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Potential of near-infrared spectroscopy for quality evaluation of cattle leather

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ABSTRACT

Models using near-infrared spectroscopy (NIRS) were constructed based on physical-mechanical tests to determine the quality of cattle leather. The following official parameters were used, considering the industry requirements: tensile strength (TS), percentage elongation (%E), tear strength (TT), and double hole tear strength (DHS). Classification models were constructed with the use of k-nearest neighbor (kNN), soft independent modeling of class analogy (SIMCA), and partial least squares–discriminant analysis (PLS-DA). The evaluated figures of merit, accuracy, sensitivity, and specificity presented results between 85% and 93%, and the false alarm rates from 9% to 14%. The model with lowest validation percentage (92%) was kNN, and the highest was PLS-DA (100%). For TS, lower values were obtained, from 52% for kNN and 74% for SIMCA. The other parameters %E, TT, and DHS presented hit rates between 87 and 100%. The abilities of the models were similar, showing they can be used to predict the quality of cattle leather.

1. Introduction

The chemical stabilization of animal skins for leather production dates to ancient times, and was initially carried out with vegetable tannins. Nowadays, chromium is the most common curing agent, due to the moderate tanning cost and good leather quality [1,2]. Leather is used in numerous applications, such as automotive upholstery, shoes, clothing, furniture and many other items [3].

The quality of the leather also depends on the way that the animals are raised. Proper care is necessary during field breeding. The feeding of the animals should be adequate for maintenance of body reserves. Also, the animals are subject to parasites, burns and sharp objects. During slaughter, care is also necessary to avoid damaging the hide [4].

Several physical-mechanical parameters of traction and tearing are defined in standard protocols to verify and guarantee the quality of hides [5]. In Brazil, the test procedures are described by the Brazilian Technical Standards Association (ABNT) [6–11]. These tests are laborious and use a considerable number of samples, which is a significant disadvantage considering that finished leather is sold by area.

The use of infrared spectroscopy for leather analysis has previously been reported by Canals et al. (2013). The authors determined the tanning degree in vegetal tanning process control in different conditions, such as combined tannins, hide substance and leather substance, by using NIRS and mid-FTIR spectroscopy. An appropriate model of partial least squares (PLS) was calculated for each condition, with the prediction and quantification errors expressed as order of magnitude, which is accepted by the tanning industry [12]. The authors also proposed the use of NIRS to determine leather fat and the defatting process, monitored competitively with other proposed methods [13]. Infrared spectroscopy has also been applied for analysis of tannin characterization in historical leathers [14] and mapping of leather fiber panels [15]. Finished tanned leather was evaluated by NIRS and mid-FTIR spectroscopy by applying PCA and canonical variate analysis. With the subsequent use of the k-nearest neighbor (kNN) method, two classification models for finishing treatment became available [16].

Classification models for quality control of cattle and sheep leathers by using laser-induced breakdown spectroscopy (LIBS) were recently proposed. The classification generates models able to predict results in comparison with the reference values for the physical-mechanical parameters [17].

In this study, we investigated the suitability of using NIR spectroscopy and classification models to evaluate the quality of bovine leather. For this purpose, reference values were obtained through physical-mechanical tests and models were built using three different chemometric classification techniques: (i) kNN, Euclidean distance between samples to classify closest neighbors; (ii) SIMCA (soft independent modeling of class analogy), PCA (principal component analysis) calculated for each class; and (iii) PLS-DA (partial least squares - discriminant analysis), which defines the dependent variables using PLS factors [18]. After

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constructing the models, we applied them as classification tools for leather, to replace time-consuming physical-mechanical tests.

2. Experimental

2.1. Samples

The samples were obtained from animals at the experimental farm of Embrapa Pecuaria Sudeste, located in the state of São Paulo, Brazil. The slaughtered animals were 342–725 days old, had weight range of 292–597 kg, and belonged to the following genetic groups: CANE (father Canchim and mother Nellore); CASN (father Canchim and mother ½ Senepol + ½ Nellore); CATA (father Canchim and mother ½ Angus + ½ Nellore); HNE (father Hereford and mother Nellore); HSN (father Hereford and mother ½ Senepol + ½ Nellore); and HTA (father Hereford and mother ½ Angus + ½ Nellore). In the subsequent experiments, we employed two sets of leather samples tanned with Cr: (a) 201 finished leather samples, and (b) 113 semi-finished samples, for a total of 314 samples.

2.2. Physical-mechanical Tests

The skins were tanned with chromium sulfate. After tanning, the finished (post-tanning) and semi-finished samples were cut with blades in a hydraulic press in the longitudinal (L) and transversal (T) directions, according to ABNT NBR ISO 2418:2015 [6]. All samples were then acclimated for 48 h to laboratory conditions at 23 ± 2 °C and relative humidity of 50 ± 5%, according to ABNT NBR 10455:2014 [7], before being submitted to physical-mechanical tests. The thickness of the leather specimens was measured according to ABNT NBR ISO 2589:2014 [8]. Four physical-mechanical parameters were measured by using a dynamometer (Maqtest, Franca, SP, Brazil): 1) determination of the tensile strength (TS) (ABNT NBR ISO 3376:2014) [9]; 2) percentage of extension or elongation (%E) (ABNT NBR ISO 3376:2014) [9]; 3) determination of tear strength (tongue tear) (TT) (ABNT NBR ISO 3377-1:2014) [10]; and 4) double hole tear strength (DHS) (ABNT NBR ISO 3377-2:2014) [11]. All of these tests were performed in six repetitions (3 L and 3 T directions).

2.3. Near-infrared (NIR) Spectra Acquisition

For NIR spectra acquisition, a sample measuring 5.0 × 5.0 cm was cut using a hydraulic press with cutting knives (Metalurgica Açoreal, P-23, Campo Bom, RS, Brazil). All spectra were obtained with a NIRFlex N-550 spectrometer (BUCHI, Flawil, Switzerland). Samples were scanned in the region from 1000 to 2500 nm in reflectance mode in Petri dishes in the same conditions previously described (23 ± 2 °C, relative humidity 50 ± 5%). Each spectrum was obtained by averaging 32 scans with 4 cm^{-1} resolution.

2.4. Data Analysis and Classification Models

The classification models combined the NIR spectrum of the analyzed leather sample with the physical-mechanical test results. Data analysis was carried out with the Pirouette software v. 4.5 (Infometrics Inc., Woodinville, WA, USA). The NIR spectra were submitted to the following transformation steps: first (1) normalized by signal norm, (2) first derivative calculation (window = 5 points), and (3) mean centering. Three classification models (kNN, SIMCA, and PLS-DA) were used to predict the leather quality. The total number of samples (314) was divided into two classes. Both classes were composed of 157 samples and were organized according to the physical-mechanical tests values. Table 1 shows the characteristics of each class. In the case of tensile strength (TS), for example, classes 1 and 2 present the following ranges: 10.00–24.08 and 24.13–43.75, respectively. Each class was further divided into calibration and validation datasets with 126 (80%) and 31 (20%) samples, respectively, according to ASTM 1655–05 [19].

3. Results and Discussion

3.1. Wavelength Selection

Raw NIR spectra are presented in Fig. 1a. Each spectrum is the average of three spectra. Our first attempt was to build models using the whole spectrum, but there was no improvement in figures of merit, so we decided to perform wavelength selection. The region from 1000 to 1400 nm (marked area in Fig. 1a) did not provide useful information, with regression vectors near zero, so it was excluded. The new spectra obtained were then submitted to data processing to correct baseline as well as to detect differences among spectra. The processed data after normalization, first derivative calculation, and mean-centering are presented in Fig. 1b.

In Fig. 1a, the peaks between 1800 and 2000 nm are mainly related to the first overtone of O—H stretching and O—H combination bands of water, respectively. Spectral regions between 1700 and 1800 nm and between 2100 and 2500 nm are related to the first overtone of C − H stretching and C − H + C − H and C − H + C– C combination bands, respectively [18,20].

Fig. 2 shows the PLS-DA regression vectors for classes 1 (Fig. 2a) and 2 (Fig. 2b) of tensile strength. With the regression vector, it is possible to observe the most important wavelengths for each class characterization. In the PLS, regression vectors are calculated using both score values, from X matrix and y vector. The wavelengths between 2200 and 2400 are positively and negatively correlated to classes 1 and 2, respectively.

3.2. Classification Model Proposal

The samples were divided into two classes, as previously mentioned and specified in Table 1. These specifications were organized according to ABNT NBR 13525:2016 [21] and show the orientation values for acceptance of leather quality according to physical-mechanical parameters. These values were used as orientation parameters to establish the classes. Attempts were made to keep about 50% of the samples in each class. These categories were then used to calculate classification models using the NIR spectra, in order to verify the predictive capacity of the spectra for sample classification.

To evaluate the performance of the models, we calculated four figures of merit: accuracy, sensitivity, specificity and false alarm rate. The accuracy represents the percentage of correct predictions of the model, while the sensitivity for class 1 is the ability of the model to predict class 2 samples correctly. In the case of specificity, the value

Table 1
Physical and mechanical values from the tests.

Tests and reference values (ABNT NBR 13525:2016) [21]		Range of results obtained (average L and T)	Range for class 1 (n = 157)	Range for class 2 (n = 157)
Tensile tests	Tensile strength (TS, N mm^{-2})	10.00–43.75	10.00–24.08	24.13–43.75
	Elongation (%E, %), ≥40%	46.41–116.92	46.41–77.90	78.10–116.92
Tear tests	Tear strength (TT, N mm^{-1})	62.41–262.39	62.41–108.19	108.20–262.39
Double hole tear strength	Strength (DHS, N) ≥60 N	62.67–274.17	62.67–99.83	100.17–274.17