	0.955
Selection A	**75**	**4**	**0.270**	**4.368**	**0.966**
Selection B	35	5	0.363	7.906	0.929
Correlogram[a]	25	4	0.462	12.821	0.922
External val.[b]	75	4	0.232[c]	0.7001	

[a] Variable selection by the correlogram applied to Selection A for a cut-off = 0.35.

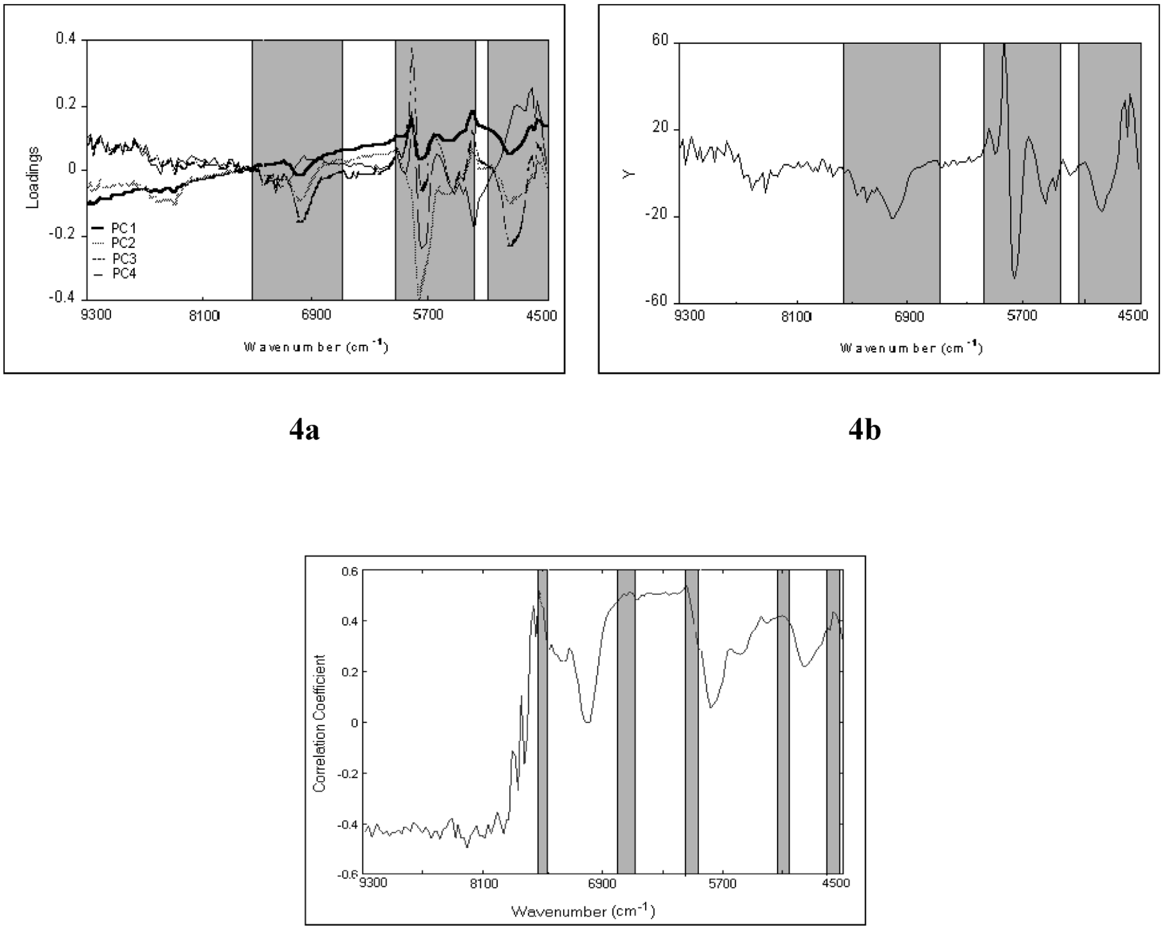
[b] External validation using the PLS model from Selection A.

[c] SEP (standard error of prediction).

slightly better than the standard deviation of the experimental data. On the other hand, the range of experimental concentrations is high and the RER (see Eq. 3) of 9.49 looks satisfactory.

The three selected wavenumbers are in the region 5090–5280 cm^{-1}, which corresponds to the water absorption band. Another spectral region (7143–6667 cm^{-1}), although assigned to water absorption,[21] and selected in Selection B, was not found to have much relevance when constructing the final calibration model.

Iodine. For the iodine analysis, 73 samples were used to build the regression model (60 in the calibration set and 13 for external validation). As before, 160 variables were selected when applying the boxcar averaging. The iodine index (II) for these samples is distributed between 2.2 and 6.3 g iodine/100 g sample, with a higher number of samples with analyte concentration in the range 2.5–3.5. In this case, there are also some samples with II



4a

4b

4c

FIG. 4. Iodine index in ESO (II). (**a**) Loading vectors. (**b**) Regression vector for a PLS model with 4 LVs. (**c**) Correlogram for the full spectrum. The selected wavenumbers are illuminated.

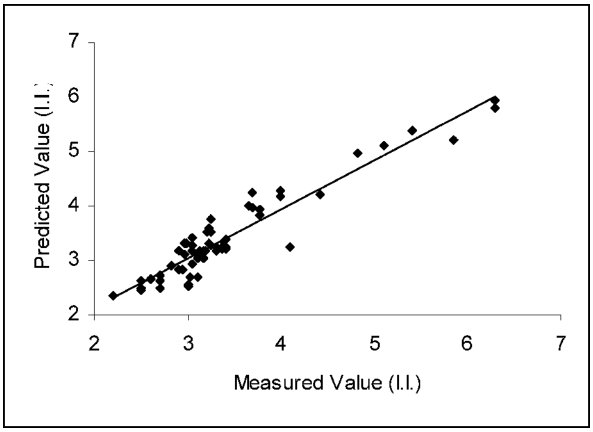


FIG. 5. Measured iodine index vs. values predicted by leave-one-out cross-validation for a PLS model with 4 LVs.

values higher than the value accepted by the quality control.

For this analyte and the next one, the procedure used was the same as for water calibration: boxcar averaging, followed by Selection A, Selection B, and last, the variable selection by the correlogram. The results obtained can be seen in Fig. 4 and Table III. The correlogram (Fig. 4c), applied to the subset of 75 variables, did not result in high correlation coefficients with respect to II, so a low cutoff value had to be used (0.35). For this analyte, the first selection method, A, gave better SECV and PRESS values for a model with 4 LVs and a high correlation coefficient (0.974). From the results in Table III, it can be seen that for iodine index, 4 LVs were used to obtain a fairly good calibration model. The plot of experimental II vs. values predicted by cross-validation can be seen in Fig. 5.

The external validation was performed using 13 samples in the model given by Selection A (results in Table III). From the experimental and predicted II in Table IV, it can be seen that only three samples are predicted with an error higher than 10%. For this analyte, the concentrations are fairly uniform and the RPD = 4.00 is an indication that the instrument is predicting the experimental values better than the standard original data. The value of RER = 14.19 confirms this fact.

The selected variables correspond to wavelengths in the regions 7430–6600, 6100–5400, and 5100–4500 cm^{-1}. The first absorption band (7430–6600 cm^{-1}) is related to the combination of stretching and deformation of C–H bonds and could also be assigned to the –OH first overtone. The absorption band in the region 6100–5400 cm^{-1} is related to the stretching of –CH in olefins, while that of 5100–4500 cm^{-1} is involved in the combined stretching of C=C double bonds in conjugated chains.[22]

Epoxide. For the epoxide modeling, 43 samples were used (35 in the calibration set and 8 for external validation) and the results are shown in Fig. 6 and Table V. The epoxide index (EI) takes its values in the narrow range from 6.21 to 6.61.

Selection A was the method that produced the best calibration model, and 65 variables were selected in this step (Figs. 6a and 6b). The variable selection made through the correlogram (Fig. 6d), with the cutoff value set at 0.20, did not improve the model. Eight samples were used for external validation. The PLS model from Selection A (65 variables and 4 LVs) was used for best results. The results in Table V indicate that it was possible to build a model with a very good prediction ability that was able to follow the quality of the product. The plot of measured EI vs. values predicted by cross-validation is shown in Fig. 7.

TABLE IV. Experimental, estimated, and residual values for iodine index (II) in the external validation set.

Sample		Experimental values	Predicted values		Residuals
2		2.98	3.171		0.191
6		3.41	3.195		−0.214
9		3.02	3.050		0.030
14		3.25	3.578		0.328
20		2.61	2.578		−0.032
26		3.19	3.087		−0.103
30		3.38	2.959		−0.421
37		2.96	2.958		−0.002
50		3.82	3.741		−0.078
59		2.45	2.801		0.351
65		4.41	4.432		0.022
68		4.82	4.804		−0.016
72		5.85	5.414		−0.436
Mean		3.550	3.521		0.029
Std.		0.959	0.856		0.240
Range		3.400			
RPD[a]	4.00		RER[b]	14.19	

[a] RPD = std(exp.)/std(residuals).

[b] RER = range(exp.)/std(residuals).

Table VI shows the measured and predicted EI values with the respective residuals for the 8 samples from the validation set. They were all very well predicted (none of them with an error above 0.5%). For this analyte, both the ratios RPD and RER yielded excellent results (26.022 and 80.695, respectively, when the ideal ratio is 10 or higher) indicating accurate analysis, especially when the analyte concentration varies in a small range.

The selected variables refer to absorption bands in the region 7100–6800, 5800–5600, 5400–5200, and 5000–4500 cm^{-1}. The first region (7100–6800 cm^{-1}) corresponds to the first overtone from the C–H stretching. The second one (5800–5600 cm^{-1}) is related to the C–H bond stretching present in fatty acids. The third region (5400–5200 cm^{-1}) could be assigned to the second overtone of C=O stretching, while the last one (5000–4500 cm^{-1}) is assigned to the combination of C=C stretching in double bonds.[23]

CONCLUSION

It has been shown in this work that the use of NIRS combined with multivariate regression is a feasible alter-

TABLE V. Results of PLS models for epoxide.

Method	# Variables	Latent var.	SECV	PRESS	R
Boxcar averaging	160	5	0.039	0.054	0.975
Selection A	**65**	**4**	**0.033**	**0.039**	**0.974**
Selection B	37	4	0.048	0.079	0.965
Correlogram[a]	4	2	0.085	0.255	0.736
External val.[b]	65	4	0.017[c]	0.002	

[a] Variable selection by the correlogram applied to Selection B for a cutoff = 0.20.

[b] External validation using the PLS model from Selection A.

[c] SEP (standard error of prediction).

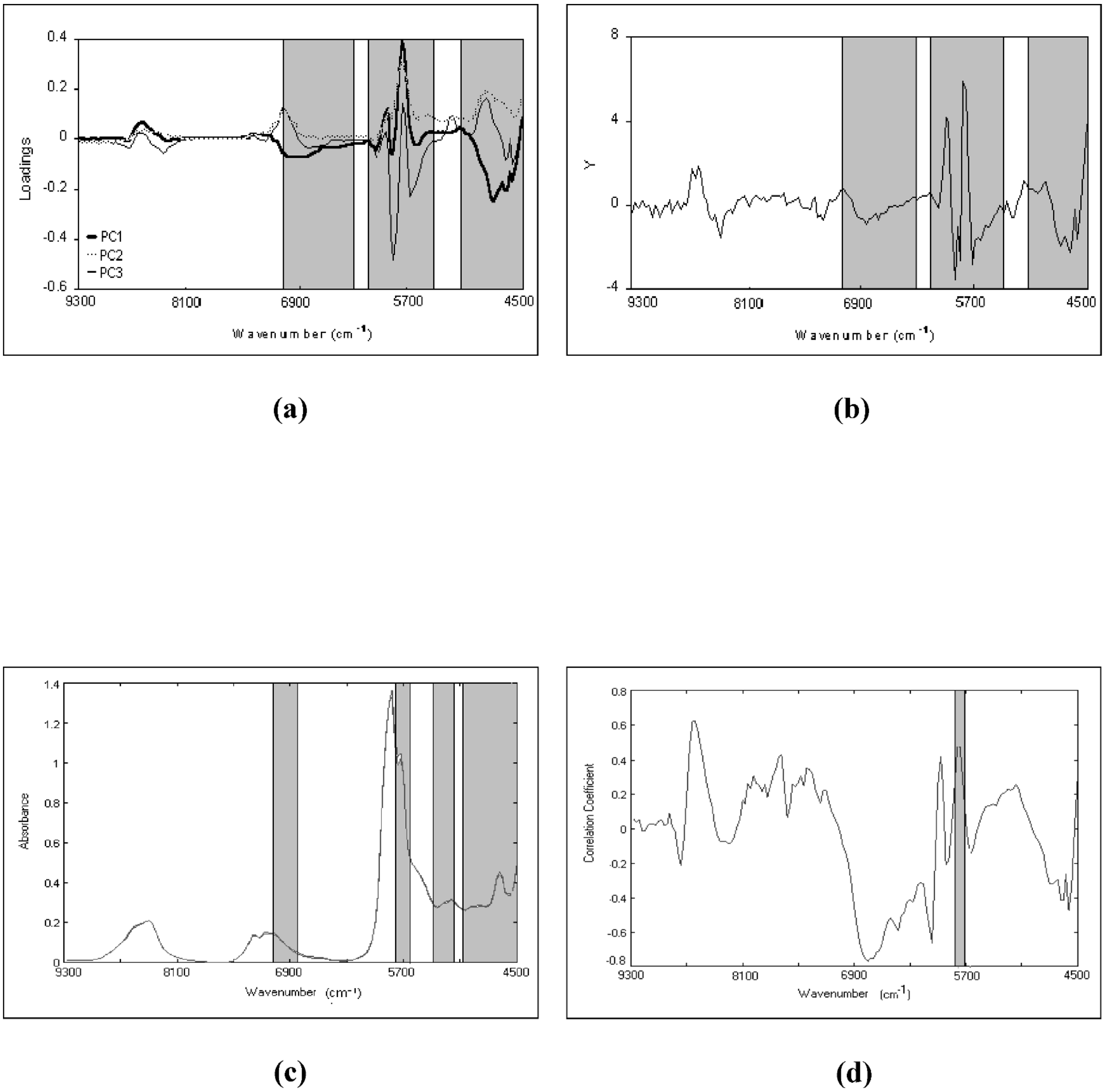


FIG. 6. Epoxide index in ESO (EI). (**a**) Loading vectors. (**b**) Regression vector for a PLS model with 4 LVs. (**c**) Spectra showing two samples, one with high and the other with low epoxide index. (**d**) Correlogram for the full spectrum. The selected wavenumbers are illuminated.

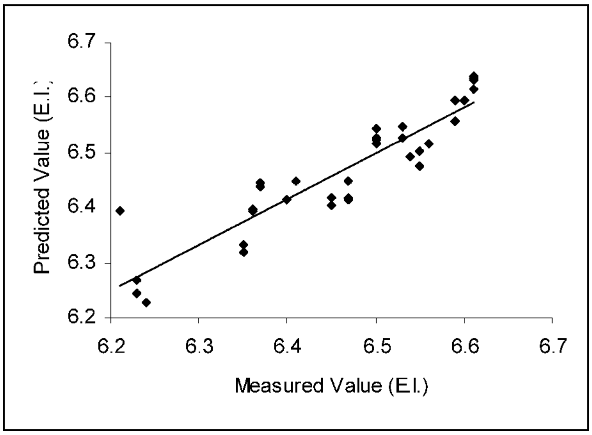


FIG. 7. Measured epoxide index vs. values predicted by leave-one-out cross-validation for a PLS model with 4 LVs.

native to the widely established techniques, especially in industrial processes. The use of a PLS method was successful to construct regression models of high quality. It has also been shown that by using simple and intuitive

TABLE VI. Experimental and estimated values and residuals for epoxide index (EI) in the external validation set.

Sample		Experimental values	Predicted values		Residuals
2		5.73	5.710		−0.020
3		6.21	6.199		−0.010
10		6.60	6.596		−0.004
15		6.56	6.540		−0.020
23		6.41	6.415		0.005
28		6.54	6.517		−0.023
41		6.47	6.443		−0.027
44		6.24	6.234		−0.006
Mean		6.35	6.332		0.013
Std.		0.29	0.288		0.011
Range		0.89			
RPD[a]	26.022		RER[b]	80.695	

[a] RPD = std(exp.)/std(residuals).
[b] RER = range(exp.)/std(residuals).

variable selection methods, such as loadings/regression vector analysis and the correlogram, the number of variables can be significantly reduced without impairing the model quality. The statistical parameters used, RPD and RER, indicated that NIRS determination was accurate for the EI and fairly good for II. For water % the results were shown to be satisfactory.

From the results obtained, it can be concluded that the proposed methodology is appropriate for monitoring the epoxidation of soybean oil and evaluating the additive's quality in the industrial process, where time, effort, and money are crucial.

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