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Near-Infrared Spectroscopy Analysis of Seed Coats of Common Beans (*Phaseolus vulgaris* L.): A Potential Tool for Breeding and Quality Evaluation

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ABSTRACT: Near-infrared spectroscopy (NIRS) is a well-established technique for determining the components of foods. Sample preparation for NIRS is easy, making it suitable for breeding and/or quality evaluation, for which a large number of samples should be analyzed. We aimed to assess the feasibility of NIRS to estimate parameters that seem to influence consumers' perception of the seed coat of common beans: dietary fiber (DF), uronic acids (UA), ashes, calcium, and magnesium. We used reference methods to analyze ground seed coats of 90 common bean samples with a wide range of genetic variability and cultivated at many locations. We registered the NIR spectra on intact beans and ground seed coat samples. We derived partial least-squares (PLS) regression equations from a set of calibration samples and tested their predictive power in an external validation set. For intact beans, only RER values for ashes and calcium are good enough for very rough screening. For ground seed coat samples, the RPD and RER values for ashes (3.49 and 14.09, respectively) and calcium (3.57 and 12.70, respectively) are good enough for screening. RPD and RER values for DF (2.60 and 9.15, respectively) and RER values for magnesium (6.57) also enable rough screening. A poorer correlation was achieved for UA. We conclude that NIRS can help in common bean breeding research and quality evaluation.

KEYWORDS: *common beans, NIR, breeding, seed coat*

INTRODUCTION

In recent years, legumes have been attributed with health benefits such as the inhibition of carcinogenesis[1,2] and increased antioxidant capacity,[3,4] enhancing their reputation in developed countries and leading to a demand for higher sensory qualities. Breeders' efforts have focused mainly on improving production and nutrition-related chemical composition while largely neglecting sensory traits. Recent efforts to obtain or recover varieties with high organoleptic quality to supply a growing market have resulted in new bean inbred lines derived from prestigious Spanish landraces[5,6] used in the Protected Designations of Origin (PDOs) "Mongeta del Ganxet" and "Fesols de Santa Pau".

The evaluation of sensory attributes requires trained panelists working with cooked beans, so handling large numbers of samples is time-consuming and expensive. Thus, chemical or instrumental approaches to describe materials objectively would be useful to evaluate genetic and environmental variation in sensory traits in breeding programs and to evaluate the sensory quality of marketable beans.

A few studies dealing with the relationship between chemical composition and texture properties of common beans have been reported, but their results are not conclusive for a broad range of common beans. Low mealiness is favored by high-protein and low-amylose contents in the whole seed of common beans,[7] and firmness is related to calcium, magnesium, and soluble pectin contents.[8,9] Consumers prefer low seed coat perception, a property evaluated by rating how much the seed coat is noticed throughout the mastication of eating cooked beans. Paradoxically, larger proportions of seed coat with respect to the whole seed do not result in increased seed coat perception.[10] Seed coat perception correlates negatively with the pectin content but not with calcium or magnesium,[7] although it is well-known that seed coat perception increases dramatically with increased water hardness.

Bean seed coats are composed of sclereid cells characterized by thick cell walls composed mainly of fiber having undergone a secondary process of lignification.[11] Pectin is found in the middle lamellae and its degree of solubilization determines the degree to which cells separate from one another. Both calcium and magnesium can cross-link with carboxylate groups of uronic acids, decreasing the solubilization of pectin, and this should increase seed coat perception. Presumably, seed coat perception is influenced not only by the content of components but by their relative ratios and the interactions among them as well, which would explain the limited correlations found to date. Large systematic studies are needed to elucidate this matter, and one such study is underway in our laboratory.

Nevertheless, standard chemical analyses are also time-consuming, even for a first rough classification of entries, because determining the compounds most relevant to sensory characteristics requires enzymatic approaches, which are slow, difficult, and expensive. Near-infrared spectroscopy (NIRS) is a well-established technique for determining the components of foods[12] that can be used on easily prepared samples. NIRS has been used to analyze legumes: to determine protein, essential amino acids, fatty acids, carbohydrates, and inorganic

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phosphorus in soy and soy products[13−17] and to determine protein, moisture, fat, fatty acids, ash, starch, alcohol insoluble solids, total dietary fiber, and functional properties in peas and chickpeas.[18−21] However, few studies have used NIRS in common beans. Hermida et al.[22] obtained a robust calibration for moisture, protein, starch, and fat in beans ground to a fine powder, and Hacisalihogu et al.[23] predicted protein, starch, and seed weight in intact common bean seeds. As expected, statistical values, such as RPD, were higher for ground samples than for unprocessed beans.

Despite the limited correlations described above, we consider that data about the composition of common beans could contribute to a better understanding of the chemical bases underlying seed coat perception, and this information could be useful in breeding programs. Thus, we aimed to assess the feasibility of NIRS for predicting the content of dietary fiber (DF), uronic acids (UA), ashes, calcium, and magnesium in the seed coats of common beans to determine the suitability of this technique for evaluating the large numbers of samples required for breeding research or quality control of marketable beans.

MATERIALS AND METHODS

The experiment was carried out on 90 accessions of Spanish landraces and inbred lines selected to encompass a wide range of chemical variation. The beans were cultivated in six locations in Catalonia (northeastern Spain) and two locations in Asturias (northern Spain) over 5 years (2004−2008). We included traditional varieties from Catalonia (Bermà, Bitxo, Carai, Castellfollit, Confit, Floreta, Ganxet, Genoll de Crist, Joan, Planxeta, Rosada, Sastre, Tabella Brisa, and Vilanoví) and from Asturias (Andecha, Cimera, and Xana) as well as recombinant inbred lines of Xana × Cornell. The group of accessions had large variability in seed coat perception and composition and included white and colored beans.

Reference Analysis. The seed coat of common beans accounts for only 8−15% of the mass of the seed, so it must be separated from the endosperm prior to analysis to enable its composition to be accurately determined. To this end, seeds were soaked in deionized water for 24 h, and the seed coat was manually separated from the endosperm and then dried and ground using a laboratory mill (Perten, 3100) with a 0.4 mm screen. The ground seed coat samples obtained were stored in polyethylene bags at −18 °C in a nitrogen-modified atmosphere. Before analysis, samples were further dried at 50 °C for 4 h.

The following traits were analyzed in duplicate by reference methods in the milled seed coat samples: ashes, calcium, magnesium, DF, and UA. The ash content was determined according to AOAC method 923.03.[24] Approximately 1 g of milled seed coat was burned at 450 °C, cooled in a desiccator, and weighed soon after reaching room temperature. Ash extract was obtained by dissolving ashes in 7.5 mL of 3 M nitric acid solution and adding water to make 50 mL. Calcium and magnesium in diluted ash extract were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 3200RL, Perkin-Elmer, Norwalk, CT). DF and UA were measured by the Englyst procedure, using a commercial kit (Englyst Fiberzym kit, Novo Nordisk Bioindustries, Surrey, U.K.). This routine measures DF as nonstarch polysaccharides (NSP) using enzymatic−chemical methods and has evolved from the principles laid down by Southgate.[25] About 300 mg of seed coat was taken. Starch was hydrolyzed enzymatically; NSP were isolated by precipitation in ethanol and then hydrolyzed by sulfuric acid. The constituent neutral sugars and UA were measured by colorimetry.

Spectra Measurement. Spectra were taken from two kinds of materials: intact beans and ground seed coat. NIR spectra were registered directly on the 90 samples of ground seed coat using a model 6500 spectrophotometer (Foss NIRSystems, Silver Spring, MD) equipped with a reflectance detector and a rapid content analyzer module. About 5 g of ground seed coat was placed in a 3 cm diameter cell holder and gently compressed with a cylindrical piece of metal. Spectra were recorded every 2 nm between 1100 and 2500 nm and averaged from 32 scans.

For the 90 samples of unprocessed beans, spectra were registered in a FOSS XDS near-infrared spectrometer with rapid content analyzer module. Spectra were recorded every 0.5 nm between 400 and 2500 nm and averaged from 32 scans. About 100 g of intact beans was placed in a rectangular metallic holder.

For both kinds of materials, the reflectance at each wavelength was expressed as $\log(1/R)$. Three spectra were registered for each sample, and the average spectrum was used for computations. The ceramic plates supplied with the instruments were used to obtain the blank spectrum. Vision software, version 2.51 (Foss NIRSystems), was used to control the recorder, collect the spectra, and import the data.

Statistical Analyses. First, the reproducibility of the reference analysis methods was evaluated through the standard error of laboratory (SEL), calculated as

$$\mathrm{SEL} = \sqrt{\frac{\sum_{i=1}^{N} (x_{i,1} - x_{i,2})^2}{2N}} \quad (1)$$

where $x_{i,1}$ and $x_{i,2}$ are the replicate values obtained for each reference analysis and N is the entire number of samples.

Spectra of ground seed coats and intact beans were treated independently. They were all first treated by standard normal variate (SNV) to remove the multiplicative interference of scatter and particle size.[26] Then, their first and second derivatives were calculated by the Savitzky and Golay method to reduce peak overlap and eliminate baseline shift.[27] Principal components analysis (PCA) was used to compare spectra. Partial least-squares (PLS) regression was used to obtain the equations to correlate NIR spectra and chemical content.

For any trait analyzed (ashes, calcium, magnesium, DF, and UA), accessions were divided in two groups so that about tow-thirds could be used for calibration and one-third for external validation. Calibration and validation accessions were randomly selected, but they were adjusted so that their content standard deviations were similar to ensure that the range and distribution of the two groups would be comparable. PLS regressions for calibration were evaluated using leave-one-out cross-validation (CV). The coefficient of determination (R^2) and standard error (SE) were calculated for both cross-validation and external validation or prediction (P). For all of the parameters analyzed, the mathematical pretreatment that yielded the minimum standard error of cross-validation (SECV) value was considered to be optimal. The model's predictive ability was assessed with the dimensionless parameters RPD and RER defined in eqs 2 and 3

$$\mathrm{RPD} = \frac{\mathrm{SD}_x}{\mathrm{SEP}} \quad (2)$$

$$\mathrm{RER} = \frac{\max(x_1, ..., x_n) - \min(x_1, ..., x_n)}{\mathrm{SEP}} \quad (3)$$

in which SD_x is the standard deviation of validation data and SEP is the standard error of prediction.

Outlier samples having spectra that differed from the population were detected using the Mahalanobis distance (H) by PCA of SNV's spectra. An upper limiting value of $H = 3$ was chosen. Furthermore, outlier calibration samples that could not be predicted by the model were identified as t-outliers. The limit for acceptance was $t \leq 2.5$, where $t = |y_i - x_i| / \mathrm{SECV}$ and y_i and x_i are the predicted and reference content of sample i, respectively. Computations were done using commercial software (Unscrambler v. 9.2, Camo AS, Thondheim, Norway) and R statistical system (available free of charge through http://www.r-project.org).

RESULTS AND DISCUSSION

All of the constituent contents, determined by the reference analysis, varied over a wide enough range to enable satisfactory calibrations (Table 1). The magnitude of the variation is

Table 1. Descriptive Statistics of Cultivated Common Beans (g kg^{-1} Dry Matter)

		calibration set			validation set		
trait	SEL	range	mean	SD	range	mean	SD
DF	15.58	529.57−914.63	738.59	100.76	534.39−909.22	738.92	106.62
UA	5.05	68.89−174.24	124.88	24.74	71.56−171.49	120.97	26.93
ash	1.78	31.63−90.63	53.56	12.65	33.97−87.43	54.90	13.25
Ca	0.65	4.11−25.59	12.64	4.45	4.98−23.64	13.19	5.25
Mg	0.13	1.60−4.96	2.90	0.66	1.62−4.80	2.88	0.72

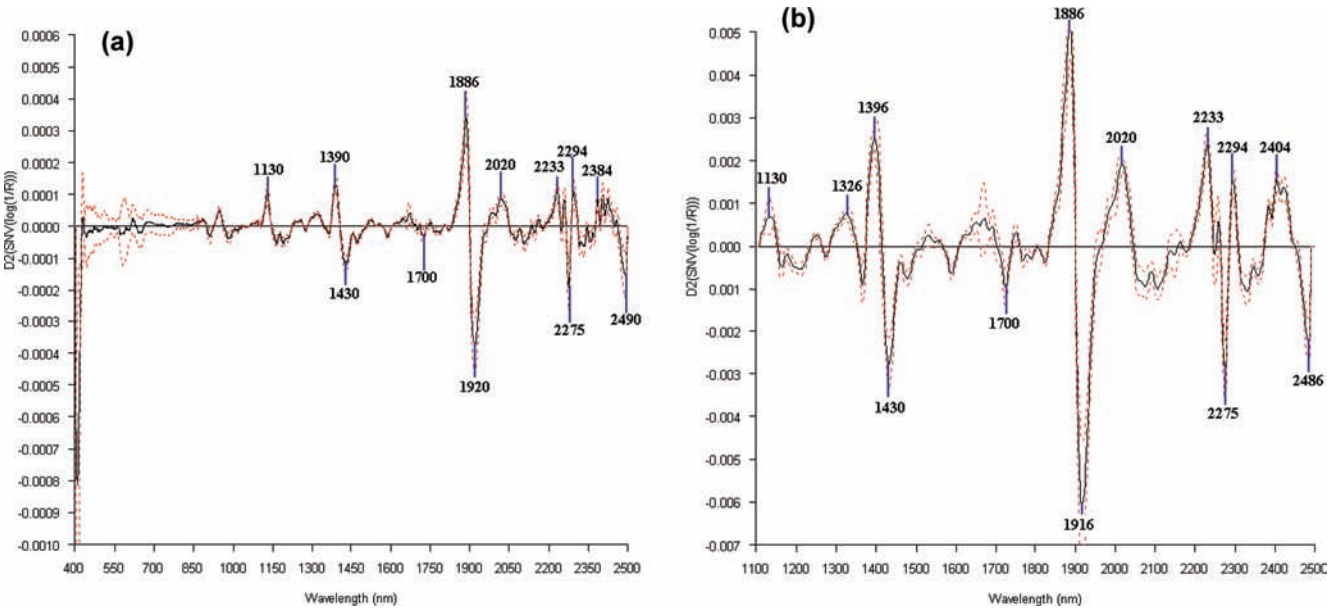

Figure 1. SNV+2D treatment of mean NIR spectra: (a) intact beans; (b) ground seed coat. Continuous line: spectrum; dashed line, standard deviation.

Table 2. Statistical Descriptors for the NIR Determinations (Wavelength 1100−2500 nm)

trait	sample	treatment	outliers	PLS terms	R^2_{CV}	SECV	R^2_{val}	SEP	RPD	RER	SEP/SEL
DF	intact	SNV	2	6	0.692	51.40	0.411	86.22	1.23	4.35	5.54
	ground	SNV+2D	0	7	0.890	32.70	0.865	40.95	2.60	9.15	2.63
UA	intact	SNV+2D	3	5	0.635	13.70	0.506	19.20	1.40	5.20	3.80
	ground	SNV+2D	0	3	0.676	13.44	0.549	18.09	1.49	5.52	3.58
ash	intact	SNV+1D	0	5	0.841	5.05	0.761	6.54	2.03	8.19	3.67
	ground	SNV+2D	1	5	0.933	3.20	0.922	3.80	3.49	14.09	2.13
Ca	intact	SNV+1D	5	5	0.778	1.99	0.821	2.19	2.40	8.52	3.38
	ground	SNV+2D	0	5	0.904	1.38	0.922	1.47	3.57	12.70	2.27
Mg	intact	SNV	8	7	0.447	0.47	0.437	0.54	1.33	5.84	4.10
	ground	SNV+2D	0	8	0.761	0.31	0.557	0.48	1.50	6.57	3.64

probably due to the genetic diversity of the entries, together with the environmental effects of location and year. DF is the major component of common bean seed coats, and it can account for >90% of the composition of the seed coat. Fiber includes the UA, which make up about one-fifth of the DF. Our findings for calcium and magnesium content agree with those reported by Moraghan et al.,[30] who showed that both metals accumulate more in seed coat than in cotyledon. Correlations were found between some chemical parameters: calcium versus ashes (r = 0.85, P < 0.001), calcium versus UA (r = 0.31, P < 0.001), DF versus magnesium (r = 0.34, P < 0.001), and ashes versus UA (r = 0.25, P < 0.05).

The SNV spectrum shows the usual shape of spectra of food samples that have a complex composition: many overlapping chemical-bond vibrations result in broad bands and poorly defined peaks. The second-derivative treatment yields the spectra shown in Figure 1. From 1100 to 2500 nm, similar peaks and troughs can be identified for both kinds of samples, although higher signal intensity is observed for ground samples. A few peaks are observed for wavelengths below 1100 nm. The peak at 1130 nm can be attributed to the C−H stretch second

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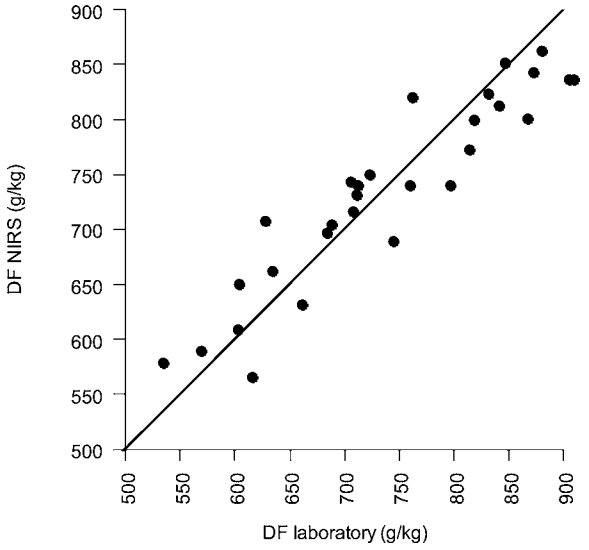

Figure 2. Predicted versus reference dietary fiber content for ground seed coat validation samples.

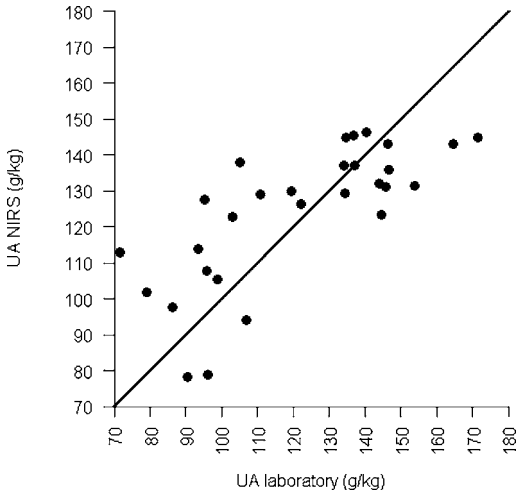

Figure 3. Predicted versus reference uronic acids content for ground seed coat validation samples.

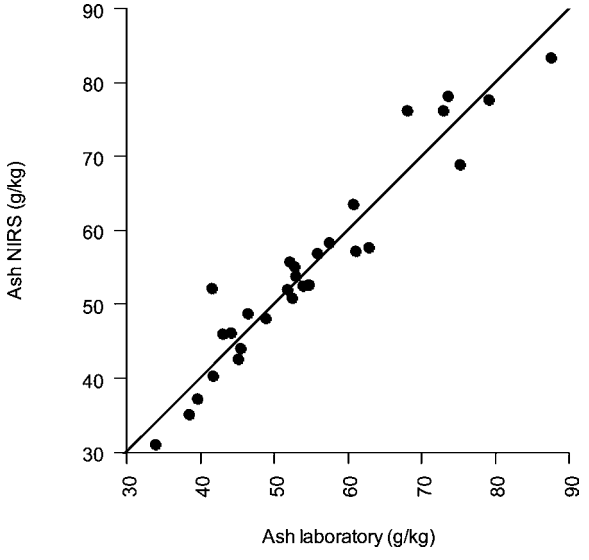

Figure 4. Predicted versus reference ash content for ground seed coat validation samples.

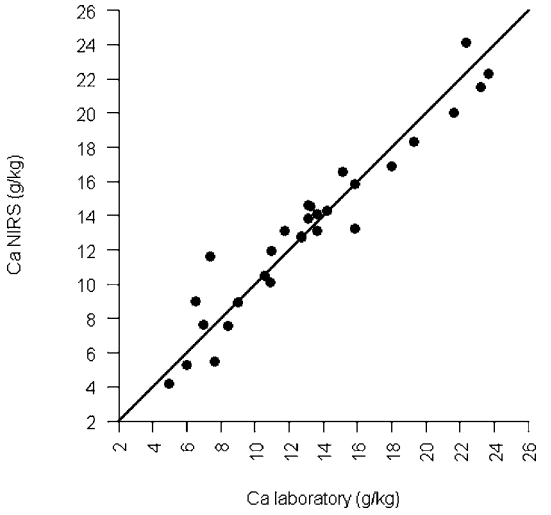

Figure 5. Predicted versus reference calcium content for ground seed coat validation samples.

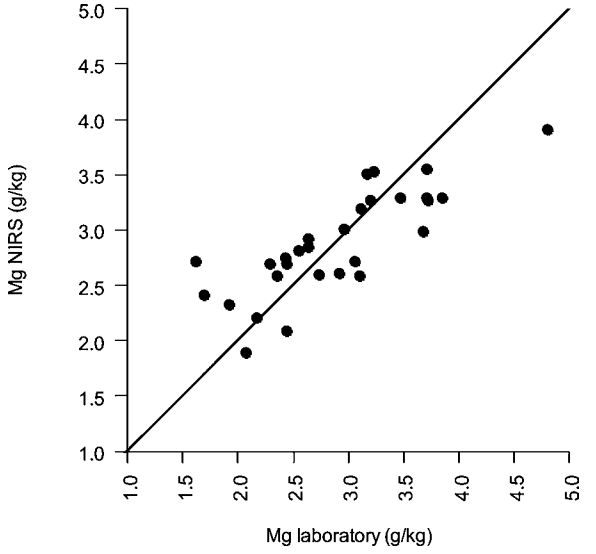

Figure 6. Predicted versus reference magnesium content for ground seed coat validation samples.

overtone, whereas the C−H and O−H stretch first overtones are seen around 1400 nm. Aromatic C−H bonds are perceived at 1700 nm. The main absorption was seen at 1886, 1916, and 2020 nm; these wavelengths can correspond to water or carboxylic acids and their derivates, such as amides or carboxylates. Signals between 2200 and 2300 nm have been assigned to O−H (water) plus C−C stretch groups, and peaks above 2300 nm are related to C−H combination tones.[28,29]

First, a PCA was run for the spectra with SNV treatment of all the samples. For ground samples, PC1 and PC2 explain 77 and 12% of the variation, respectively, and only one *H*-outlier was found. For intact beans samples, PC1 and PC2 explain 60 and 26% of the variation, respectively, and three *H*-outliers were found. Although the spectra of the *H*-outliers differed from those of the others, they were in the range of the set values for all target components. Nevertheless, these samples were not included in further computations. The remaining samples were divided into two groups: 59 and 57 for calibration of ground and intact beans, respectively, and 30 for external validation.

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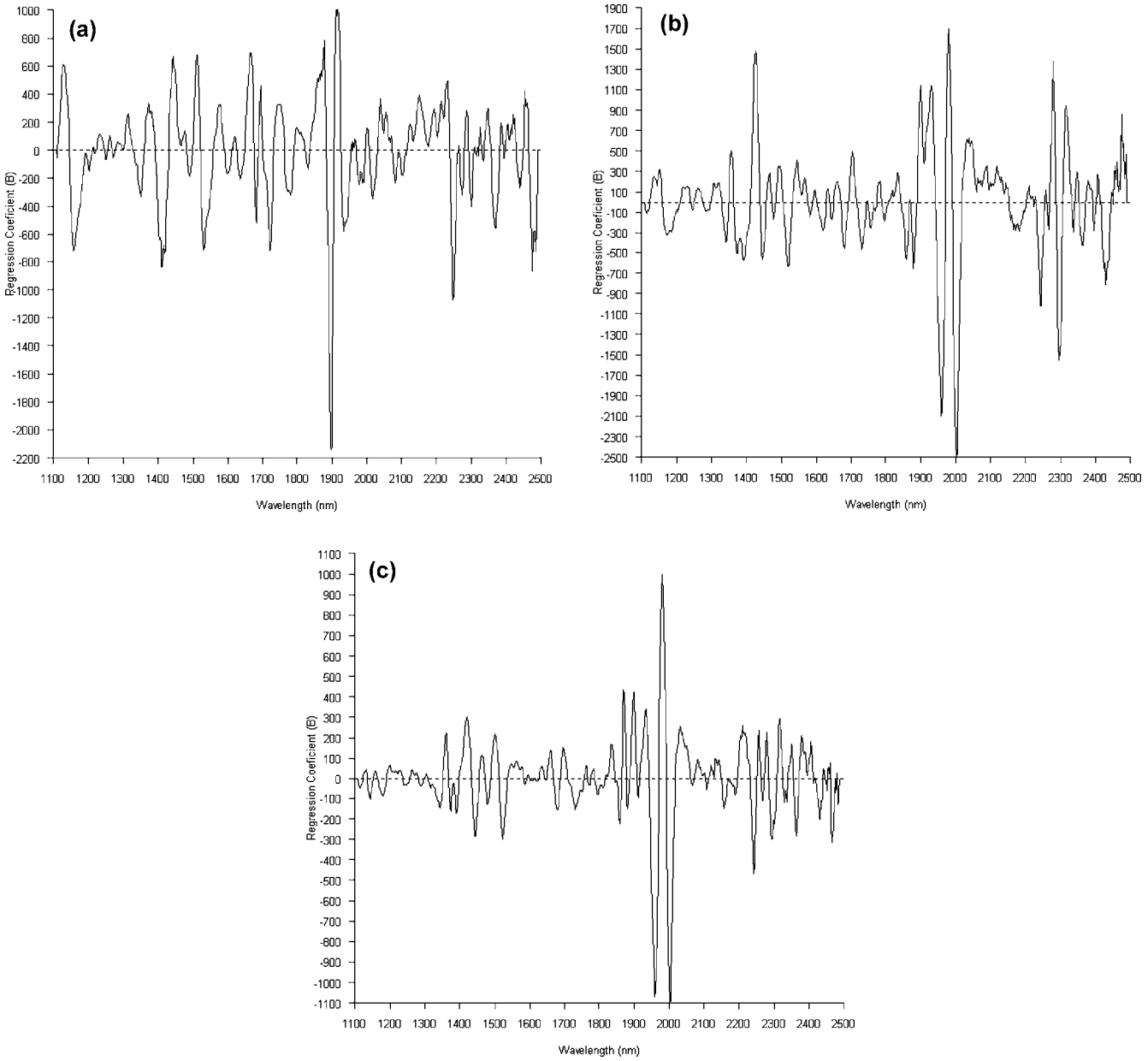

Figure 7. Regression coefficients for second-derivative models: (a) uronic acids; (b) ashes; (c) calcium.

To obtain the calibration equations, we defined the optimal number of PLS terms as the number of factors that did not significantly decrease the SECV when they were increased. Nevertheless, to prevent overfitting, an upper limit of optimal PLS terms was set at 1 PLS factor per 10 samples of calibration plus 2.[31] More *t*-outliers were detected for intact beans than for ground seed coat (Table 2). The predictive power of the models developed was tested with the external validation samples. Statistics for the optimal treatments considering the spectrum region comprised between 1110 and 2500 nm are presented in Table 2. For DF, ashes, and calcium, the predictive power of the models is better for ground samples than for intact beans, although the predictive power for UA and magnesium was similar for both types of samples. For intact beans, only RER values for ashes and calcium are good enough to enable very rough screening, whereas the rest of the RPD and RER values are worse. Taking the whole spectrum from 400 to 2500 nm does not improve the accuracy of predictions for intact beans samples.

Figures 2−6 show the comparison of laboratory- and NIRS-predicted content of ground validation set samples. For DF, the validation yielded RPD and RER values of 2.60 and 9.15, respectively. This means NIRS predictions enable rough screening, which can be very useful in the early stages of a breeding program. However, the RPD and RER values for UA (1.49 and 5.52, respectively) limit the application of NIRS. Although NIRS has been widely used to determine DF in different foods,[32,33] references to UA or pectin are scarce, probably due to their lower content and the fact that their molecules are associated with other fiber components, which makes it more difficult to find specific absorption bands.[34,35]

NIRS can determine mineral content because these elements establish bonds with certain functional groups of organic compounds. Both electrostatic and chelating bonded mineral elements can cause certain peaks in the infrared spectrum.

Therefore, ashes and several elements have been analyzed by NIRS in foods or plants.[17,36−39] In the seed coat of beans, the association of calcium or magnesium with carboxylate groups of UA can lead to their cross-linking. On the one hand, RPD and RER values obtained for ashes (3.49 and 14.09, respectively) and calcium (3.57 and 12.70, respectively) are considered fair and suggest that NIRS can be used for screening. On the other hand, the RER value for magnesium (6.57) is acceptable for rough screening, but the RPD value (1.50) is too low. To understand the different results obtained for the two metals, it is important to note that calcium is 5 times more abundant than magnesium in the seed coat of beans.

The regression coefficients for DF and magnesium (not shown) are erratically spread throughout the entire spectrum, with no wavelength region showing a differentiated contribution to the calibration equations. However, on the one hand, wavelengths around 1400 nm and above 2240 nm show high regression coefficients for the calibration for ashes and calcium (Figure 7). These wavelengths have been attributed to the interactions between minerals and O−H tones and C−H combination tones, respectively.[36,40] On the other hand, the regression coefficients for UA, calcium, and ashes show the extreme values in the region of 1880−2080 nm (Figure 7), where the most intensive peaks are present in the second-derivative spectrum. According to the literature, for the determination of mineral elements, such wavelengths have been attributed to the interaction between mineral ions and O−H tones, especially water.[36] Furthermore, a higher absorption in this region has been reported for polygalacturonic acids with respect to other carbohydrates,[34] due to the presence of carboxylic acids and their derivates. Thus, carboxylic acids and carboxylates and their interactions with calcium can be responsible for the elevated regression coefficients for calcium and UA from 1880 to 2080 nm. The strong correlation between ashes and calcium content ($r = 0.85$, $P < 0.001$) can also explain the relevance of these compounds for ashes. Magnesium should interact with UA in the same way as calcium does, but the lower magnesium content makes it difficult to obtain more significant regression coefficients in this zone.

A PLS regression taking into account only the wavelengths between 1880 and 2080 nm, instead of the whole spectrum, improved the predictive accuracy for calcium: the RPD and RER values obtained (4.21 and 14.96, respectively) were slightly higher than those obtained with the whole registered spectrum (3.57 and 12.70, respectively). However, the RPD and RER values for UA and ashes did not improve. Another attempt was performed for calcium and ashes considering the wavelengths regions 1340−1525, 1880−2080, and 2240−2430 nm simultaneously, but it did not yield better results.

Another parameter used to assess the goodness of fit of a predictive model is the SEP/SEL ratio,[19,31,41] which compares the predictive accuracy of NIR measurements and the precision of the reference method. The values of SEP/SEL obtained for dietary fiber, ash, and calcium (between 2 and 3) indicate good precision for NIRS determinations according to the criteria described by Ruiz-Jimenez,[31] whereas the values obtained for uronic acids and magnesium (between 3 and 4) indicate medium precision.

It should be pointed out that although validation accessions were not used at all to develop the calibration equations, they were taken from the same pool as the calibration ones. Then, the model should be amplified, retested, and revalidated with data of other accessions that we will use in future studies on breeding.

In summary, to optimize the selection process in a breeding program, a great number of phenotypes must be quickly evaluated to decide which progenies will be used to found the next generation. NIR spectra of milled common bean seed coats can provide enough information about the chemical components related to sensory attributes to help in the phenotyping work, although the knowledge of the correlations between both chemical and sensory characteristics should be improved. NIRS can also help in monitoring the sensory properties of marketable seeds. Time and money saved through the use of this technique can increase both the efficiency of the breeding programs and the quality control of the marketable beans.

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