



# Comparison and application of near-infrared (NIR) and mid-infrared (MIR) spectroscopy for determination of quality parameters in soybean samples



D.S. Ferreira<sup>a,\*</sup>, O.F. Galão<sup>b</sup>, J.A.L. Pallone<sup>a</sup>, R.J. Poppi<sup>c</sup>

<sup>a</sup> Faculty of Food Engineering – UNICAMP, CEP 13083-862, PO Box 6121, Campinas, SP, Brazil

<sup>b</sup> State University of Londrina, CEP 86051-990, PO Box 6001, Rodovia Celso Garcia 445 Km 38, Londrina, PR, Brazil

<sup>c</sup> Institute of Chemistry – UNICAMP, CEP 13082-970, PO Box 6154, Campinas, SP, Brazil

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## ABSTRACT

Grain composition is directly related to maintenance of quality. Chemical analyses have been determined using traditional and laborious methods, which are time-consuming and generate chemical waste. This justifies the development of fast and accurate alternative methodologies to control the grain composition. Near-infrared (NIR) and mid-infrared (MIR) spectroscopy techniques associated with chemometric tools have been applied in the development of several analytical methodologies for agricultural products. The aim of this study is to develop and compare these two spectroscopic techniques to determine the parameters of quality, such as moisture, protein, lipid and ash content, in 20 varieties of soybean, which are grown in the cities of Ponta Grossa and Londrina, Brazil, totally 40 samples. It was used near-infrared and mid-infrared spectroscopy, with diffuse reflectance measurements, associated with multivariate calibration methods based on partial least squares algorithm. The determination coefficient ( $R^2$ ) for moisture, ash, protein and lipid content were 0.72, 0.73, 0.88 and 0.81 for NIR and 0.63, 0.87, 0.91 and 0.67 for MIR, respectively, having an RMSECV (root mean square error of cross-validation) < 2.09%. The results show that both infrared (NIR and MIR) techniques have predictive abilities.

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## 1. Introduction

The quality of the grains is an important parameter for cultivation and also for the economic value. In many countries, the price of the grain is determined by the content of protein, starch and for the hardness. There are different methodologies for evaluation of these quality parameters, such as the chemical composition and the infrared technology, which allows to determine different constituent in grains, including in online systems in the plantation itself (Maertens, Reyns, & De Baerdemaeker, 2004).

Infrared spectroscopy is pointed as a fast and reliable way of investigation of the quality and safety of food (Downey, 1998). Several studies have been described the ability of that technique in characterizing products in chemical, physical and sensorial terms, as well as, proposals for classification. Mid-infrared (MIR) and near-

infrared (NIR) spectroscopy techniques have been applied in authentication processes in order to assess whether the product is strictly in accordance with the label described or if it complies with the current legislation (Borin, Ferrão, Mello, Maretto, & Poppi, 2006; Hourant, Baeten, Oroles, & Meurens, 2000; Reid, Woodcock, O'Donnell, Kelly, & Downey, 2005; Vlachos et al., 2006).

Since the beginning of the 1960s, the NIR technology is associated with the analyses of grains and derived products, being Karl Norris the pioneer in the analytical development of NIR methodologies. His team of the Department of Agriculture of the United States was capable to determine the content of moisture of seed extracts using NIR spectra associated with the multivariate calibration (Hart, Norris, & Golumbic, 1962). In 1975, NIR was adopted by the Canadian Grain Commission as an official method of analysis of proteins in wheat (Williams, 1975). In 1980, the technique was adopted by the Federal Grain Inspection Service of the United States, and the wheat protein test by NIR was finally approved by the American Association of Cereal Chemists (AACC) in 1989 (Osborne, 2000).

Several authors have described the possibility of direct measures of protein, moisture, dry weight and starch of several grains by NIR (Engel, Long, Carlson, & Reed, 1997; Maertens et al., 2004;

\* Corresponding author. Present address: Rua Monteiro Lobato, 80, CEP 13083-862 PO Box: 6121, Campinas SP, Brazil. Tel.: +55 19 33053882; fax: +55 19 35212153.

E-mail addresses: [eng.dsfg@gmail.com](mailto:eng.dsfg@gmail.com) (D.S. Ferreira), [galao@uel.br](mailto:galao@uel.br) (O.F. Galão), [j.pallone@fea.unicamp.br](mailto:j.pallone@fea.unicamp.br) (J.A.L. Pallone), [ronei@iqm.unicamp.br](mailto:ronei@iqm.unicamp.br) (R.J. Poppi).

Montes et al., 2006). For that, calibration models were built between the NIR spectra and the quality parameters by the PLS algorithm, with standard error of cross-validation (SECV) around 0.57 and 0.31% for protein and moisture in wheat, respectively (Maertens et al., 2004).

In the field of analysis of oils, MIR has been effectively used to determine the *cis* and *trans* content, iodide, saponification number, peroxide and free fatty acids in oil and fat samples (Innawong, Mallikarjunan, Irudayaraj, & Marcy, 2004; Van De Voort, Sedman, & Russin, 2001). MIR has also been described to detect olive oil adulteration with several vegetable oils (sunflower oil, soybean oil, sesame oil and corn oil) and to monitor the oxidation process (Vlachos et al., 2006).

MIR spectroscopy allows the identification of fundamental vibrational transitions and comprises the spectral range from 2500 to 50,000 nm, while the NIR spectra, the spectral range from 780 to 2500 nm, which contains overtone information and combinations of these vibrations, being more difficult to be interpreted (Reid et al., 2005). The interpretation of these infrared spectra usually involves the combination of multiple samples, where each one possesses a great number of correlated characteristics. Thus, specific algorithms should be applied to reduce the complexity of the data, aiming the identification of parameters of interest in the spectrum. The multivariate calibration is broadly applied to extract the relevant information from the spectrum obtained to forecast the chemical concentration of the sample. However, the main problem associated with these methods is the nonlinearity of the data (Balabin, Safieva, & Lomakina, 2007).

Few studies compare the NIR and MIR techniques for specific applications, including discrimination of edible oils and fats (Yang, Irudayaraj, & Paradkar, 2005), quantification of essential oils (Schulz, Schrader, Quilitzsch, Pfeffer, & Krüger, 2003) and evaluation of chemical differences in red and white wines, applying different strains of *Oenococcus oeni* for fermentation (Cozzolino, McCarthy, & Bartowsky, 2012). Tarr, Diepeveen and Appels (2012) applied FTIR (MIR) and Raman to supplement the information obtained by NIR to monitor the barley grain during the process of production of malt. The authors described that, through the construction of a PLS calibration model is difficult, it was possible to monitor quality parameters for malt by NIR. FTIR was used for the reception of images of the surface of the barley grain in the region between 4000 and 700  $\text{cm}^{-1}$ .

The aim of this work is to compare the use of two infrared spectral regions (MIR and NIR), in association with chemometric

**Table 1**

Spectroscopic parameters for soy flour in each near-infrared (NIR) and mid-infrared (MIR) spectral range.

	Unit	MIR	NIR
Spectral range	$\text{cm}^{-1}$	400–4000	4000–8000
	nm	25000–2500	2500–1250
Resolution	$\text{cm}^{-1}$	4	4
Number of scans (spectrum and white)		64	32
White		KBr	BaSO <sub>4</sub>

tools, for determination of the content of moisture, proteins, lipids and ashes in soybean.

## 2. Material and methods

### 2.1. Samples

The soybean varieties evaluated were: BRS 48, 184, 213, 232, 233, 257, 258, 259, 260, 261, 262, 267, 268, 282, 242RR, 244RR, 245RR, 246RR, 255RR and 256RR. Each variety was simultaneously cultivated in the cities of Londrina and Ponta Grossa (Brazil), totally 40 samples. Samples were dried in oven at 40 °C for 24 h before grinding. The chemical analyses were performed in the State University of Londrina (UEL, PR, Brazil) resulting in contents of moisture, lipids, ashes and proteins (AOAC, 2006).

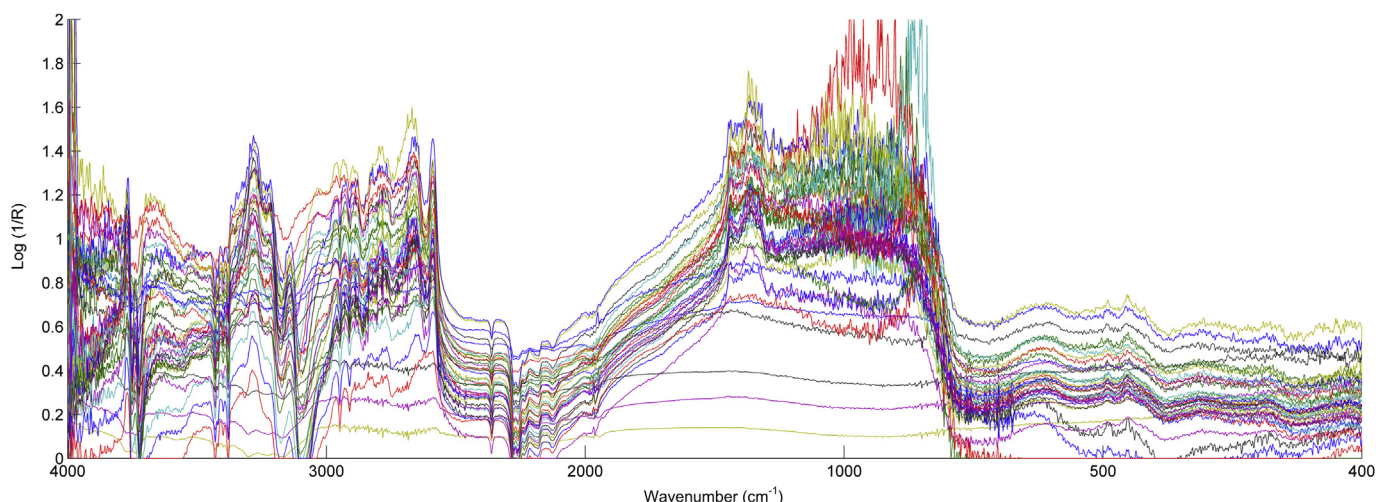
### 2.2. Near-infrared and mid-infrared spectroscopy

The 40 samples of soybean were analyzed by spectroscopy in the mid-infrared and near-infrared region. The equipment used were an FT-NIR Spectrum 100N from Perkin Elmer (United States) and FT-IR MB-100 from Bomem (Quebec, Canada), according with the parameters described in Table 1.

A small portion of samples was placed in powder accessory and the measure of diffuse reflectance was accomplished using the software Spectrum of NIRA – v. 6.3.1.0132 (Perkin Elmer) or Win Bomem Easy (ABB Bomem). The samples were scanned in triplicate and the mean value was used.

### 2.3. Chemometric analyses

The calibration was accomplished by partial least squares (PLS) regression. The results obtained by NIR and MIR were treated by the



**Fig. 1.** MIR spectra for soybean samples, obtained in the range between 4000 and 400  $\text{cm}^{-1}$ , without pretreatment.

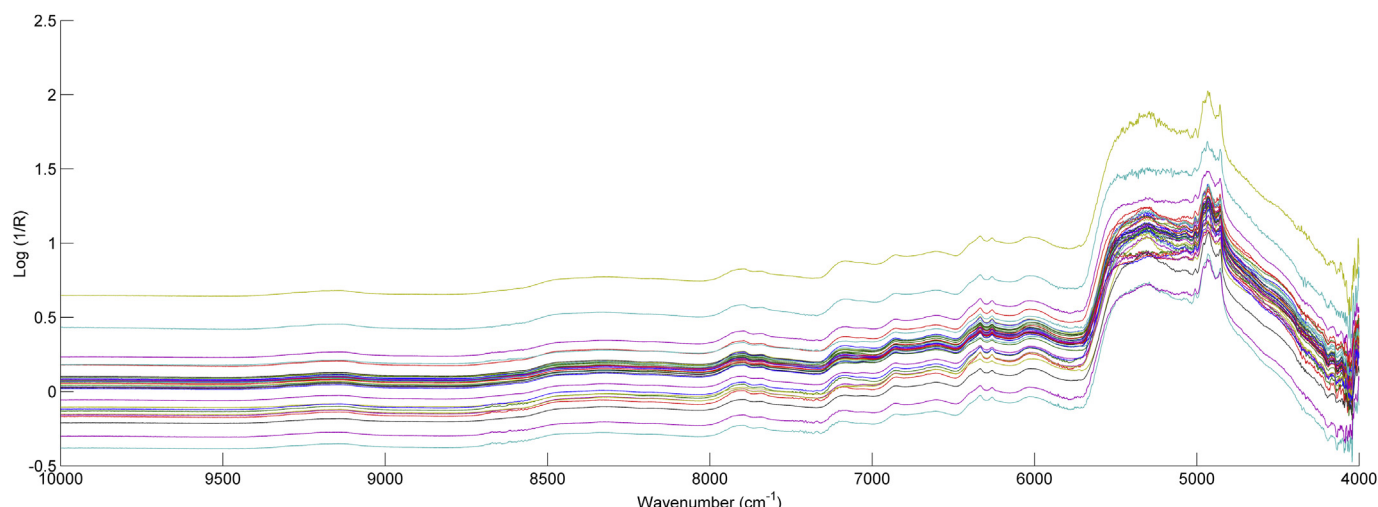


Fig. 2. NIR spectra for soybean samples, obtained in the range between 10,000 and 4000  $\text{cm}^{-1}$ , without pretreatment.

program PLS Toolbox v. 5.8 (Eigenvector, Research, Inc., USA) developed for the Matlab 7.8 (MathWorks, USA).

From the total of 40 soybean samples, 30 were used for the development of the calibration model and 10 were used for the external validation (set of prediction); the choice of samples for the calibration and prediction was performed by the Kennard-Stone algorithm (Kennard & Stone, 1969).

The spectra were preprocessed by the combination of several mathematical treatments: first and second derivatives, normal standard variate transformation (SNV) and the spectral data were mean centered (MC) before calibration. The number of PLS factors was determined by cross-validation (leave-one-out) (Geladi & Kowalski, 1986).

The quality of the models was checked by calculation of the root mean square error of calibration (RMSEC), root mean square error of cross-validation (RMSECV), root mean square error of prediction (RMSEP) and determination coefficient ( $R^2$ ) (Williams & Norris, 2001). Values closer to one for  $R^2$  and low values for RMSE indicate the good performance of the model for the prediction of the quality parameters of soybean.

The outliers were identified and removed when necessary by residual  $\times T^2$  plot. Hotelling's  $T^2$  means square of distance of sample from model. The residuals mean distance of sample from the model that can be explained by random error (Naes, Isaksson, Fearn, & Davies, 2002).

### 3. Results and discussion

It was obtained 40 spectra from the soybean samples for each technique, mid-infrared and near-infrared (MIR and NIR), which are presented in Figs. 1 and 2 without pretreatment.

The characteristics of the MIR and NIR spectra for the soybean samples (Figs. 1 and 2) represent functional groups associated

mainly to the content of moisture, proteins, lipids and carbohydrates. The vibrational absorptions in NIR correspond to the vibrational transactions between the fundamental energy level and the energy levels of a higher order and/or combination bands. In this sense, it can be highlight the spectral range comprised between 5200 and 5100  $\text{cm}^{-1}$  related to the O–H functional group (1st overtone of the combination mode), 5000–5600  $\text{cm}^{-1}$  related to the C–H functional group (1st overtone of  $\text{CH}_3$  and  $-\text{CH}=\text{CH}-$ , of fatty acids), 4400–4033  $\text{cm}^{-1}$  related to the C–H group and also 5000–4500  $\text{cm}^{-1}$  related to the N–H and C=O stretching, corresponding to proteins. The absorptions in MIR correspond to the vibrational transactions between the fundamental energy level and the first excited vibrational level, where the spectral range from 1200 to 900  $\text{cm}^{-1}$  is known as fingerprint, where most of the fundamental vibrational frequencies are found. In the MIR region, it was possible to identify the C–O, C–C and C–O–H stretching; moreover, it can be highlight the region between 3040 and 2850  $\text{cm}^{-1}$  related to the C–H groups for asymmetrical and symmetrical stretching's of  $\text{CH}_2$  and  $\text{CH}_3$ , characterizing fatty acid chains, and 1654  $\text{cm}^{-1}$  related to N–H vibrational stretching, for proteins (Espinoza, Lucas, & Littlejohn, 1999; Hourant et al., 2000; Kays, Windham, & Barton, 1998; Liu, Cho, Sakuri, Miura, & Ozaki, 1994; Shenk, Workman, & Westerhaus, 2007).

In chemometrics, the spectral and concentrations are inserted as matrices. It was used as depended variables (Y) the reference values for the parameters moisture, protein, lipids and ashes, obtained through laboratory methods, as shown in Table 2. The

Table 2

Range of values obtained by the reference methods for soybean samples from different farming regions.

Farming region	Moisture (%)	Protein (%)	Lipid (%)	Ash (%)
Londrina	6.70–8.50	32.91–39.41	18.16–23.86	5.65–6.55
Ponta Grossa	7.40–8.80	37.26–42.16	17.95–23.98	4.91–6.49
Mean $\pm$ SD	7.79 $\pm$ 0.01	38.35 $\pm$ 1.98	20.92 $\pm$ 1.53	5.80 $\pm$ 0.39
SE	0.038	0.274	0.162	0.069

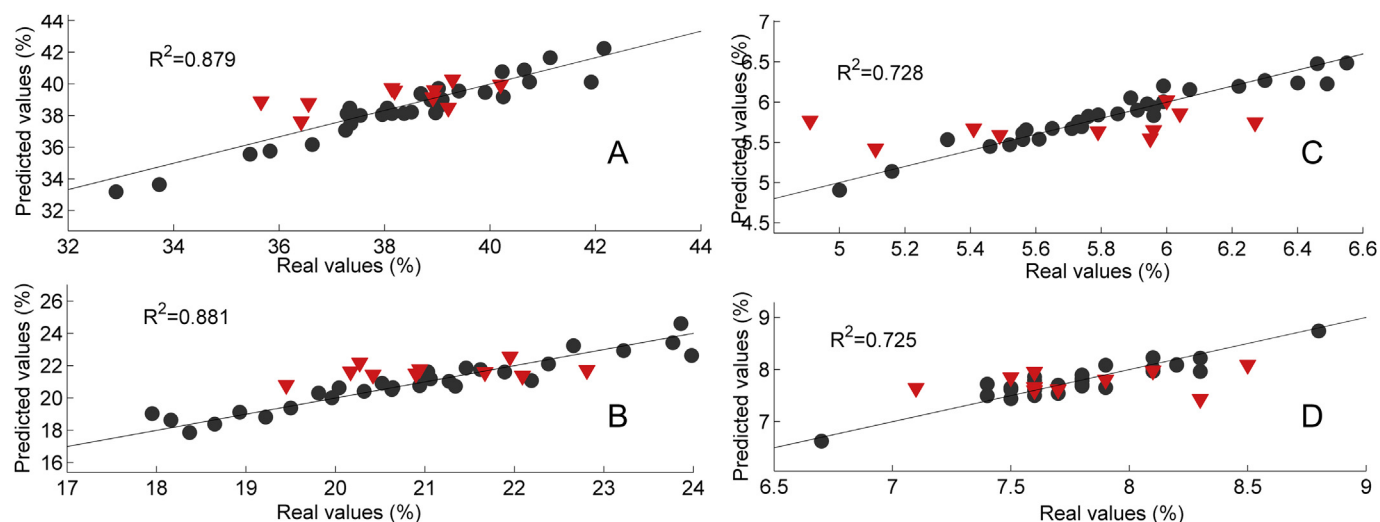
SD – standard deviation, SE – standard error of analysis.

Table 3

Multivariate analysis (PLS) of the parameters for soybean with NIR and MIR spectroscopic techniques.

	Moisture		Ash		Protein		Lipid	
	NIR	MIR	NIR	MIR	NIR	MIR	NIR	MIR
RMSEC	0.12	0.13	0.11	0.06	0.33	0.39	0.38	0.14
$R^2$	0.72	0.63	0.73	0.87	0.88	0.91	0.81	0.67
RMSECV	0.52	0.47	0.44	0.41	1.76	1.74	2.09	1.44
RMSEP	0.35	0.41	0.36	0.25	1.32	1.06	1.08	1.87
LV	8	5	9	7	9	8	6	8
Treatment	2nd deriv.	1st deriv.-MC	MC	SNV	SNV	SNV	2nd deriv.-MC	SNV
	-MC		-MC	-MC	-MC	-MC		-MC

$R^2$  – determination coefficient, RMSEC, RMSEP, RMSECV – root mean square error of calibration, prediction and cross-validation, VL – latent variables, MC – mean centered data, SNV – standard normal variate.



**Fig. 3.** Relation between the real values and the values predicted by the calibration models obtained by NIR for the content of protein (A), lipid (B), ash (C) and moisture (D). (●) Calibration values, (▼) Prediction values.

matrix **X** was composed of the reflectance at different wave-numbers of each sample, where each row of the matrix is represented by a different sample and the columns represent the respective reflectances for the samples studied at each wave-number (Beebe & Kowalski, 1987).

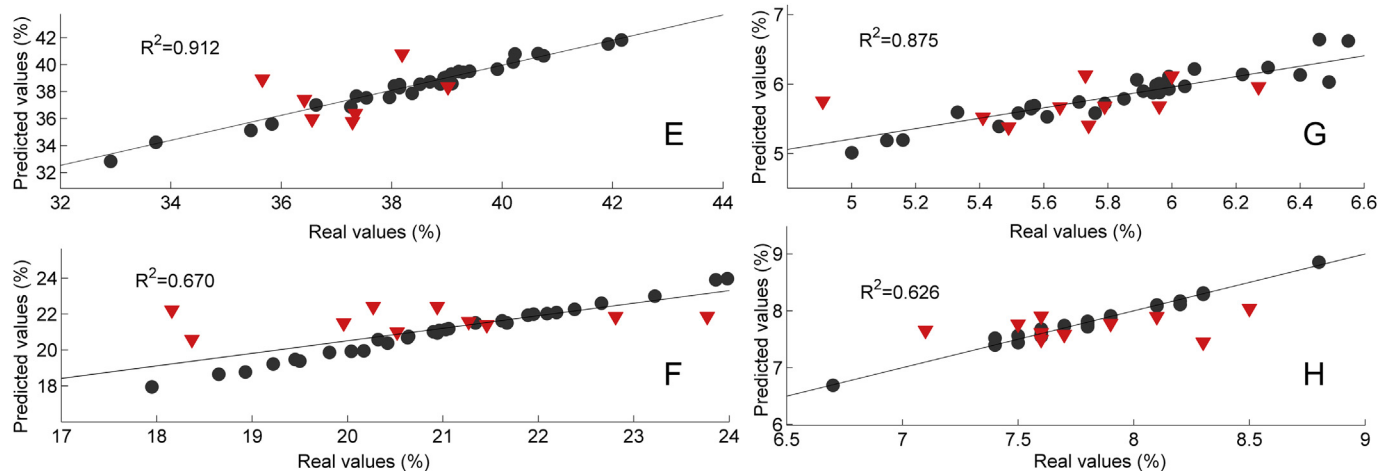
The MIR and NIR techniques have enabled the development of calibration models for the quantification of the content of moisture, protein, lipid and ash, presented in Table 3. Regardless of the farming region, it was used all soybean samples for the construction of the model and its validation. Cross-validation was applied to all models to obtain the number of principal components for each model. To extract the relevant chemical information of the spectra it was used the “loading” vectors (Haaland & Thomas, 1988). The SNV pretreatment in the MIR and NIR spectra corrected the effects of the multiplicative scatter provoked by particle size distribution, common in reflectance spectroscopy, allowing the best calibration models (Rodríguez-Saona, Fry, & Calvey, 2000), while the first and second derivatives accentuated the spectral information for the MIR and NIR techniques, respectively. The second derivative applied to the MIR spectra did not improve the calibration model as

the data contained a lot of noise (Fig. 1), and this pretreatment further enhances this interference. An optimal number of latent variables, from 5 to 9, were chosen for each model without incorporating significant noise.

According to Table 3, the calibration, cross-validation and prediction errors were low and the determination coefficient was similar for NIR and MIR ( $R^2$  from 0.63 to 0.91 for MIR and 0.72 to 0.88 for NIR). The presented results can be compared with NIR spectroscopy of Brazilian soybean, as reported by Ferreira, Pallone, and Poppi (2012) ( $R^2$  from 0.50 to 0.81), which obtained good models calibration, but a large calibration set was used and the data were not compared with other method as performed in this study.

The plot of predicted against measured values (Figs. 3 and 4) for the contents of protein, lipids, ashes and moisture showed good correlation for both MIR and NIR spectral regions.

For the representation of a good relation between the experimentally determined values and the predicted values for the set of 10 validation samples, it was calculated the relative error, which is the ratio between the measured value minus the predicted value divided by the measured value. Table 4 shows the measured and



**Fig. 4.** Relation between the real values and the values predicted by the calibration models obtained by MIR for the content of protein (E), lipid (F), ash (G) and moisture (H). (●) Calibration values, (▼) Prediction values.



**Table 4**

Comparison between the measured value and the value predicted by the regression model applied to the NIR and MIR spectra for proteins and lipids.

Sample	Proteins					Lipids				
	Value measured	NIR	RE <sup>a</sup> (%)	MIR	RE <sup>a</sup> (%)	Value measured	NIR	RE <sup>a</sup> (%)	MIR	RE <sup>a</sup> (%)
1	36.56	38.96	6.56	35.79	2.10	18.16	18.63	2.58	20.10	10.68
2	35.66	38.02	6.61	37.12	4.09	21.27	21.23	0.18	21.51	1.12
3	38.19	39.24	2.74	38.28	0.23	20.94	20.80	0.66	23.65	12.94
4	39.21	39.00	0.53	37.11	5.35	23.77	23.92	0.63	23.47	1.26
5	36.42	37.98	4.28	37.40	2.69	22.81	21.25	6.83	23.06	1.09
6	39.29	40.22	2.36	37.08	5.62	20.27	22.13	9.17	20.36	0.44
7	40.20	39.67	1.31	38.28	4.77	19.96	21.15	5.96	21.46	7.51
8	38.14	39.47	3.48			21.46	21.74	1.11	21.40	0.27
9	38.95	39.62	1.72			18.37	17.70	3.64	20.60	12.13
10	38.92	39.24	0.82			20.52	20.99	1.85	20.92	1.94

<sup>a</sup> RE - Relative error: Calculated as the difference between the measured value and the predicted value versus the measured value.**Table 5**

Comparison between the measured value and the value predicted by the regression model applied to the NIR and MIR spectra for ashes and moisture.

Sample	Ashes					Moisture				
	Value measured	NIR	RE <sup>a</sup> (%)	MIR	RE <sup>a</sup> (%)	Value measured	NIR	RE <sup>a</sup> (%)	MIR	RE <sup>a</sup> (%)
1	5.95	5.62	5.55	6.04	1.51	7.90	7.16	9.37	7.81	1.14
2	6.27	5.83	7.01	6.30	0.48	7.50	7.31	2.53	7.40	1.33
3	5.79	5.61	3.11	5.87	1.38	7.60	8.14	7.10	7.71	1.45
4	6.04	5.90	2.32	6.08	0.66	7.70	7.78	1.04	7.76	0.78
5	6.00	6.01	0.17	5.98	0.33	7.70	7.94	3.12	7.65	0.65
6	5.96	5.68	4.69	5.66	5.03	7.50	7.65	2.00	7.65	2.00
7	4.91	5.74	16.90	4.79	2.44	7.40	8.04	8.65	7.39	0.13
8	5.41	5.66	4.62	5.39	0.37	8.10	8.13	0.37	8.12	0.25
9	5.49	5.60	2.00	5.46	0.54	8.50	8.44	0.70	8.40	1.18
10	5.11	5.40	5.67	5.11	0	8.20	8.04	1.95	8.16	0.49

<sup>a</sup> RE - Relative error: Calculated as the difference between the measured value and the predicted value versus the measured value.

predicted values for proteins and lipids and Table 5 shows the content of ash and moisture. In general, the relative error was low for both models generated with NIR and MIR; however, the results suggest the use of NIR for prediction of protein (0.5–6.5%) and lipids (0.6–9.2%) and the use of MIR for ashes (0–5.0%) and moisture (0.1–2.0%).

For the calibration model with MIR (Table 4), for protein content, some outliers were removed after analysis of the residual plot (residual  $T^2 \times Q$ ).

From the results presented here, it was found that both the NIR and MIR techniques can be applied to quality parameters determination in soybean samples from Brazil. Guo, You, Prisecaru, Costescu and Nelson (2000) also concluded that the NIR technique is rapid, accurate and cost effective for analyzing the composition of protein, lipids, moisture, carbohydrates and fiber in soybeans (USA) and its derived products (milk and tofu), with  $R^2 \cong 0.99$  and RMSE < 1.0%. Delwiche, Pordesimo, Panthee, and Pantalone (2007) did not prove the feasibility of the NIR technique for the quantitation of proteins and fractions thereof in whole soybean grains in Tennessee (USA) and obtained  $R^2$  from 0.02 to 0.73% and RMSEP from 0.15 to 11.9. As this study, Balabin and Smirnov (2011) also showed that the two techniques are fast, robust and cost effective, and they also detected melamine, an adulterant applied in milk products to increase the nitrogen content and overestimate the protein content of the food. However, the authors analyzed samples of milk, infant formula and milk powder by NIR and MIR and related the use of two nonlinear techniques for chemometric calculations. Haughey, Graham, Cancouët, and Elliott (2013) also detected melamine after application as adulterant in animal feed made with soybean, with coefficients of determination ( $R^2$ ) from 0.89 to 0.99 in the calibration models. No studies were found that relate these two techniques to the Brazilian soybean samples.

#### 4. Conclusions

It was concluded that both MIR and NIR techniques generated consistent PLS models and with good predictive abilities. The total time required for the preparation and analysis of samples was less than 5 min, compared to the 10–16 h required for the determination of the content of moisture, proteins, lipids and ashes by reference methods. Considering the results, both the MIR and NIR techniques can be effectively applied in the industry as an analytical tool to monitor the quality of soybean and simultaneously measure several parameters of quality.

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#### References

- Van De Voort, F. R., Sedman, J., & Russin, T. (2001). Lipid analysis by vibrational spectroscopy. *European Journal of Lipid Science and Technology*, 103(12), 815–826.
- AOAC. (2006). In W. Horwitz, & G. W. Latimer (Eds.), *Official methods of analysis of AOAC International* (18th ed.). Gaithersburg, Maryland: AOAC International.
- Balabin, R. M., Safieva, R. Z., & Lomakina, E. I. (2007). Comparison of linear and nonlinear calibration models based on near infrared (NIR) spectroscopy data for gasoline properties prediction. *Chemometrics and Intelligent Laboratory Systems*, 88(2), 183–188.
- Balabin, R. M., & Smirnov, S. V. (2011). Melamine detection by mid- and near-infrared (MIR/NIR) spectroscopy: a quick and sensitive method for dairy products analysis including liquid milk, infant formula, and milk powder. *Talanta*, 85(1), 562–568.
- Beebe, R. K., & Kowalski, B. R. (1987). An introduction to multivariate calibration and analysis. *Analytical Chemistry*, 59(17), 1007–1017.
- Borin, A., Ferrão, M. F., Mello, C., Maretto, D. A., & Poppi, R. J. (2006). Least-squares support vector machines and near infrared spectroscopy for quantification of common adulterants in powdered milk. *Analytica Chimica Acta*, 579(1), 25–32.

- Cozzolino, D., McCarthy, J., & Bartowsky, E. (2012). Comparison of near infrared and mid infrared spectroscopy to discriminate between wines produced by different *Oenococcus oeni* strains after malolactic fermentation: a feasibility study. *Food Control*, 26(1), 81–87.
- Delwiche, S. R., Pordesimo, L. O., Panthee, D. R., & Pantalone, V. R. (2007). Assessing glycinin (11S) and  $\beta$ -conglycinin (7S) fractions of soybean storage protein by near-infrared spectroscopy. *Journal of the American Oil Chemists' Society*, 84(12), 1107–1115.
- Downey, G. (1998). Food and food ingredient authentication by mid-infrared spectroscopy and chemometrics. *TrAC Trends in Analytical Chemistry*, 17(7), 418–424.
- Engel, R., Long, D., Carlson, G., & Reed, J. F. (1997). On-the-go grain protein sensing is near. Does it have a future in precision nitrogen. Management for wheat? *Better Crops With Plant Food*, 81(4), 20–24.
- Espinoza, L. H., Lucas, D., & Littlejohn, D. (1999). Total organic carbon content in aqueous samples determined by near-IR spectroscopy. *Applied Spectroscopy*, 53(1), 103–107.
- Ferreira, D. S., Pallone, J. A. L., & Poppi, R. J. (2012). Fourier transform near-infrared spectroscopy (FT-NIRS) application to estimate Brazilian soybean [*Glycine max* (L.) Merrill] composition. *Food Research International*, 51, 53–58.
- Geladi, P., & Kowalski, B. R. (1986). Partial least-squares regression: a tutorial. *Analytica Chimica Acta*, 185(1), 1–17.
- Guo, J., You, T., Prisecaru, V., Costescu, D., & Nelson, R. L. (2000). NIR calibrations for soybean seeds and soy food composition analysis: total carbohydrates, oil, proteins and water contents. *Proteins (AACC 1995)*.
- Haaland, D. M., & Thomas, E. V. (1988). Partial least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information. *Analytical Chemistry*, 60(11), 1193–1202.
- Hart, J. R., Norris, K. H., & Golumbic, C. (1962). Determination of the moisture content of seeds by near-infrared spectrophotometry of the methanol extracts. *Cereal Chemistry*, 39, 94–99.
- Haughey, S. a., Graham, S. F., Cancouët, E., & Elliott, C. T. (2013). The application of near-infrared reflectance spectroscopy (NIRS) to detect melamine adulteration of soya bean meal. *Food Chemistry*, 136, 1557–1561.
- Hourant, P., Baeten, V., Oroles, M. T. M., & Meurens, M. A. R. C. (2000). Oil and fat classification by selected bands of near-infrared spectroscopy. *Applied Spectroscopy*, 54(8).
- Innawong, B., Mallikarjunan, P., Irudayaraj, J., & Marcy, J. E. (2004). The determination of frying oil quality using Fourier transform infrared attenuated total reflectance. *LWT – Food Science and Technology*, 37(1), 23–28.
- Kays, S. E., Windham, W. R., & Barton, F. E. (1998). Prediction of total dietary fiber by near-infrared reflectance spectroscopy in high-fat- and high-sugar-containing cereal products. *Methods*, 856(1997), 854–861.
- Kennard, R. W., & Stone, L. A. (1969). Computer aided design of experiments. *Technometrics*, 11(1), 137–148.
- Liu, Y., Cho, R., Sakuri, K., Miura, T., & Ozaki, Y. (1994). Studies on Spectra/Structure correlations in near-infrared spectra of proteins and polypeptides. Part I: a marker band for hydrogen bonds. *Applied Spectroscopy*, 48(10), 1249–1254.
- Maertens, K., Reyns, P., & De Baerdemaeker, J. (2004). On-line measurement of grain quality with NIR technology. *American Society of Agricultural Engineers*, 47(4), 1135–1140.
- Montes, J. M., Utz, H. F., Schipprack, W., Kusterer, B., Muminovic, J., Paul, C., et al. (2006). Near-infrared spectroscopy on combine harvesters to measure maize grain dry matter content and quality parameters. *Plant Breeding*, 125(6), 591–595.
- Naes, T., Isaksson, T., Fearn, T., & Davies, T. (2002). *Outlier detection. A user-friendly guide to multivariate calibration and classification* (pp. 177–189). Chichester, UK: NIR Publications.
- Osborne, B. (2000). Near-infrared spectroscopy in food analysis. In R. A. Meyers (Ed.), *Encyclopedia of analytical chemistry* (pp. 1–14). Chichester: John Wiley & Sons Ltd.
- Reid, L. M., Woodcock, T., O'Donnell, C. P., Kelly, J. D., & Downey, G. (2005). Differentiation of apple juice samples on the basis of heat treatment and variety using chemometric analysis of MIR and NIR data. *Food Research International*, 38(10), 1109–1115.
- Rodriguez-Saona, L. E., Fry, F. S., & Calvey, E. M. (2000). Use of fourier transform near-infrared reflectance spectroscopy for rapid quantification of castor bean meal in a selection of flour-based products. *Journal of Agricultural and Food Chemistry*, 48(11), 5169–5177.
- Schulz, H., Schrader, B., Quilitzsch, R., Pfeffer, S., & Krüger, H. (2003). Rapid classification of basil chemotypes by various vibrational spectroscopy methods. *Journal of Agricultural and Food Chemistry*, 51(9), 2475–2481.
- Shenk, J. S., Workman, J. J., & Westerhaus, M. O. (2007). Application of NIR spectroscopy to agricultural product. In E. W. Ciurczak, & D. A. Burns (Eds.), *Handbook of near-infrared analysis* (3rd ed.). (pp. 347–386) CRC Press.
- Tarr, A., Diepeveen, D., & Appels, R. (2012). Spectroscopic and chemical fingerprints in malted barley. *Journal of Cereal Science*, 56(2), 268–275.
- Vlachos, N., Skopelitis, Y., Psaroudaki, M., Konstantinidou, V., Chatzilazarou, A., & Tegou, E. (2006). Applications of Fourier transform-infrared spectroscopy to edible oils. *Analytica Chimica Acta*, 573–574, 459–465.
- Williams, P. C. (1975). Application of near infrared reflectance spectroscopy to analysis of cereal grains and oilseeds. *Cereal Chemistry*, 52(4), 561–576.
- Williams, P., & Norris, K. H. (2001). *Near-infrared technology in the agricultural and food industries* (2nd ed.). (pp. 296) University of Wisconsin-Madison/American Association of Cereal Chemists.
- Yang, H., Irudayaraj, J., & Paradkar, M. (2005). Discriminant analysis of edible oils and fats by FTIR, FT-NIR and FT-Raman spectroscopy. *Food Chemistry*, 93(1), 25–32.