DOI: 10.5433/1679-0359.2026v47n2p357

Evaluation of dry rubber content of natural rubber sheets by near-infrared spectroscopy: benchtop versus portable instruments

Avaliação do teor de borracha seca (*DRC*) em lâminas de coágulos de borracha natural por espectrometria de infravermelho próximo (*NIRS*): instrumento de bancada versus portátil

Regina Kitagawa Grizotto[1]*; Adriana Novais Martins[2]; Gilberto Batista de Souza[3]; Marli Dias Mascarenhas Oliveira[4]; Antônio Lucio Mello Martins[5]; Elaine Cristine Piffer Gonçalves[1]

Highlights

Multivariate statistical model can be used to evaluate the quality of natural rubber.
Near-infrared spectroscopy (NIRS) enabled rapid, nondestructive analysis of DRC.
NIRS DRC analysis can support quality-based payment systems for natural rubber latex.
Portable and benchtop NIRS devices showed similar performance predicting rubber DRC.

Abstract

The aim of this study was to develop a rapid and accurate method for determining dry rubber content (DRC) in natural rubber sheets using near-infrared spectroscopy (NIRS), an analytical method that is performed via both benchtop and portable spectrometers. Samples of rubber coagula for benchtop NIRS (n = 936) and portable NIRS (n = 987) were collected from a rubber processing cooperative between January 2024 and July 2025 under edaphoclimatic conditions during the dry, transition, and wet seasons. Three different collection methods were used: Conventional, frame, and turning. The coagulum samples were processed into rubber sheets and analyzed for DRC. NIR spectra were subsequently acquired using the transflectance method and the accuracy and precision of the models

[1] Researcher, Colina Regional Development and Research Unit, Agência Paulista de Tecnologia dos Agronegócios, APTA, Colina, SP, Brazil. E-mail: regina.grizotto@sp.gov.br; elaine.piffer@sp.gov.br;
[2] Researcher, Marilia Regional Development and Research Unit, APTA, Marília, SP, Brazil. E-mail: adriana.martins@sp.gov.br
[3] Researcher, SouzaGB Consultoria, Londrina, PR, Brazil. E-mail: souzagilbertob@gmail.com
[4] Researcher, Agricultural Economics Institute, IEA, São Paulo, SP, Brazil. E-mail: marlimascarenhasoliveira@gmail.com
[5] Researcher, Pindorama Regional Development and Research Unit, APTA, Pindorama, SP, Brazil. E-mail: almartins@sp.gov.br
* Author for correspondence

Received: Dez. 02, 2025 Approved: Jul. 03, 2026

were evaluated. The NIR spectra were correlated with reference values to develop chemometric models of calibration using partial least squares (PLS) regression. The calibration equation for benchtop NIRS exhibited R^2, root mean square error of calibration (RMSEC), root mean square error of cross-validation (RMSECV), slope, and offset values of 0.63, 2.04, 2.18, 0.63, and 24.5, respectively. In comparison, portable NIRS presented calibration parameters of 0.51, 2.37, 2.40, 0.51, and 32.0, respectively, for the same coefficients. The precision and accuracy (external validation) of the fitted models were tested using an independent sample set (n = 163) not included in the calibration step and randomly selected by the chemometric software. The external validation results revealed that both benchtop and portable NIRS exhibited similar performance in predicting the DRC in natural rubber sheets, with very close values of R^2, root mean square error of prediction (RMSEP), SEP, Pearson's correlation coefficient (r), and bias. The R^2 values of 0.68 for benchtop NIRS and 0.61 for portable NIRS, as well as the other performance metrics [residual prediction deviation (RPD) and range error ratio (RER)], reveal that the models should be applied with caution in direct operational use. Overall, both the benchtop and portable NIRS models exhibited potential for predicting DRC in natural rubber sheets. However, before routine analytical application, the models should be further improved through the inclusion of new samples and continuous recalibration. Although the benchtop model exhibited slightly higher accuracy, analyses must be performed under laboratory conditions. Conversely, the portable model offers the advantage of real-time and in situ analysis.
Key words: Chemometrics. DRC. Natural rubber. NIR spectroscopy. PLS. Seasonal variation.

Resumo

O objetivo deste trabalho foi desenvolver um método rápido e preciso para determinação do teor de borracha seca (*DRC*) em lâmina de coágulo de borracha, utilizando a espectroscopia no infravermelho, *Near Infrared* (*NIR*) *Spectroscopy* (*NIRS*), como técnica analítica, em espectrômetros de bancada e portátil. Amostras de coágulos de borracha natural para o *NIRS* de bancada (n = 936) e *NIRS* portátil (n = 987) foram coletadas de uma cooperativa processadora de borracha, no período de janeiro de 2024 a julho de 2025, nas condições edafoclimáticas das épocas de seca, de transição e de águas. Foram utilizados três diferentes métodos de coleta: convencional, quadrado e revolvimento. Os coágulos foram processados na forma de lâminas e analisados o *DRC*. Após, os espectros *NIR* das amostras foram obtidos utilizando o método transflectância, e a acurácia e a precisão do modelo foram investigadas. Os espectros *NIR* foram associados aos resultados laboratoriais para construir modelos quimiométricos de calibração pelo método de regressão por mínimos quadrados parciais (PLS). A equação de calibração utilizando o NIRS de bancada apresentou valores dos parâmetros de calibração R2, RMSEC, RMSECV, *Slope* e *Offset* de 0,63; 2,04; 2,18; 0,63; 24,5, respectivamente. Por sua vez, o NIRS portátil apresentou parâmetros de calibração 0,51; 2,37; 2,40; 0,51; 32,0, respectivamente para os mesmos coeficientes. Os modelos ajustados foram testados quanto a precisão e exatidão (validação externa) utilizando um conjunto independente de amostras (n = 163) não incluídas na construção dos modelos de calibração e selecionadas aleatoriamente pelo software quimiométrico. Os resultados da validação externa mostraram que os *NIRS* de bancada e portátil apresentaram habilidades similares na predição do DRC de coágulo de borracha em lâminas, com R^2, RMSEP, SEP, r (Pearson) e *bias* muito próximos. Os valores de R^2 iguais a 0,68 (*NIRS* de bancada) e 0,61 (*NIRS* portátil) e demais métricas (*RPD* e *RER*),

indicam que os modelos ainda devem ser aplicados com cautela em uso operacional direto. De modo geral, os métodos desenvolvidos tanto para o *NIRS* de bancada como o portátil apresentam potencial para predizer os valores de *DRC* em coágulo de borracha em lâminas. Entretanto, antes da aplicação rotineira nas análises, os modelos devem ser aprimorados por meio da inclusão de novas amostras e de recalibrações contínuas. Embora o modelo de bancada tenha a vantagem de ser ligeiramente mais preciso, as análises precisam ser realizadas sob condições laboratoriais. Em contrapartida, o modelo portátil tem a vantagem de ser usado em tempo real e em análise *in situ.*
Palavras-chave: Quimiometria; DRC; Coágulo de borracha; Espectrometria NIR ; PLS; Variação sazonal.

Introduction

The dry rubber content (DRC) of latex is the weight percentage of dry rubber present in 100 g of latex, precipitated by the action of an acid solution, whose liquid (whey) part is separated from the solid part by pressure (Maraphum et al., 2022). After being pressed, the rubber clot can undergo drying at varying parameters from 16 h to 70 °C (Maraphum et al., 2022), 10 h to 105 °C (Suchat et al., 2015) or other parameters (Puttipipatkajorn & Puttipipatkajorn, 2020). In Brazil, there is no consensus regarding the parameters for determining the DRC of natural rubber clots by processing plants. The research team of the São Paulo Agribusiness Technology Agency (Agência Paulista de Tecnologia dos Agronegócios - APTA) of the Secretariat of Agriculture and Supply of the State of São Paulo audited and determined that, as in the case of soil analysis laboratories, there is no standardized methodology for DRC analysis in Brazilian rubber processing plants; each unit has its own methodology. Even today, most Brazilian producers are paid by the weight of the rubber measured in the field and the buyer establishes the amount to be paid to the producer without considering the DRC (Gonçalves et al., 2024a,b). To address the lack of standardization of the methodology for determining the DRC, the APTA research team, with support from the private sector, has been working since 2023 to define the methodology to form the basis of payments to producers in the future.

Near-infrared spectroscopy (NIRS) has been considered an alternative to conventional analytical methods in the laboratory (wet method) because of the lack of use of chemical reagents, low operational cost and rapid acquisition of results without causing destruction of the sample. It is an analytical technique widely used in the development of predictive models of the chemical composition of various agricultural products (Abreu et al., 2023a,b; Campos et al., 2024; Cozzolino & Labandera, 2002; Lobos et al., 2019; Murphy et al., 2019; Rambo et al., 2020; Serafim et al., 2020; Trópia et al., 2023), among others. NIRS analysis reveals the vibration of functional groups present in matter in the infrared region (750 nm to 2500 nm) that are correlated with chemical measurements, allowing the development of multivariate calibration models (Pasquini, 2003).

NIR spectrometers are extremely versatile instruments that do not cause destruction of the sample, and the portable version is suitable for field applications. Studies conducted in Thailand have reported that NIRS can be used to evaluate the quality of rubber clots in terms of moisture content (Suchat et al., 2015; Puttipipatkajorn & Puttipipatkajorn, 2020), total solids content (Maraphum et al., 2022), and DRC (Maraphum et al., 2022; Siano et al., 2022) and even reveal evidence of fraud (Maraphum et al., 2022). Therefore, we assume that it is possible to develop mathematical models for the evaluation of DRC in Brazilian samples using NIRS.

Thus, this study was conducted on the basis of the following hypotheses: i) It is possible to develop a robust chemometric model for estimating the DRC in rubber clots using NIRS, even when the samples are obtained under nonexistent conditions of controlled collection, coagulation and storage; and ii) the variability among the different practices adopted by farmers can be incorporated into the model, resulting in the development of a predictive tool representative of the real conditions in rubber processing plants. In this context, the objective of this study was to construct chemometric calibration models to estimate the DRC in rubber clots, using two types of NIR spectrometers, benchtop and portable, and to compare the calibration and validation parameters of the models. For the benchtop version, the NIRFlex N-500® (Büchi Labortechnik, Flawil, Switzerland) model was used; for the portable version, the MicroNIR OnSite-W model (Viavi Solutions, Milpitas, USA) was used.

Material and Methods

Natural rubber clots

A total of 79 lots from different farmers, containing approximately 15 kg of rubber clots per lot, were collected from a processing company in the northern region of the state of São Paulo, Brazil, during the period from 01/18/2024 to 07/01/2025, under the edaphoclimatic conditions of the wet season, transition period and drought. The rural producers of natural rubber curds were located in the northwestern region of the state of São Paulo, west of the state of Minas Gerais and east of Mato Grosso do Sul, Brazil. In these regions, from where the samples were obtained, the wet season, with the highest rainfall, is from November to February; the transition period occurs in March, April, May and October; and the dry season, with lower rainfall, is from June to September.

Each lot (15 kg) was divided into 3 sublots of 5 kg each according to the clot collection procedure followed in the company: 1) Conventional; 2) frame/square; and 3) turning/mechanical separation of the load. Conventional collection is adopted by the cooperative and consists of randomly removing clots from the sides of the heap. Frame/square-type collection consists of randomly throwing a 1 x 1 m square mold at 4 different points of the load, and 4 clots, one from each point, are collected. Collection by turning/mechanical separation consists of separating the load with the aid of a tractor and removing the samples from 6 points of the central part. The objective of investigating the 3 types of collection was to

randomize and reduce the effect of human variation regarding the choice of clots.

The rubber clot processing company works in the cooperative system and receives lots from several rural producers in the states of São Paulo, Minas Gerais and Mato Grosso do Sul. The frequency of collection varied according to the season: Once a week in the wet season and, according to supply, in the dry season, owing to the natural decrease in latex production. The seasonal range is highly important in the construction of robust linear regression models, given the variability of the DRC results as a function of high or low rainfall.

Preparation of rubber clot slides

The clot lots (15 kg), subdivided into sublots (3 kg), were prepared in the form of slides at APTA Regional de Marilia (APTA Regional-Marilia) on the day following collection. The preparation consisted of pressing the clots in a *calender*, a crepe model with a 200 mm diameter and 400 mm wide rollers (Usitecnica, Olimpia, Brazil). The calender results in the joining of the clots under pressure until a blanket is obtained. Each mat was passed 5 times through the calender until a sheet of approximately 7 mm was obtained (Figure 1a). From the central part of the slides, samples of 130 x 130 x 7 mm (L x P x A) (Figure 1a, 1b) were removed and sent for DRC analysis in the same research unit.

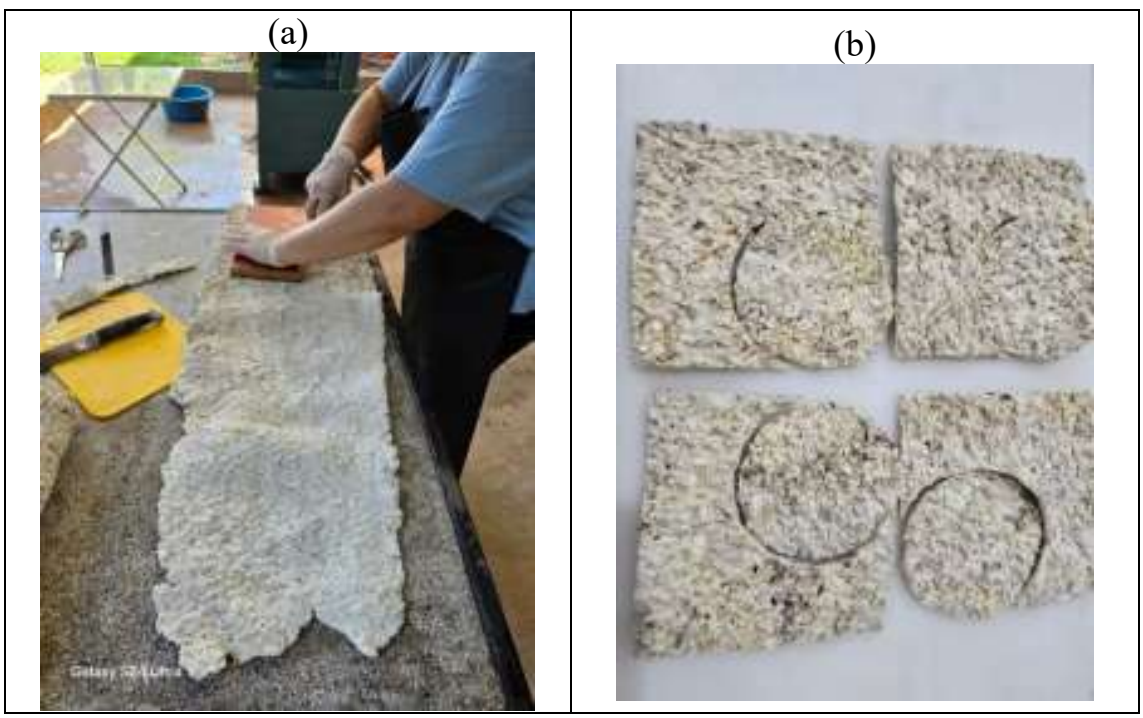


Figure 1. Image of the 7-mm-thick rubber clot slide. (a) Sections measuring 130 × 130 × 70 mm for spectrum collection in portable NIRS, and (b) details of the 9-cm diameter disc for spectrum collection in benchtop NIRS.

Analysis of DRC by the laboratory reference method (LRM)

In total, 948 samples (79 lots x 3 types of collection x 4 replicates) of laminated rubber (130 x 130 x 7 mm) were subjected to DRC analysis via the LRM at the APTA Regional-Marilia. The DRC was determined by drying the samples in an oven with air circulation at 120 °C for 4 hours until a constant weight was reached, with 4 repetitions, according to the methodology adapted from the International Organization for Standardization (ISO) 126 standard (Associação Brasileira de Normas Técnicas [ABNT], 2011). DRC was calculated by gravimetry according to Equation 1.

$$DRC = \left(\frac{P2}{P1}\right) \times \left(\frac{P4}{P3}\right) \times 100 \text{ Eq. 1}$$

where:

P1 – Initial weight of the total sample (kg)

P2 – Total weight of the mat after lamination (calendering) (kg)

P3 – Weight of the mat subsample (g)

P4 – Weight of the mat subsample after oven drying (g)

Analysis of DRC by NIRS

DRC analysis in portable and benchtop NIR spectrometers was performed at APTA Regional de Colina (APTA Regional-Colina). Nine hundred thirty-six samples (n = 936) of laminated rubber (130 x 130 x 7 mm) (Figure 1a) were analyzed on a portable MicroNIR OnSite-W spectrometer (Viavi Solutions, Milpitas, CA, USA), and nine hundred eighty-seven samples (n = 987) were analyzed on a NIRFlex benchtop spectrometer N-500® (Büchi Labortechnik, Flawil, Switzerland).

For each sample, 12 spectral measurements were obtained at different points, and the mean was calculated, which was used in the development of the regression model. In the portable NIR spectrometer, 12 measurements were obtained by manually activating the equipment at different points of the sample to capture the spectrum with a mean spectral resolution of 6 nm in the region of 908 to 1676 nm using Spectral Software v.4.3.5.1. 105 (Viavi Solutions, Milpitas, USA). Each spectral measurement consisted of 200 spectra with a 6.5 ms acquisition time for each spectrum, resulting in a total time of 1.3 s for the acquisition of a spectral measurement. In the benchtop NIR spectrometer, the 12 measurements were programmed in the spectrum capture software NIRWare Operator version 1.6.6000 (Büchi, Flawil, Switzerland). The spectral data were collected in the region of 1000 to 2500 nm (10,000 to 4000 cm^{-1}) with a resolution of 8 cm^{-1}. Each spectral measurement consisted of an average of 32 spectra, resulting in an acquisition time of 30 seconds for each sample. Owing to the specificity of benchtop NIRS, it was necessary to section the subsamples into 9 cm diameter discs (Figure 1b). Both devices measured the variations in the dipole moment (electronegativity difference) as a result of the vibrational movement of its atoms present in matter but differed in terms of configuration, as shown in Table 1.

Table 1
Bromatological composition of the Control Diet (CD) and Silage Diet (SD) on a dry matter basis

Characteristics	NIRFlex N-500 ®	MicroNIR OnSite-W
Type	Bench	Portable
Manufacturer	Büchi Labortechnik	Viavi
Wavelength range (nm)	800 to 2500 nm	900 to 1700 nm
Wavelength range (cm^{-1})	4000 to 12.000 cm^{-1}	-
Resolution (nm)	1.25 x 106 nm	6 nm
Resolution (cm^{-1})	8 cm^{-1}	33 cm^{-1}
Scan by spectrum	32	-
Signal/Noise	10.000:1	25.000:1
Bulb type	Tungsten-halogen	Integrated vacuum tungsten
Laser type	12 VDC HeNe, up to 633 nm	-
Monochromator	FT-NIR polarization Interferometer	LVF – Linear Variable Filter
Detector	Single element InGaAs	128 elements InGaAs D AD
Dimensions	350 x 250 x 450 mm (w x h x l)	194 x 47 mm (w x h)
Weight	15 kg	275 g
Type	Bench	Portable
Manufacturer	Büchi Labortechnik	Viavi

Statistical analysis

Descriptive analysis of DRC values in rubber clots via the LRM was performed using the PROC MEANS procedure. For the regression model and Pearson's correlation, the PROC REG and PROC CORR procedures, respectively, were used. The DRC data were analyzed by *fitting mixed* models using the MIXED procedure, considering the following fixed effects: Type of collection, time of collection, and interaction between the type and time of collection, and repetitions as a random effect. The effects were separated by least square (LS) means using Tukey's test at a 5% SAS probability for collection time and collection type. The data were analyzed using SAS® OnDemand for Academics software (SAS Institute Inc., Cary, NC, USA).

The multivariate calibration models for the DRC were constructed using the chemometric software Unscrambler X, version 10.4 (CAMO Software, Oslo, Norway). The dataset was randomly divided into two groups, with one group for calibration and cross validation and the other group for external validation, resulting in the formation of two subgroups of independent samples. Of the total samples analyzed using the NIRflex (n = 936) and MicroNIR (n = 987) methods, 773 and 824 samples, respectively, were used for calibration, and 163 samples from each model were randomly separated by the Unscrambler software for external validation. Thus, the same dataset was used for both calibration and external validation, but with different sets of samples at each step. To obtain a more uniform spectrum,

the 12 spectral replicates of each sample were reduced to the average of one spectrum per sample. Initially, the spectral data were converted into logarithms of the inverse of the reflectance [log(1/*R*)], where *R* is the reflectance value obtained for each wavelength. After this transformation, some chemometric pretreatments were applied to the spectral matrix. To reduce overlapping *bands* and to correct the spectral baseline, the Algorithm 1st derivative Savitzky–Golay (sg-1) with a window of 1 to 15 points was applied. In addition, total normalization (*normalization full, n-full*) was applied to reduce system-based variations, such as differences in the size of the parts or sample thickness, of the NIRFlex and MicroNIR. Afterward, the spectral data (matrix X) were linearly combined with the DRC values determined in the laboratory through linear regression via partial least squares (PLS) regression, which is a statistical technique for multivariate data analysis. The model was built by PLS calibration, with cross-validation applied internally to optimize the number of latent variables and evaluate the predictive capacity, preventing *overfitting.* Cross-validation (*Random cross-validation*) with 20 segments consisted of the sequential removal of a group of samples from the calibration set for model validation. The predicted values were continuously compared with the reference values and the deviations were used to calculate the root mean square error of cross-validation (RMSECV).

After the mathematical treatments were applied, the samples considered *outliers* were excluded from the dataset and a new PLS regression model was subsequently developed. The *outliers* were evaluated using the statistical tool Hotelling's T^2 and *Q-residuals* [squared prediction error (SPE)] derived from the PLS model, with a significance level of 5%. The interpretation was performed jointly, considering both the distance in the model space (T^2) and the reconstruction error (*Q-residuals*), allowing us to differentiate between structurally extreme samples and samples that fit poorly into the model. The removal or retention decisions were based on the original data and the chemical consistency of the samples.

The PLS regression was performed considering the following statistical indices: 1) The coefficient of determination (R^2) of the calibration sets (R^2_C) and cross-validation (R^2_{CV}); 2) the square root of the standard error of calibration [root mean square error of calibration (RMSEC)]; 3) the square root of the standard error of cross-validation [root mean square error of cross-validation (RMSECV)]; and 4) the slope and offset, which are, respectively, the slope of the curve (β_1) and the intercept (β_0) of the linear regression model:

$y = \beta_0 + \beta_1 \times X$, where X represents the predicted value and y represents the observed value (Trópia et al., 2023).

The models that had the highest R^2 value and the lowest possible RMSEC and RMSECV values were selected.

According to Guimarães et al. (2023), a correlation is considered good when $R^2 \geq 0.75$, with lower standard error of prediction (SEP) and standard error of calibration (SEC) values that are closer to each other, in addition to the lowest value of the square root of the mean prediction error [root mean square error of prediction (RMSEP)] obtained in the external validation. The systematic error (*bias*) should not be greater than 0.6

times the SEC value (Guimarães et al., 2023). The closer the *slope* is to 1 and the closer *the offset* is to zero, the better the quality of the regression (Trópia et al., 2023).

The values of the residual prediction deviation (RPD) and the range error ratio (RER) were used to evaluate the performance of the calibration models and for external validation (Maraphum et al., 2022; Puttipipatkajorn & Puttipipatkajorn, 2020; Rambo et al., 2020; Serafim et al., 2020; Siano et al., 2022; Suchat et al., 2015). The RPD is calculated by the ratio between the standard deviation of the reference values by RMSEC or RMSECV (Puttipipatkajorn & Puttipipatkajorn, 2020), and the RER is calculated by the ratio between the amplitude of the concentration range of the reference values by the SEC or SEP value (Serafim et al., 2020).

The PLS model was chosen, an external validation test was performed to estimate the precision and accuracy parameters using an independent sample group (n = 163). In addition to R^2, *slope and* offset, other statistical indices obtained in the external validation were included: Correlation, r (Pearson), RMSEP, SEP, and systematic error (*bias*). The RMSEP exhibited agreement between the values estimated by the NIRS and the reference values (LRM). RMSEP = standard error + *slope* + *bias*; SEP = standard error + *slope* (Guimarães et al., 2023). Thus, the RMSEP is considered the most complete index for estimating the standard error (Guimarães et al., 2023). Parallel to the use of chemometric tools to evaluate the external validation parameters, a paired Student's t test was performed to compare the mean DRC values predicted by the calibration models of the NIRFlex and MicroNIR equipment, using an independent set of samples (n = 116) not used in the development of the calibration models. The test was used to evaluate the agreement and predictive performance of the two devices.

Results

Results of the descriptive analyses of the DRC data of the rubber clot samples obtained by the LRM used in the construction of the regression models via benchtop NIRS (n = 936) and portable NIRS (n = 987) are presented in Tables 2a and 2b, respectively. The results revealed low variation in the DRC values, with a coefficient of variation (CV) of 5% (Table 2a and 2b) and a standard error of the mean (SEM) between 0.15 and 0.23 (Table 3a and 3b), at different times of the year (wet, transition and dry) and under different types of collection (conventional, frame/square and turning/mechanical load separation). Analysis of variance (ANOVA), through a fixed effects test applied to the laboratory DRC data obtained for NIRFex (n = 936) (Table 3a) and MicroNIR (n = 987) (Table 3b) revealed that there was a difference ($p < 0.0001$; $p < 0.001$) in the collection time effect (E) of the two devices. No differences were observed for the type of collection (TC), with $p = 0.3726$ for NIRFlex (Table 3a) and $p = 0.4942$ for MicroNIR (Table 3b), nor for the interaction between the effects (E □ TC), with $p = 0.2288$ for NIRFex (Table 3a) and $p = 0.093$ for MicroNIR (Table 3b). A Tukey test was performed, which revealed differences between the means of the DRC values, with higher values ($p < 0.05$) for samples collected in the dry season, i.e., 67.23% (NIRFlex) (Table 3a) and 66.39% (MicroNIR) (Table 3b), and lower values ($p < 0.05$) for samples collected in the wet season, i.e., 65.09% (NIRFlex)

(Table 3a) and 65.25% (MicroNIR) (Table 3b). For samples collected during the transition period, means of 66.04% (NIRFlex) (Table 3a) and 66.03% (MicroNIR) (Table 3b) calculated between the 3 types of collection were statistically equal ($p > 0.05$).

Table 2.a
Descriptive analysis of dry rubber content (DRC) values of rubber clots obtained by the laboratory reference method (LRM) by collection time (n = 936) and type of collection (n = 936) used in the calibration of the NIRFlex benchtop NIRS

Collection time	n[1]	Mean	Minimum	Maximum	EP[2]	CV[3]
Wet	219	65.11	54.57	73.35	0.23	5%
Transition	501	66.04	58.10	74.90	0.15	5%
Dry	216	67.23	60.10	73.25	0.23	5%
Total	**936**					
Type of collection						
Conventional	315	66.24	56.06	74.90	0.20	5%
Frame	308	65.84	54.57	73.98	0.21	5%
Turning	313	66.20	55.81	73.35	0.21	5%
Total	**936**					

[1] Number of samples; [2] Standard Error; [3] Coefficient of Variation

Table 2.b
Descriptive analysis of dry rubber content (DRC) values of rubber clots obtained by the laboratory reference method (LRM) by collection time (n = 987) and type of collection (n = 987) used in the calibration of the MicroNIR portable NIRS

Collection time	n[1]	Mean	Minimum	Maximum	EP[2]	CV[3]
Wet	224	65.24	54.57	73.73	0.23	5%
Transition	476	66.03	58.10	74.90	0.17	5%
Dry	287	66.40	60.10	73.25	0.20	5%
Total	**987**					
Type of collection						
Conventional	327	66.03	58.39	74.90	0.20	5%
Frame	331	65.74	54.57	73.98	0.19	5%
Turning	329	66.11	55.81	73.35	0.20	5%
Total	**987**					

[1] Number of samples; [2] Standard Error; [3] Coefficient of Variation

Table 3.a
Analysis of Variance: Fixed effects test for Time of collection (E), Type of Collection (TC), and Interaction (E x TC) of the dry rubber content (DRC) of rubber clots obtained by the laboratory reference method (LRM) (n = 936) for benchtop NIRS calibration (NIRFex)

Season	Type of collection			Mean	*p* -Value			
	Traditional	Frame	Turning	Type of collection	SEM [1]	Season (E)	Collection Type (TC)	E x CT
Wet	65.70 [b, A]	64.47 [b, A]	65.10 [b, A]	65.09	0.23			
Transition	66.15 [a,b, A]	65.68 [b, A]	66.28 [b, A]	66.04	0.15	< 0.0001	0.3726	0.2288
Dry	67.02 [a, A]	67.52 [a, A]	67.15 [a, A]	67.23	0.23			

[1] Standard Error of the Mean
Different lowercase letters in columns indicate differences according to Tukey's test at 5% probability. The same uppercase letters in a row indicate no differences according to Tukey's test at 5% probability.

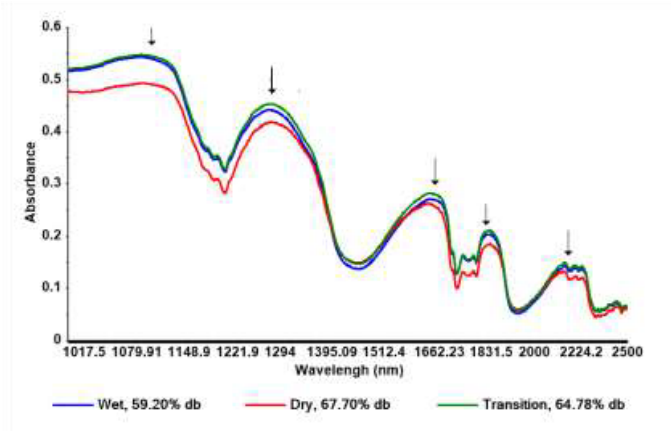
Table 3.b
Analysis of Variance: Fixed effects test for Time of collection (E), Type of Collection (TC), and Interaction (E x TC) of the dry rubber content (DRC) of rubber clots obtained by the laboratory reference method (LRM) (n = 987) for calibration in portable NIRS (MicroNIR)

Season	Type of collection			Mean	*p* -Value			
	Traditional	Frame	Turning	Type of collection	SEM [1]	Season (E)	Collection Type (TC)	E x CT
Wet	65,92 [a, A]	64.84 [b, A]	64.99 [b, A]	65.25	0.20			
Transition	66.13 [a, A]	65.65 [b, A]	66.30 [b, A]	66.03	0.16	< 0.001	0.4942	0.0930
Dry	65.94 [a, A]	66.61 [a, A]	66.63 [a, A]	66.39	0.23			

[1] Standard error of the mean
Different lowercase letters in columns indicate differences according to Tukey's test at 5% probability. The same uppercase letters in a row indicate no differences according to Tukey's test at 5% probability.

The raw spectra, i.e., without any chemometric pretreatment, obtained from three samples of rubber clot slides selected from the different edaphoclimatic seasons (wet, transition and dry) through the respective benchtop (Figure 2a) and portable NIRS (Figure 2b) systems are shown in Figure 2. The wavelength ranges varied according to the specificity of the equipment, i.e., 1000 to 2500 nm for the benchtop NIRFlex spectrometer and 900 to 1700 nm for the portable MicroNIR spectrometer. The raw spectra obtained via benchtop NIRS (Figure 2a) revealed a greater number of peaks compared with those obtained via portable NIRS (Figure 2b). This difference in spectral behavior is due to the greater number of points used to form the spectra (1501 points per average spectrum or sample) of benchtop NIRS compared with the data matrix (125 points per average spectrum or sample) of portable NIRS. In the raw spectra of portable NIRS, there were three distinct absorbance peaks in different wavelength

ranges: 1063 to 1106 nm (peak 1), 1273 to 1280 nm (peak 2) and 1620 to 1658 nm (peak 3). In turn, in benchtop NIRS raw spectra, 5 peaks were observed in the ranges of 1054 to 1109 nm (peak 1), 1266 to 1288 nm (peak 2), 1625 to 1645 nm (peak 3), 1822 to 1829 nm (peak 4) and 2222 to 2234 nm (peak 5). In the region from 1000 to 2500 nm (Figure 2a) or in the region from 908 to 1300 nm (Figure 2b), the red line indicating lower absorbance corresponded to the dry season sample with a higher DRC (67.70% dry base). The upper lines indicated higher absorbance, which were associated with lower DRC, corresponding to samples collected in the wet season (54.20% dry base) and transition period (64.78% dry base). Maraphum et al. (2022) reported that the band corresponding to water vibrates in the range of 1152 to 1205 nm and 1715 to 1779 nm in natural rubber clots. Puttipipatkajorn and Puttipipatkajorn (2020) reported that different moisture levels of rubber clots on 3 mm slides resulted in different spectral behaviors, which is in agreement with the findings of this study. Samples with lower moisture content (higher DRC) had lower absorbance values, whereas samples with higher moisture content (lower DRC) had higher absorbance values in the range of 1400 to 1600 nm.



(a)

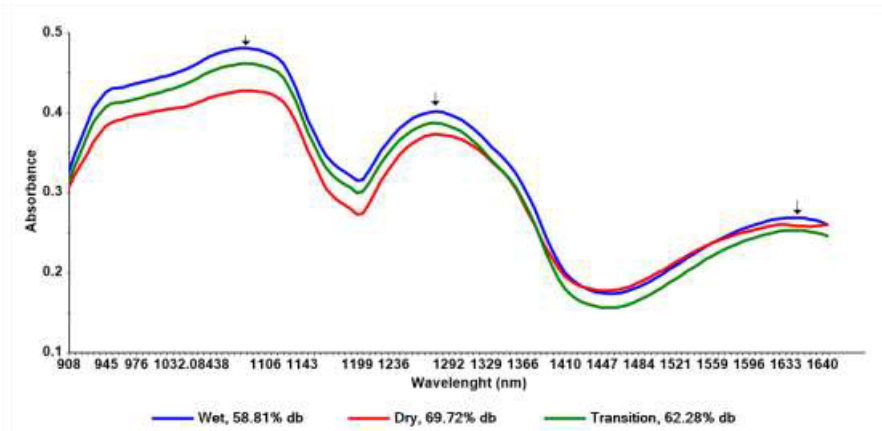
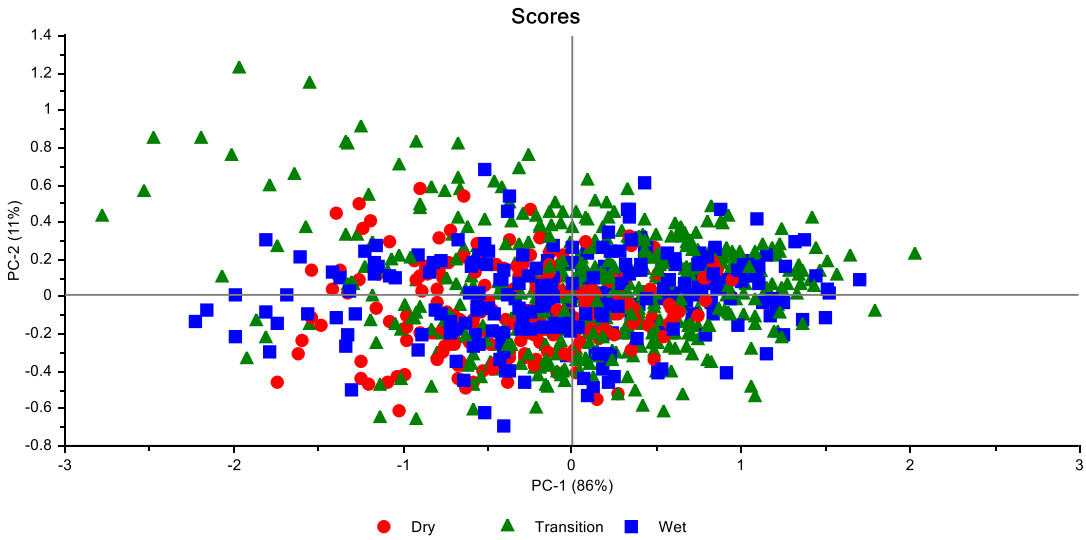
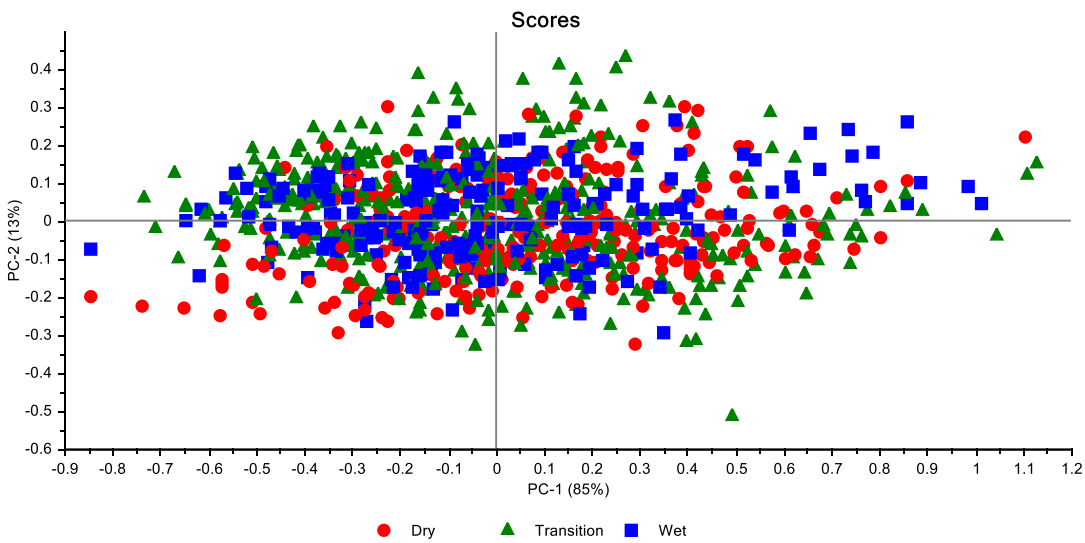


Figure 2. Raw NIR spectra obtained from three samples of rubber clot slides during the wet, transition and dry periods in a benchtop NIRFlex spectrometer (a) and a portable MicroNIR spectrometer (b). The colored lines represent the samples.

The spectral variability according to the principal component analysis (PCA) of the rubber clot samples are illustrated in Figure 3. Of the three principal components that were considered for the construction of the model, two components corresponded to 97% (Figure 3a) and 98% (Figure 3b) of the data variability, of which 86% and 85% were explained by component 1 (PC1) and 11% and 13% by component 2 (PC2) for benchtop NIRS (Figure 3a) and portable NIRS (Figure 3b), respectively.



(a)



(b)

Figure 3. Principal component analysis (PCA) of the rubber clot slide samples, grouped according to season (dry, wet and transition), in an NIRFlex (a) and portable MicroNIR (b) spectrometer.

The statistical parameters of the linear regression model for DRC are presented in Table 4 for benchtop NIRS (NIRFlex) and portable NIRS (MicroNIR). The same pretreatments (dg-1 and n- *full*) were applied to fit the models for both instruments. The numbers of samples in the calibration and cross-validation, and in the external validation, in the benchtop and portable NIRS models, were not equal because of the *outliers* detected in each procedure. The range of variation in the DRC values of the calibration model was 55.80% to 74.90% (Table 4). For benchtop NIRS (NIRFlex), the calibration (RMSEC) and cross-validation (RMSECV) errors were 2.04 and 2.18, respectively, and the coefficients of determination (R2) of the calibration and cross-validation were 0.63 and 0.57, respectively (Table 4). Conversely, for portable NIRS, RMSEC and RMSECV were close to 2.4, and R2 was equal to 0.51 (calibration) and 0.50 (cross-validation) (Table 4). The slope (Slope) and the intersection on the Y axis (Offset) of the linear regression were 0.63 ($p < 0.0001$) and 24.48 ($p < 0.0001$), respectively, for benchtop NIRS and 0.51 ($p < 0.0001$) and 32.02 ($p < 0.0001$), respectively, for portable NIRS (Table 4). Thus, the benchtop NIRS model presented better correlation coefficients in the calibration (R2cal) and cross-validation (R2cv) equal to 0.63 and 0.57, respectively, when compared with those obtained for portable NIRS, with R2cal = 0.51 and R2cv = 0.50 (Table 4). The quality indices of the predictive ability of the models, namely, the RPD and the RER, were 1.64 and 9, respectively, for the NIRFlex (Table 4) and 1.44 and 8, respectively, for the MicroNIR (Table 4).

The results of the descriptive analysis and the statistical parameters of the sample groups used in the model accuracy test (external validation), considering all the samples (n = 163) and after the removal of samples with residues greater than ±4 for NIRFlex (n = 144) and MicroNIR (n = 140) are shown in Table 5. With the withdrawal of discrepant samples, all the validation statistical parameters were satisfactory; for example, the coefficient of determination (R2), RMSEP, SEP, RPD and RER values for benchtop NIRS were 0.68, 1.84, 1.83, 1.78 and 9, respectively. For portable NIRS, the same parameters were 0.61, 1.95, 1.94, 1.60 and 8, respectively. The prediction errors were similar but slightly lower for NIRFlex (RMSEP = 1.84) than for MicroNIR (RMSEP = 1.95). Analysis of the systematic error (bias) revealed similar values between the devices, which were 0.199 for portable NIRS and -0.166 for benchtop NIRS. The Pearson correlation coefficients were 0.83 ($p < 0.0001$) for benchtop NIRS and 0.78 ($p < 0.0001$) for portable NIRS indicating good correlation between the values predicted by NIRS and the laboratory reference values.

Table 4

Statistical parameters of the linear regression model, with the calibration (C) and cross-validation (CV) sets for predicting the dry rubber content (DRC) of rubber clots in benchtop NIRS (NIRFlex) and portable NIRS (MicroNIR)

NIR	Pre-treatment	VL[1]	n[2]	Range	*Slope*[3] (C/CV)	*Offset*[4] (C/CV)	RMSEC[5]	RMSECV[6]	R^2[7] (C/CV)	RPD[8]	RER[9]	Calibration date
NIRflex	dg1[10], n-full[11]	11	773	55.80–74.90	0.63/0.60	24.48/26.64	2.04	2.18	0.63/0.57	1.64	9	07/21/2025
MicroNIR	dg1, n-full	7	824	55.81–74.90	0.51/0.51	32.04/32.48	2.37	2.40	0.51/0.50	1.44	8	07/18/2025

[1]Latent Variable - number of variables; [2]number of samples; [3]Angular coefficient (Slope); [4]Intercept (Offset); [5]Square Root of Standard Error of Calibration; [6]Square Root of Standard Error of Cross Validation; [7]Coefficient of determination; [8]Residual Predictive Deviation; [9]Range and Error Ratio Range Error Ratio; [10]Savitzky–Golay first derivative; [11]Total normalization

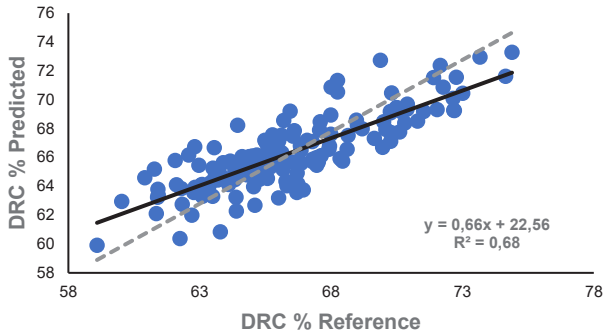
Table 5

Descriptive analysis and statistical parameters of the external validation of dry rubber content (DRC) of rubber clots, obtained by benchtop NIRS (NIRFlex) before (n = 163) and after the removal of outliers (n = 144) and portable NIRS (MicroNIR) before (n = 163) and after the removal of outliers (n = 140)

Spectrometer	n[1]	Mean	Minimum	Maximum	DP[2]	*Offset*[3]	*Slope*[4]	R^2[5]	r[6]	RMSEP[7]	SEP[8]	*RPD*[9]	RER[10]	*Bias*[11]
NIRflex	163	66.49	54.57	74.89	3.56	31,02	0,53	0.46	0.68	2.62	2,62	1,35	8	-0,189
NIRflex	144	66.55	59.09	74.89	3.26	22,56	0,66	0,68	0,83	1.84	1,83	1.78	9	-0,166
MicroNIR	163	65.57	57.11	75.13	3.36	34,12	0,48	0,38	0,40	2,64	2,64	1.27	6	0,237
MicroNIR	140	65.54	58.29	73.13	3.11	24,69	0,63	0,61	0,78	1,95	1,94	1.60	8	0,199

[1] number of samples; [2]standard deviation; [3]Intercept (Offset) ; [4]Angular coefficient (Slope); [5]coefficient of determination; [6]Pearson correlation; [7]Root Mean Square Error of Prediction; [8]Standard Error of Prediction; [9]Residual Predictive Deviation; [10]Range Error Ratio ; [11]Systematic error

Paired t tests revealed that there was no significant difference between the DRC values predicted by the PLS models obtained with the NIRFlex and MicroNIR equipment (t = 0.025; p = 0.9802), indicating the absence of systematic bias between the methods. The predicted means of DRC were practically identical, corresponding to 64.522 for NIRFlex and 64.518 for MicroNIR. The Pearson correlation coefficient (r = 0.767) indicated a moderate to strong positive association between the values obtained by the NIRFlex and MicroNIR devices, indicating that both exhibit consistent behavior, although not perfectly concordant. The regressions between the reference values (LRM) and the predicted values for benchtop and portable *NIRS* in the external validation are shown in Figure 4. The relationships between the DRC values obtained by the LRM and those predicted by NIRS revealed low coefficients of determination R^2 values of the regressions, 0.68 (Figure 4a) and 0.61 (Figure 4c), respectively. The Pearson correlation coefficient (r) was 0.83 ($p < 0.0001$) for benchtop NIRS and 0.78 ($p < 0.0001$) for portable NIRS, indicating good correlation between the predicted values (NIRS) and laboratory reference values. The distribution analysis of the residuals of the PLS model for benchtop (Figure 4b) and portable NIRS (Figure 4d) revealed random dispersion around zero, with no systematic trend along the concentration range evaluated for both devices. There was also no evident nonlinear behavior, suggesting the stability of the equipment in the external validation. In the benchtop NIRS, small punctual deviations were observed but lacked structural characteristics, indicating good predictive performance of the equipment (Figure 4b). Compared with the benchtop model, the portable NIRS model (Figure 4d) had greater error dispersion and presence of extreme values. These results reveal the adequate performance of both devices in the external validation with greater variability associated with the portable device.



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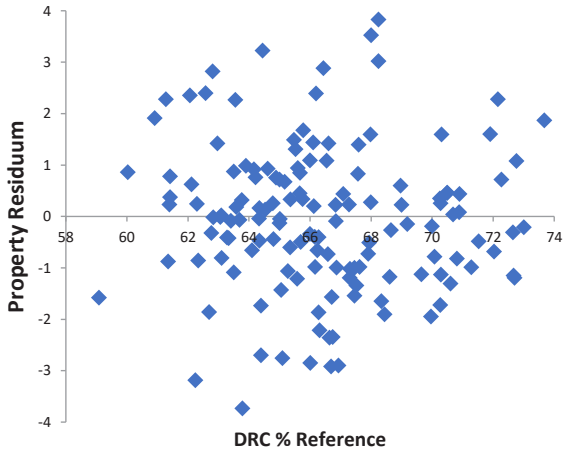

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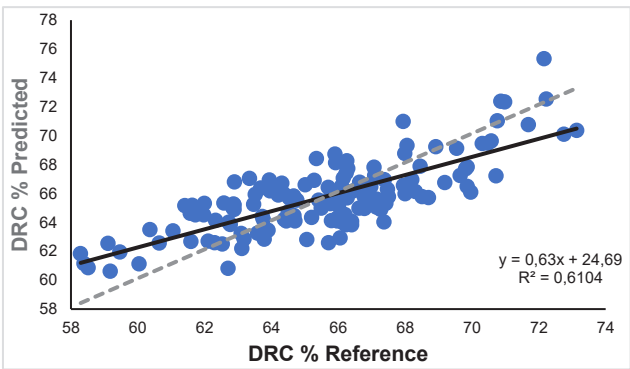

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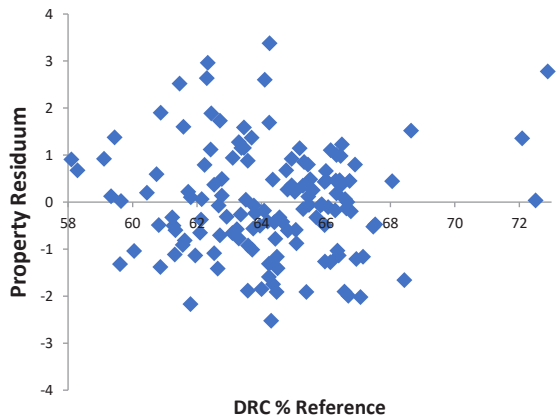

(d)

Figure 4. Relationships between the reference and predicted values for DRC of rubber clots obtained in the external validation by benchtop NIRS via NIRFlex (a) (n = 144) and portable NIRS via MicroNIR (c) (n = 140). The blue dots indicate individual observations. Relationships between the predicted values and the residuals of the cross-validation for DRC in rubber clot slides, measured by benchtop NIRS (b) and portable NIRS (d). The solid black line represents the relationship between the reference and predicted values (a, c). The dashed line is the bisector (Y = X) (a, c).

Discussion

Safe and rapid determination of the DRC in the rubber coagulum is highly important for the production chain because it introduces the possibility of remuneration on the basis of quality instead of only weight, as currently occurs in Brazil with most rural natural rubber producers. The determination of DRC by NIRS is considered reliable because it is a technique with high analytical frequency (Pasquini, 2003) and is capable of obtaining measurements in a few minutes (Grizotto et al., 2019). It is much faster than laboratory-based methods that require 16 h for DRC determination (Maraphum et al., 2022).

An interesting finding was the influence of seasonal variation on DRC values. Higher DRC values were obtained for samples collected in the dry season, which lasts from June to September in Brazil. During this season, characterized by lower rainfall, there is a natural decrease in latex production. In contrast, for samples collected in the wet season (November to February) and during the transition season (March to May and October), the DRC values decreased. These findings may be important for decision-making regarding the implementation of systems that favor the production of latex during the dry season, such as the irrigation of rubber plantations. The differences in the absorbances of the raw spectra acquired for samples collected in different edaphoclimatic seasons (wet, transition and dry) provide insights into the significant differences in the DRC values of the samples collected during these periods.

With respect to the types of collection (conventional, frame/square and turning/mechanical separation), there were no differences ($p < 0.05$); i.e., the randomness or the human effect in the choice of clots was not proven, which is reflected in higher or lower DRC values. However, standardization of the method of clot collection may increase the uniformity of the methodology for determining DRC by the research team.

The objective of the evaluation of chemometric models was to determine the accuracy, precision and robustness in the prediction of chemical properties. NIR spectroscopy of agricultural products is challenging because the nonuniform characteristics of the samples can affect the quality of the spectra (Maraphum et al., 2022). In an initial study on rubber clots, Grizotto et al. (2024) reported high heterogeneity of the material, which resulted in the use of low-accuracy calibration models in portable and benchtop NIRS, suggesting the inclusion of new samples for recalibration.

The models developed for benchtop (NIRFlex) and portable NIRS (MicroNIR) exhibited coefficients of determination (R^2) within the range of 0.50 to 0.63 and may be classified as inaccurate by Guimarães et al. (2023). An explanation for the low value of R^2 can be attributed to the heterogeneity of the rubber clots, since the samples came from different farmers from different regions of Brazil under conditions of different storage times on the farm. Furthermore, the presence of water molecules in the samples may have hindered the adjustment of the NIRS calibration models. Although water sometimes obscures the detection of other constituents, such as proteins, lipids and other chemical components (Lobos et al., 2019), NIRS technology has been successfully used in the prediction of moisture content in foods

with high water content, such as meat (Alomar et al., 2003; Alvarenga et al., 2021; Bonin et al., 2020) and freshly harvested forage (Cozzolino & Labandera, 2002; Decruyenaere et al., 2009; Lobos et al., 2019; Murphy et al., 2019), taking advantage of the strong water absorption bands in the near-infrared region (Puttipipatkajorn & Puttipipatkajorn, 2020).

On the one hand, the heterogeneity of the samples is a problem for model development because of spectral nonuniformity; on the other hand, this heterogeneity provides robustness to the model in the prediction of unknown samples, as long as a range of clot types and a large number of samples are included. In homogeneous materials, such as natural latex, Maraphum et al. (2022), in a study evaluating DRC (n = 115), reported excellent values of R^2, RMSEC, and RMSEP (0.97, 1.58 and 1.20, respectively), using the online portable NIRS model AvaSpec-NIR256 from Avantes (Holland). Similarly, Puttipipatkajorn and Puttipipatkajorn (2020), in a study on natural latex coagulated in the laboratory (n = 300), reported excellent R^2, RMSEC and RMSEV values, 0.99, 0.177 and 0.227, respectively, for portable NIRS model DLP NIR Scan Nano (Texas Instr., USA). In a study on coagulated latex (n = 180) under laboratory conditions, Suchat et al. (2015) obtained R^2, SEC, and SEP values of 0.98, 1.68 and 1.48, respectively, for a portable NIRS NIRSystem 6500 (Foss NIR Systems, USA). Despite the exceptional values of R^2 and low calibration errors, Suchat et al. (2015) emphasized that their model is not ready for use, since only a certain type of latex sample can be used for prediction by the model. The authors emphasized that the model was developed for acidified and coagulated latex in a specific manner of RRIMM 600 clones and that other forms of preparation or clones could produce latex with different characteristics.

The error indices of the regression models (RMSEC, RMSECV, and RMSEP) were similar, indicating internal consistency of the calibrations and good behavior in the external validation. The values of the systematic error (*bias*) of the two types of spectrometers were low, with values well below 60% of the SEC value, according to Guimarães et al. (2023), suggesting the absence of significant systematic error in the predictions. In terms of overall performance, the quality indices of the predictive ability of the models, RPD and RER, were below the limits usually recommended for robust quantitative applications (RPD > 2.0 and RER ≥ 10) and were more suitable for screening purposes. in accordance with the criteria reported in the literature. The exclusion of discrepant samples improved these indices but not enough to change their classification. According to the literature, RPD values higher than 2.0 (Maraphum et al., 2022) or 2.5 (Williams & Sobering, 1996) indicate satisfactory performance of the models, whereas values lower than 1.4 (Maraphum et al., 2022) or 1.5 (Williams & Sobering, 1996) reflect low predictive ability. For the RER, values greater than 5 are considered acceptable for *screening* samples (Rambo et al., 2020), whereas values above 10 indicate models with high predictive capacity (Williams & Sobering, 1996).

The precision test (external validation), performed with a group of samples unknown by the model, is an important step for the validation of the regression model. The use of a group of unknown samples and the RMSEP is recommended because it

produces reliable results, independent of any data used in the construction of the model (Pasquini, 2003). In terms of the equipment, compared with MicroNIR, NIRFlex consistently resulted in lower prediction error and lower dispersion of residues, indicating greater analytical stability of the benchtop equipment. However, the differences between the devices were small and do not represent a relevant practical advantage, suggesting similar predictive performances under the analyzed conditions. These results are in line with those reported in the literature, which indicate greater robustness of benchtop spectrometers in multivariate calibrations, especially in quantitative applications (Pasquini, 2018). Nevertheless, the use of portable spectrometers, such as MicroNIR and others, has increased in virtually all areas in which conventional benchtop spectrometers were originally used (Pasquini, 2018).

Analysis of the distribution of the residuals revealed good adherence to the linear regression model because it is possible to visually perceive the normal distribution of the data, indicating the absence of a trend in the constructed models. The correlations (r) between the predicted and laboratory values were positive, with values equal to 83% for benchtop NIRS and 78% for portable NIRS after the outliers were removed. These results reinforce the ability of the models to capture the variation in DRC, even when real variability associated with different producers, collection practices and processing conditions is included.

The dataset, composed of a large number of samples collected over two years and in various seasons, contributed to the representativeness of the regression models, but it also introduced variability that limited the absolute predictive performance of the models. Thus, continuous updating of the models with the inclusion of new samples is recommended.

Finally, the main operational advantage of NIR spectroscopy is its analytical speed, allowing the determination of the DRC to occur within minutes, in contrast to the conventional method, which can require up to 16 hours for completion. From an operational point of view, benchtop NIRS exhibited slightly higher accuracy; however, controlled conditions are needed to perform the analyses. The portable model, in turn, has the advantage of being mobile and able to be transported to the processing site, enabling the results to be obtained in real time. In addition to DRC determination, the NIRS technique has the potential to be used for the evaluation of other rubber quality parameters. Thus, the use of NIRS technology may assist operators in obtaining quick results and contribute to the implementation of payment systems based on the quality of the natural rubber coagulum.

Conclusion

Chemometric models were developed to estimate the DRC in natural rubber slides using NIRS with both benchtop and portable equipment. Both devices exhibited the potential to quickly estimate the DRC values in rubber sheets, even in the context of variability associated with different producers, collection practices and processing conditions.

Although the developed models did not meet the most rigorous criteria of predictive ability reported in the literature, the results reveal satisfactory performance for sample screening purposes. The benchtop equipment exhibited slightly better performance in terms of accuracy and error stability, whereas the portable equipment exhibited high potential for practical application because of the possibility of using it directly in the processing plant and obtaining results in real time.

However, the direct operational application of chemometric models should be done with caution, requiring the expansion of the dataset, with the inclusion of new samples from different producing regions and periodic recalibration of the models. The estimation of DRC by NIR spectroscopy is highly important for the rubber production chain, allowing the analysis of a greater number of samples in a short period of time, with the potential to assist quality control programs and remuneration systems based on the quality of the natural rubber clot.

Acknowledgments

The authors thank the COOPBOR (Cooperative of Natural Rubber Producers), FUNDEPAG (Fundação de Desenvolvimento da Pesquisa Agropecuária), and FAPESP (Fundação de Apoio à Pesquisa do Estado de São Paulo) for their financial support for this study. The authors thank the company, Spectral Solutions Comércio e Serviços Ltda, and Mr. Guilherme Holland, for their trust in the use of portable NIRS.

References

Abreu, J. G., Kazama, D. C. S., Sauceda, M., Ferreira, E. A., Peixoto, W. M., & Detlefsen, G. (2023a). NIRS estimation of the nutritive value of *Urochloa* sp. (Syn. *Brachiaria* sp.) forages. *Revista Uniaraguaia, 18*(2), 18-28. https://sipe.uniaraguaia.edu.br/index.php/REVISTAUNIARAGUAIA/article/view/1281

Abreu, J. G., Kazama, D. C. S., Sauceda, M., Peixoto, W. M., Assis, L. M. B., Baldissarelli, V. Z., Butzge, J. L., Herrera, D. M., & Herrera, D. S. (2023b). NIRS estimation fo the nutritive value of *Megathyrsus maximus.* (Syn. *Panicum* sp.) forages. *Journal of Experimental Agriculture International, 45*(8), 126-137. doi: 10.9734/JEAI/2023/v45i82165

Alomar, D., Gallo, C., Castañeda, M., & Fuchslocher, R. (2003). Chemical and discriminant analysis of bovine meat by near infrared reflectance spectroscopy (NIRS). *Meat Science, 63*(4), 441-450. doi: 10.1016/S0309-1740(02)00101-8

Alvarenga, T. I. R. C., Hopkins, D. L., Morris, S., McGilchrist, P., & Fowler, S. M. (2021). Intramuscular fat prediction of the *semimebranosus* muscle in hot lamb carcaces using NIR. *Meat Science, 181,* 10804, 2021. doi: 10.1016/j.meatsci.2020.108404

Associação Brasileira de Normas Técnicas (2011). ABNT NBR ISO 126: *látex de borracha natural: determinação do teor de borracha seca.* ABNT.

Bonin, M. N., Silva, S. L., Bünger, L., Ross, D., Feijó, G. L. D., Gomes, R. C., Rennó, F. P.,

Santana, M. H. A., Rezende, F. M., Ítavo, L. C. V., Novais, F. J., Surita, L. M., Bonin, M. N., Pereira, M. W., & Ferraz, J. B. S. (2020). Predicting the shear value and intramuscular fat in meat from Nellore cattle using Vis-NIR spectroscopy *Meat Science, 163,* 108077. doi: 10.1016/j.meatsci.2020.108077

Campos, R. L.C., Oliveira, R. H. M., Macedo, M. C. M., & Gomes, R. C. (2024). *Predicting the nutritional value of tropical forages by Near Infrared Reflectance Spectroscopy (NIRS).* EMBRAPA Gado de Corte. (Boletim de Pesquisa e Desenvolvimento, 56).

Cozzolino, D., & Labandera, M. (2002). Determination of dry matter and crude protein contents of undried forages by near-infrared reflectance spectroscopy. *Journal of the Science of Food and Agriculture, 82*(4), 380-384. doi: 10.1002/jsfa.1050

Decruyenaere, V., Lecomte, P., Demarquilly, C., Aufrere, J., Dardenne, P., Stilmant, D., & Buldgen, A. (2009). Evaluation of green forage intake and digestibility in ruminants using near infrared reflectance spectroscopy (NIRS): developing a global calibration. *Animal Feed Science and Technology, 148*(2), 138-156. doi: 10.1016/j.anifeedsci.2008.03.007

Gonçalves, E. C. P., Oliveira, M. D. M., Martins, A. L. M., Martins, A. N., Almeida, L. C., & Grizotto, R. K. (2024a). Análise dos desafios e das oportunidades da produção de borracha natural no Brasil In L. F. da Silva, J. R. S. Oliveira, & F. L. F. de Jesus. (Orgs.), *Cultivando o futuro, tendências e desafios nas ciências agrárias* (Cap. 1, pp. 1-14). Atena Editora.

Gonçalves, E. C. P., Oliveira, M. D. M., Martins, A. N., Martins, M. A., & Grizotto, R. G. (2024b). A crise da borracha natural: de maior produtor a grande erradicador. *Pesquisa & Tecnologia, 21*(1), 1-7. https://agricultura.sp.gov.br/apta-regional/revista/2024janeiro-junhoa-crise-da-borracha-natural-de-maior-produtor-a-grande-erradicador

Grizotto, R. K., Martins, A. N., Martins, A. L. M., Oliveira, M. D. M., & Gonçalves, E. C. P. (2024). Espectroscopia na região do infravermelho próximo para avaliação do teor de borracha seca em coágulo de borracha natural. *Pesquisa & Tecnologia, 21*(1), 1-7. https://agricultura.sp.gov.br/apta-regional/revista/2024janeiro-junhoespectroscopia-na-regiao-do-infravermelho-proximo-para-avaliacao-do-teor-de-borracha-seca-em-coagulo-de-borracha-natural

Grizotto, R. K., Siqueira, G. R., & Resende, F. D. (2019). Uso do NIRS como ferramenta na pecuária de precisão. In A. J. C. Nuñez, A. E. Furtini Neto, D. T. Lima, D. P. Almeida, H. L. B. Nascimento, J. Restle, R. H. Fernandes, & U. O. Biego (Eds.), *Anuário de pesquisa pecuária - resultados 2018 -2019.9* (Cap. 1, pp. 81-85). Instituto de Ciência e Tecnologia COMIGO.

Guimarães, I. C. S. B., Silva, T. H., Picchi, C. C., & Fukushima, R. S. (2023). Assessing the repeatability and reliability of NIRS to predict nutritional values and to evaluate two lignin methods in *Urochloa* spp grasses. *Grasses, 2*(2), 112-126. doi: 10.3390/grasses2020010

Lobos, I., Moscoso, C. J., & Pavez, P. (2019). Calibration models for the nutritional quality of fresh pastures by near-infrared reflectance spectroscopy. *Ciencia e Investigación Agraria, 16*(3), 234-242. doi: 10.7764/rcia. v46i3.2020

Maraphum, K., Wanjantuk, P., Hanpinitsak, P., Paisarnsrisomsuk, S., Lim, C. H., & Posom, J. (2022). Fast determination of total solids content (TSC) and dry rubber content (DRC) of para rubber latex using near-infrared spectroscopy. *Industrial Crops and Products, 182*, 1-9. doi: 10.1016/j.indcrop.2022.115507

Murphy, D. J., O'Brien, B., O'Donovan, M., Condon, T., Claffey, A., & Murphy, M. D. (2019). A preliminary near infrared spectroscopy calibration for the prediction of undried fresh grass quality. *Proceeding of the European Conference on Precision Livestock Farming, ECPLF 2019,* Cork, Ireland, 9.

Pasquini, C. (2003). Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. *Journal of the Brazilian Chemical Society, 14*(2), 198-219. doi: 10.1590/S0103-50532003000200006

Pasquini, C. (2018). Near infrared spectroscopy: a mature analytical technique with new perspectives – a review. *Analytica Chemica Acta, 1026,* 8-36. doi: 10.1016/j.aca.2018.04.004

Puttipipatkajorn, A., & Puttipipatkajorn, A. (2020). Development of calibration models for rapid determination of moisture content in rubber sheets using portable near-infrared spectrometers. *Journal of Innovative Optical Health Sciences, 13*(2), 2050009. doi: 10.1142/S1793545820500091

Rambo, M. K. D., Ferreira, M. M. C., Melo, P. M., Santana, C. C., Jr., Bertuol, D. A., & Rambo, M. C. D. (2020). Prediction of quality parameters of food residues using NIR spectroscopy and PLS models based on proximate analysis. *Food Science and Technology, 40*(2), 444-450. doi: 10.1590/fst.02119

Serafim, C. C., Guerra, G. L., Mizubuti, I. Y., Castro, F. A. B., Prado-Calixto, O. P., Galbeiro, S., Parra, A. R. O., Bumbieris, V. H., Jr., Pértile, S. F. N., & Rego, F. C. A. (2020). Use of near-infrared spectroscopy for prediction of chemical composition of Tifton 85 grass. *Semina: Ciências Agrarias, 42*(3), 1287-1302. doi: 10.5433/1679-0359.2021v42n3p1287

Siano, D., Puttipipatkajorn, D. A., Puttipipatkajorn, A., Noypitak, S., & Terdwongworakul. A. (2022). Application of near infrared spectroscopy for quality evaluation in Para rubber industry. *IOP Conference Series: Materials Science and Engineering, 1234*(1), 12037. doi: 10.1088/1757-899X/1234/1/012037

Suchat, S., Theanjumpol, P., & Karrila, S. (2015). Rapid moisture determination for cub lump natural rubber by near infrared spectroscopy. *Industrial Crops and Products, 76,* 772-780. doi: 10.1016/j.indcrop.2015.07.070

Trópia, N. V., Silva, F. A. S., Andrade, D. R., Matos, E. M. A., Cidrini, F. A. A., Borges, K. M., Ebani, F. Y. C., Roque, J. V., Zanetti, D., & Valadares, S. C., Fº. (2023). Development and validation of regression models from NIR spectra to predict the composition of sugarcane, soybean meal, and cornmeal. *Semina: Ciências Agrarias, 42*(44), 859-880. doi: 10.5433/1679-0359.2023v44n2p859

Williams, P., & Sobering, D. (1996). How do we do it: a brief summary of the methods we use in developing near infrared calibrations. In A. M. C. Davies, & P. L. Williams (Eds.). *Near Infrared spectroscopy: the future waves* (pp. 185-188). NIR Publications.