Texture Prediction in Intact Green Asparagus by Near Infrared (NIR) Spectroscopy combined with Linear and Non-Linear Regression Strategies

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Abstract

Texture-related parameters were assessed in intact green asparagus at harvest and during postharvest storage using near-infrared spectroscopy combined with MPLS and LOCAL algorithms. Three spectrophotometers were evaluated for this purpose: a monochromator (range 400–2500 nm), a diode-array Vis–NIR spectrophotometer (range 400–1700 nm), and a handheld micro-electro-mechanical system (MEMS) spectrophotometer (range 1600–2400 nm). 300 green asparagus spears (cv. 'Grande') were used to obtain calibration models based on reference data and NIR data. Results for maximum shear force showed that LOCAL algorithm improved the predictive capacity of models constructed using all three NIRS instruments, increasing r^2 by 24%, 16% and 56% and reducing the SEP(c) values by 11%, 8% and 14%, respectively. For cutting energy, the LOCAL also improved the predictive capacity of the models (r^2 increased by 3% for the monochromator and the diode-array instrument and by 6% for the MEMS device; and the SEP(c) decreased by 3% in the three instruments). It is worth noting that while the monochromator and diode-array instruments displayed similar predictive capacity for the parameters tested, the MEMS instrument achieved slightly poorer results but has clear advantages for the measurement of texture in intact asparagus, being economical, portable, and easy to use *in situ*.

Keywords *In situ* NIRS sensors; MEMS technology; Intact green asparagus; Texture parameters; LOCAL algorithm.

Introduction

Texture, like external appearance, is one of the properties most influencing consumer acceptance or rejection of green asparagus (Bhowmik et al. 2000; Fuchs et al. 2008; Sanz et al. 2009).

Asparagus texture is determined by a number of pre-harvest and post-harvest factors, including: variety, type of agriculture, climate conditions, spear length and diameter, cut location, and postharvest storage conditions and duration. Growers, processors and consumers would benefit from any method enabling them to assess the impact of these factors on spear acceptability and shelf life (Rodríguez-Arcos et al. 2002a; Rodríguez et al. 2004).

Szczesniak (2002) notes the requirements to be met by an ideal texture-measurement system, which include: ease of use, speed, repeatability, good correlation with sensory methods, a mechanism of action similar to chewing, complete measurement of the attribute, accurate knowledge of what is being measured, and finally applicability to varying sizes. Asparagus texture has traditionally been assessed using destructive instrumental or sensory techniques (Rodríguez-Arcos et al. 2002b), thus permitting the quality evaluation of only a small number of samples from any given batch.

Near-infrared (NIR) spectroscopy is a particularly promising analytical technique for the quality assurance, certification and traceability of fruit and vegetables from grower to consumer (Saranwong and Kawano 2007; Sánchez and Pérez-Marín 2011); it is fast and non-destructive, and meets many of the criteria for texture measurement listed above. NIRS technology may therefore provide asparagus growers and processors with a viable alternative for product analysis.

Early research by Pérez-Marín et al. (2002) into the prediction of texture in green asparagus using NIRS technology measured maximum shear force and cutting energy on dried, ground samples using a monochromator instrument. Later, Flores-Rojas et al. (2009) measured the same two parameters in intact green asparagus using only monochromator and diode-array instruments. No published studies to date have addressed the prediction of texture in intact green asparagus using a portable, MEMS-based spectrophotometer. Moreover, the authors of these two papers only applied multivariate analysis methods based on global calibrations, using linear regression strategies, and particularly modified partial least squares (MPLS) regression. When using these methods, the selection of samples included in the calibration set is a critical process that greatly affects the precision and accuracy of the calibrations performed; the samples selected for calibration should include all possible sources of variation encountered during prediction, in order to increase the robustness of the calibration, although this usually decreases the accuracy of prediction (Shenk et al. 1997). In this respect, it has been reported that non-linear algorithms such as the LOCAL regression algorithm developed by Shenk et al. (1997) notably improve the precision and accuracy of the models as compared to those obtained using linear regression strategies, and that this algorithm obviates the need to choose between accuracy and robustness (Shenk et al., 2001; Sánchez et al., 2012). The LOCAL algorithm additionally appears to offer a promising regression strategy for predicting physical, texture-related attributes (Sánchez et al. 2011; Sánchez et al. 2012), enabling parameters such as maximum shear force and cutting energy to be modeled more effectively using local or specific equations.

The present study sought to investigate the viability of using NIRS technology in conjunction with non-linear regression strategies such as LOCAL to evaluate the texture of intact green asparagus both at harvest and during postharvest storage, and to compare the results with those obtained with models constructed using a global calibration strategy. At the same time, the performance of three commercial NIRS instruments was compared: a high-end monochromator suitable for laboratory measurements, used here for reference purposes, and two instruments suitable for *in situ* measurements: a diode-array spectrophotometer and a MEMS-based spectrophotometer.

Material and Methods

Asparagus

A total of 300 green asparagus spears (*Asparagus officinali*s L., cv. 'Grande'), grown in selected, controlled plots in Huétor-Tájar (Granada, Spain) using organic (N = 120 spears) and conventional (N = 180 spears) methods were harvested by hand in 2008. Conventionally-grown spears were harvested in April, May and June, whereas organically-grown spears were harvested only in April and May, since production ceased in late May.

Harvested spears were transported in refrigerated containers to the University of Córdoba laboratories, where they were kept in refrigerated storage (2ºC, 95% R.H.), with their ends in water throughout the trial period. Samples were drawn for analysis at 7, 14, 21 and 28 days; fresh untreated samples (0 days) were used as controls.

At the end of the pre-established postharvest storage period, spear texture (maximum shear force and cutting energy) was analyzed by NIR spectroscopy. For this purpose, spears were cut into three portions: tip (0-6 cm, measured from the apex of the spear), middle portion (6-12 cm) and base (12-18 cm), thus yielding a total of 900 samples (N = 540 conventionally-grown and N = 360 organically-grown).

Spectrum Collection

NIR spectra were collected on all samples in interactance-reflectance mode (instrument 1) and reflectance mode (instruments 2 and 3), using: (1) a FNS-6500 monochromator

(FOSS NIRSystems, Silver Spring, MD, USA); (2) a Perten DA-7000 diode-array spectrophotometer (Perten Instruments, North America, Inc., Springfield, IL, USA); and (3) a handheld micro-electro-mechanical system (MEMS) spectrophotometer (Phazir 2400, Polychromix, Inc., Wilmington, MA, USA). The main features of these instruments are listed in Table 1, the major difference between the three being the measuring principle involved.

The FNS-6500 scanning monochromator was interfaced to a remote reflectance-interactance fiber optic probe (NR-6539-A) with a 50 * 6 mm window. Each spear portion to be analyzed was hand-placed in the probe, ensuring direct contact between the spear section and the probe. This spectrophotometer works in the spectral range 400-2500 nm, taking readings at 2 nm intervals. Two measurements were made per section: the first at a random location representing the whole of the area analyzed (6 cm), and the second after rotating that area of the spear through 180º. Two spectra were collected for the three sections analyzed (tip, middle portion and base), and later averaged to provide a mean spectrum for that section.

NIR spectra of intact spear sections were also captured using a Perten DA-7000 parallel diode-array spectrophotometer working in the spectral range 400-1700 nm, and scanning at 5 nm intervals. This instrument does not use any moving parts in the optics, making it very stable and suitable for on-line measurement, providing fast noncontact measurement (1-3 s). The up-view mode was used for analysis; samples were placed directly on a round quartz window (diameter 127 mm); the surface was reduced to 50 * 6 mm in order to adapt to sample measurements. Two separate spectral measurements were made on each portion of the spear analyzed, rotating the sample through 180º after the first measurement. The two spectra were then averaged to provide a mean spectrum for each zone.

The Phazir 2400 is an integrated near-infrared handheld analyzer based on MEMS technology that incorporates all the essential components to deliver *in situ* applications as well as laboratory applications during postharvest storage (Geller, 2007). The instrument has no moving parts. The spectrometer scans at 8 nm intervals (pixel resolution 8 nm, optical resolution 12 nm), across a range of NIR wavelengths (1600-2400 nm). Two spectral measurements were made with this instrument, the first at a random location in the center of the analyzed area, and the second after rotating that area of the spear through 180º, with a measurement time of 1-2 s. The two spectra were averaged to provide a mean spectrum for each zone.

Texture Measurement

After spectrum collection, maximum shear force and cutting energy were measured using conventional destructive techniques.

Texture measurements were made individually at three points on the spear (3, 9 and 15 cm from the tip), following the method recommended by Wiley et al. (1956). The Warner-Bratzler cutting cell was used in conjunction with an Instron Universal Texturometer (Model 3343 Single Column, Instron Corporation, Norwood, MA, USA), fitted with a 1000 N load cell, selecting a constant displacement speed of 20 mm/min for all measurements.

The study parameters, maximum shear force (N) and cutting energy (J), were measured and recorded using Instron Bluehill 2 Software version 2.5 (Instron Corporation, Norwood, MA, USA). Changes in these parameters in each spear section were monitored during storage; a total of 900 measurements were made for each parameter.

Spectral Data Processing

The WinISI software package v. 1.50 (Infrasoft International, Port Matilda, PA, USA) was used for the chemometric treatment of data (ISI, 2000).

Prior to performing NIRS calibrations, the CENTER algorithm included in the WinISI software package was used to analyze the structure and spectral variability of the sample population. This algorithm performs an initial principal component analysis (PCA) and then calculates the distance of each sample (spectrum) from the center of the population in an n-dimensional space, using the Mahalanobis distance (GH); samples with a statistical value greater than 3 were considered outliers or anomalous spectra (Shenk and Westerhaus 1991, 1995a).

This algorithm was applied in the following near-infrared spectral regions: 1100-2200 nm (FNS-6500), 1100-1650 nm (Perten DA-7000) and 1600-2400 nm (Phazir 2400). A combined Standard Normal Variate (SNV) and Detrending (DT) method was used for scatter correction (Barnes et al., 1989), together with the first-derivative treatment "1,5,5,1", where the first digit is the number of the derivative, the second is the gap over which the derivative is calculated, the third is the number of data points in a running average or smoothing, and the fourth is the second smoothing (Shenk and Westerhaus 1995b).

The initial sample set comprised all samples from all three spear sections analyzed. Having ordered the sample set by spectral distances (from smallest to greatest distance from the center), those displaying GH values > 3 were discarded as outliers (N = 7, N = 33, and N = 32 for the FNS-6500, Perten DA-7000 and Phazir 2400 spectrophotometers, respectively). After discarding outliers from the sample set for each instrument, each initial sample set comprised 830 samples, since 1 sample was identified as an outlier for all three instruments. Subsequently, the structured sample set for the Phazir 2400 was used as the basis for establishing the calibration and validation sets to be used in constructing predictive models. One out of every 6 samples in the initial set (N = 139 samples; 16.6% of the population) was selected for the validation set, the remainder forming the calibration set (N = 691). The samples comprising the calibration and validation sets (Table 2) were the same for all three instruments, in order to facilitate subsequent comparison of results.

NIRS calibration models were then constructed to predict maximum shear force and cutting energy, using MPLS as the linear regression strategy (Shenk and Westerhaus 1995a). All regression equations were obtained using SNV-DT for scatter correction (Barnes et al., 1989). Four different mathematical derivative treatments were tested: 1,5,5,1; 2,5,5,1; 1,10,5,1 and 2,10,5,1 (Shenk and Westerhaus 1995b).

The following spectral regions were analyzed in order to construct texture-prediction models using MPLS: 500-2200 nm, 800-1650 nm, 800-2200 nm, 1100-1650 nm and 1100-2200 nm (FNS-6500); 515-1650 nm, 800-1650 nm and 1100-1650 nm (Perten DA-7000) and 1600-2400 nm (Phazir 2400). In order to eliminate spectral noise at the beginning and end of the spectral range, regions between 400-500 nm and 2200-2500 nm for the FNS-6500 instrument and between 400-515 nm and 1650-1700 nm for the Perten DA-7000 were discarded.

In the construction of calibration models using MPLS regression, six cross-validation steps were included in the process in order to select the optimum number of factors and avoid overfitting. Finally, validation errors were combined to obtain a standard error of cross validation (SECV) (Shenk and Westerhaus 1996).

The statistics used to select the best equations using MPLS were: the coefficient of determination for calibration (R^2), the standard error of calibration (SEC), the coefficient of determination for cross validation (r^2), the standard error of cross validation (SECV) and the coefficient of variation (CV), defined as the ratio between

SECV and the mean value of the reference data in the calibration set. Furthermore, the Residual Predictive Deviation (RPD) was calculated as the ratio of the standard deviation (SD) of the reference data to the SECV. This statistic, together with the CV, enables SECV to be standardized, facilitating the comparison of results obtained with sets of different means (Williams 2001).

The best predictive models obtained, selected by statistical criteria, were subsequently subjected to external validation following the protocol outlined by Shenk, et al., (2001).

The LOCAL algorithm (Shenk et al. 1997) was also applied as a non-linear regression strategy to predict the two texture-related parameters, using the same spectral regions and signal pretreatments indicated for MPLS regression.

The LOCAL algorithm is a procedure designed to locate and select, from within a large spectral database (based on the calibration set), samples with a spectrum similar to that of the unknown sample to be predicted. Selection is based on the coefficient of correlation between the spectrum of the unknown sample and each of the sample spectra forming the spectral library. The selected samples are then used as a calibration set to develop specific calibration equations, based on PLS linear regression, for predicting the unknown sample (Shenk et al. 1997).

The configuration of the LOCAL algorithm was optimized by varying the maximum number of samples selected for calibrations (k) – 70, 140, 210, 280 and 350 – and by setting at 15 the maximum number of PLS terms. Finally, the number of PLS factors discarded was set to the first three.

The effect of the different settings on the performance of LOCAL was evaluated by comparing the standard error of prediction (SEP), the coefficient of regression for external validation (r^2), the bias and the standard error of prediction corrected for bias or

SEP(c). The accuracy of the models obtained using the MPLS and LOCAL algorithms was then compared on the basis of the values obtained for the statistics SEP, SEP(c), r^2 and bias.

Results and Discussion

Prediction of Quality Parameters in Green Asparagus by MPLS Regression

The best calibration models obtained for predicting maximum shear force and cutting energy using each of the three instruments are shown in Tables 3 and 4.

As Table 3 shows, all three instruments displayed fair predictive capacity for maximum shear force. Results for the FNS-6500 and Perten DA-7000 instruments were very similar (r^2 = 0.51; SECV = 5.65 and 5.71 N, respectively), scanning over the range 1100-1650 nm with the monochromator and over the range 515-1650 nm with the diode-array instrument; in both cases, results were slightly better than those obtained using the MEMS-based instrument (r^2 = 0.38; SECV = 6.48 N) over the spectral range 1600-2400 nm. The first derivative provided the best results for predicting maximum shear force for the diode-array and MEMS instruments, while for the monochromator the best results were obtained with the second derivative.

In terms of the recommendations made by Williams (2001), the predictive capacity of the models constructed for maximum shear force (r^2 = 0.51), may be considered sufficient to classify values for this parameters as high, medium or low using the Perten DA-7000 and FOSS-6500 instruments. Models constructed using the Phazir-2400 (r^2 = 0.38) enabled values to be classed as either high or low. The difference in predictive capacity between the first two spectrophotometers and the hand-held instrument may reflect differences in measuring area; the MEMS device measures an area of only around 2 mm, whereas both the monochromator and the diode-array device perform a scan of the whole sample.

RPD values obtained for the models constructed using all three instruments were poorer than those reported by Pérez-Marín et al. (2002) using a monochromator and dried, ground samples from each spear section (RPD = 2.47), probably because this method of presentation reduces sample water content, thereby removing the main source of error in NIRS measurements on asparagus due to the fact that moisture content hampers the capture of spectra relevant for other attributes of interest (Polesello and Giangiacomo 1981). Presentation of the sample in powdered form also removes the difficulties associated with spear morphology, since the presence of bracts hinders sample-instrument interaction. Nonetheless, the lower predictive capacity of the models obtained here is offset by greater speed of analysis due to use of the intact product, and also by the non-destructive nature of the method, allowing wider sampling of all product batches. The RPD values recorded here were also slightly worse than those obtained by Flores-Rojas et al. (2009) in an analysis of the same intact spear sections (RPD = 1.74 and 1.49 using the monochromator and the diode-array instrument, respectively), although the range of the calibrations sets used by these authors was greater (13.58-90.93 N for the monochromator and 13.58-79.61 N for the diode-array device). However, their models were less accurate, with SECV values of 7.81 N and 8.43 N, for the monochromator and the diode-array instrument, respectively.

The predictive capacity of the models constructed to predict cutting energy (Table 4) using the monochromator (500-2200 nm) and the diode-array spectrophotometer (515-1650 nm) may be considered good (r^2 = 0.72 and 0.71; SECV = 0.03 J for both instruments), whilst the models obtained using the MEMS-based device (1600-2400 nm) would enable cutting energy values for spear sections to be classified as high, medium or low (r^2 = 0.52; SECV = 0.04 J), following Williams' recommendations (2001). Using the monochromator and the MEMS-based device, the best results for predicting cutting energy were obtained using the first derivative, whilst with the diode-array spectrophotometer the best results were achieved using the second derivative of the spectrum.

Other authors report slightly better results. In the study cited earlier, Pérez-Marín et al. (2002) recorded an RPD of 2.54, though using powdered samples, a form of presentation which – while ensuring a more homogeneous sample – requires time-consuming sample preprocessing, and is unsuited for *in situ* or on-line use. In a later study, Flores-Rojas et al. (2009) analyzed cutting energy in different sections of intact green asparagus spears using two NIRS instruments, reporting a slightly poorer predictive capacity (RPD = 1.95 for the monochromator; RPD = 1.57 for the diode-array spectrophotometer). They also reported, for both instruments, SECV values (0.06 J and 0.07 J, respectively) higher than those obtained in the present study.

Subsequent evaluation of the separate calibrations obtained for each of the three spear sections (tip, middle portion and base), and for the combined calibration for tip + middle portion, using MPLS regression with all three instruments tested (data not shown), confirmed that the predictive capacity of the calibration models obtained declined considerably when the sample set was restricted to one or two of the three spear portions, probably due to the consequently marked reduction in range for the parameter tested.

Redefinition of Validation Sets

Although initially, and following application of the CENTER algorithm, calibration sets for maximum shear force covered a range from 12.23 to 107.40 N in the three NIRS devices (Table 2), when constructing calibration models using MPLS regression those samples presenting values of over 52.46 N in the monochromator instrument and 54.45 N in the diode-array spectrophotometer and MEMS device were classed as outliers and removed from the final calibration set. The final range for this parameter was thus reduced; as comparison of Tables 2 and 3 confirms, the range of the external validation set initially selected using the CENTER algorithm was wider than that of the final calibration set. Therefore, 6 samples were removed from the external validation set in the three instruments, avoiding the extrapolation of the models developed.

For cutting energy parameter, the initial calibration sets covered the range 0.05-0.57 J for the three instruments tested (Table 2); this variability prompted a CV of 50%. However, when constructing calibration models using MPLS regression, samples with values exceeding 0.33 J, 0.34 J, and 0.31 J in the monochromator, diode-array and MEMS instruments, respectively, were classed as outliers and discarded; as a result, the range of the external validation set initially selected was wider than that of the final calibration set.

This meant that and for the same reason as mentioned above, again, 5 samples were eliminated in the external validation set in the monochromator (values of between 0.34 J and 0.45 J); 4 samples in the diode-array device (0.38 J < cutting energy < 0.45 J) and 7 samples in the MEMS instrument (0.32 J < cutting energy < 0.45 J).

Prediction of Quality Parameters in Green Asparagus by LOCAL Algorithm. Comparison of LOCAL vs. MPLS

SEP(c) values for the best models obtained for predicting maximum shear force and cutting energy using the LOCAL algorithm with all three spectrophotometers and the different values tested for maximum number of calibration samples (*k*), are shown in Figure 1.

For maximum shear force, the lowest values for SEP(c) obtained with the monochromator (SEP(c) = 5.84 N) and the diode-array spectrophotometer (SEP(c) = 5.79 N) were recorded using k = 280 samples, whereas the lowest SEP(c) value for the

MEMS device (6.27 N) was obtained when k = 210 samples. Moreover, the second derivative of the spectrum provided the best results in the monochromator; by contrast, the lowest SEP(c) value was obtained using the first spectral derivative in the diode-array spectrophotometer and MEMS device. Finally, the whole spectral range was used for all the instruments tested.

For cutting energy, the lowest SEP(c) values were obtained using the second derivative in the three instruments. Furthermore, both instruments, monochromator and diode-array spectrophotometer, provided the lowest SEP(c) (0.041 J and 0.043 J, respectively) over the spectral range 800-1650 nm; while for the MEMS device the best SEP(c) (0.044 J) was recorded scanning over the whole range. Finally, the number of samples used in LOCAL algorithm (k) was 350, 140 and 210 for the monochromator, diode-array spectrophotometer and MEMS device, respectively.

The predictive capacity of NIRS models constructed for maximum shear force and cutting energy using the MPLS and LOCAL regression algorithms for all three instruments is shown in Tables 5 and 6. In all cases, application of the LOCAL algorithm instead of MPLS regression improved the predictive capacity of the models for maximum shear force. For cutting energy, models constructed using LOCAL non-linear regression also displayed, for diode-array spectrophotometer and MEMS device, the same or greater predictive capacity than those obtained using the MPLS regression. However, a slightly worse predictive capacity was obtained when the spectral range 1100-1650 nm is used in the monochromator instrument, whereas the remaining spectral ranges tested in this instrument increased the predictive capacity in relation with MPLS regression.

The quality of the predictions for maximum shear force obtained with the external validation set using MPLS regression may be classed as poor, particularly in view of the low r^2 values obtained (Table 5).

Application of the LOCAL algorithm increased the values for r^2 (by 24% for the monochromator, 16% for the diode-array device and 56% for the MEMS instrument) compared to those obtained using MPLS regression, and enabled prediction of all the samples comprising the validation set. As well, the SEP(c) values were reduced (by 11% for the monochromator, 8% for the diode-array device and 14% for the MEMS instrument) by the application of the LOCAL algorithm. These results were in accordance with Shenk et al., (2001) who suggested that application of the LOCAL algorithm improved the predictive ability of models by around 10–30% compared to the MPLS regression.

The quality of the predictions for cutting energy obtained with the external validation set using MPLS regression (Table 6) may be classed as fair ($r^2 \geq 0.6$), in terms of the recommendations of Shenk et al. (2001), for the monochromator; the diode-array device and the MEMS instrument yielded r^2 values of 0.58 and 0.50, respectively.

Application of the LOCAL algorithm enabled prediction of all the same samples that were validated with MPLS regression in each instrument, and increased the value of r^2 for the models obtained using the monochromator and the diode-array instrument by 3% and the MEMS device by 6%. SEP(c) values were reduced by 3% when the LOCAL algorithm was used in the three instruments tested.

Most of the physical outliers discarded (75% for maximum shear force; 60% for cutting energy) during construction of calibration models using MPLS regression belonged – for both texture-related parameters – to the base section of the spear kept in refrigerated storage for at least 14 days. It should be noted that postharvest storage prompts an increase in spear resistance and hardness, mainly apparent in the lower sections of the spear (Rodríguez-Arcos et al. 2002a; Rodríguez et al. 2004). Because of this, the coefficient of variation for the calibration set declined by a mean 52% for maximum shear force and a mean 57% for cutting energy; thus, the models constructed used a much narrower final range (see Tables 2, 3 and 4).

As indicated earlier, samples displaying maximum shear force of over 52-55 N were generally discarded for all three NIRS instruments during the calibration procedure, as were samples with cutting energy values greater than 0.31-0.34 J. This reduction in range led to a decline in the mean and the standard deviation for the initial calibration sets (mean = 32.73 N; SD = 12.63 for maximum shear force; mean = 0.16 J; SD = 0.08 for cutting energy) with respect to the final values for the best obtained using MPLS regression (mean = 30.60 N; SD = 8.05 for maximum shear force; mean = 0.14 J; SD = 0.06 for cutting energy), indicating reduced variability within sets.

Williams (2001) notes that the value of the prediction error will be higher if most samples are clustered around the mean, which would account for the results obtained here for maximum shear force and cutting energy using the MPLS algorithm.

It is worth stressing that when the LOCAL algorithm was applied for the prediction of external validation sets, the best models for predicting maximum shear force were obtained using a k value of 280 samples for the monochromator and the diode-array spectrophotometer and k = 210 samples for the MEMS device, i.e. using a maximum of only 210 and 280 samples for each calibration, compared with the 641, 644 and 645 samples used for each instrument with MPLS regression; the best models for predicting cutting energy were again obtained with a maximum of 350 samples for the monochromator, 140 samples for the diode-array spectrophotometer and 210 samples for the MEMS device, compared with the 624, 633 and 618 used with the

MPLS algorithm. These results confirm the findings reported by Sánchez et al. (2011), who note that the population distribution for texture-related parameters, with a large number of redundant samples in the intermediate region of the range, may have an adverse effect on the model's predictive capacity using MPLS.

Conclusions

The results of this study, which used three NIR spectrophotometers with different working principles and measurement ranges and two different regression strategies, confirmed the viability of NIRS technology for the measurement of texture-related quality parameters in intact green asparagus. Application of the LOCAL algorithm proved particularly valuable for predicting maximum shear force and cutting energy in all three NIRS instruments tested. Although the best predictive models were obtained with the monochromator and the diode-array instrument, the MEMS-based spectrophotometer proved to be a viable option for evaluating texture-related quality in intact green asparagus. The diode-array and MEMS-based spectrophotometers have a promising future as part of asparagus quality-control programs, in that they are suitable for use both in the field and by the processing industry.

Compliance with Ethics Requirements

Conflict of Interest

María-José De la Haba declares that she has no conflict of interest.

Dolores Pérez-Marín declares that she has no conflict of interest.

Diego Rial-Huerta declares that he has no conflict of interest.

María-Teresa Sánchez declares that she has no conflict of interest.

This article does not contain any studies with human or animal subjects.

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Table 1 Basic technical characteristics of three spectrophotometers: monochromator (M), diode array (DA) and MEMS

Property	Instrument		
	M: FNS-6500	DA: Perten DA-7000	MEMS: Phazir-2400
Detector type	Silicon, 400–1100 nm; lead sulfide, 1100–2500 nm	76-channel silicon detector 400-950 nm; a 76-channel Indium-Gallium-Arsenide detector, 950-1700 nm	single-element InGaAs detector, 1600-2400 nm
Wavelength range (nm)	400-2500	400-1700	1600-2400
Spectral data rate	1.8 scans s^{-1}	30 scans s^{-1}	1-2 scans s^{-1}
Dispersion	Pre	Post	Post
Light source	Full spectrum	Full spectrum	Full spectrum
Analysis mode	Interactance-Reflectance	Reflectance	Reflectance

Table 2 Statistical analysis of calibration and validation sample sets, i.e., data ranges, means and standard deviations (SD) and coefficients of variation (CV) for the three instruments studied

Parameter	Set	Number	Range	Mean	SD	CV (%)
Maximum shear force (N)	Calibration	691	12.23-107.40	32.73	12.63	38.59
	Validation	139	15.58-69.61	31.83	10.56	33.18
Cutting energy (J)	Calibration	691	0.05-0.57	0.16	0.08	50.00
	Validation	139	0.05-0.45	0.16	0.08	50.00

Table 3 Calibration statistics for the best models obtained for predicting maximum shear force (N) in intact green asparagus using MPLS regression for different instruments and spectral ranges studied.

Instrument	Spectral range (nm)	Number	Mathematic treatment	Factors	Range	Mean	SD	SEC	R^2	SECV	r^2	RPD	CV (%)
FNS-6500	500-2200	645	1,10,5,1	5	13.33-54.45	30.71	8.26	5.51	0.55	5.74	0.52	1.44	18.69
	800-1650	640	2,10,5,1	4	13.33-54.45	30.58	8.09	5.48	0.54	5.65	0.51	1.43	18.48
	800-2200	636	2,10,5,1	2	12.23-54.45	30.54	8.04	5.62	0.51	5.71	0.50	1.41	18.70
	1100-1650	641	2,10,5,1	6	13.33-52.46	30.60	8.05	5.36	0.56	5.65	0.51	1.42	18.46**
	1100-2200	644	1,10,5,1	6	12.23-52.46	30.57	8.09	5.47	0.54	5.76	0.49	1.40	18.84
Perten DA-7000	515-1650	644	1,5,5,1	6	13.33-54.45	30.69	8.18	5.51	0.55	5.71	0.51	1.42	18.60*
	850-1650	646	1,5,5,1	5	13.33-54.45	30.69	8.16	5.64	0.52	5.77	0.50	1.43	18.80
	1100-1650	644	1,5,5,1	5	13.33-56.87	30.76	8.25	5.61	0.54	5.74	0.52	1.44	18.66
Phazir 2400	1600-2400	645	1,5,5,1	2	12.23-54.45	30.72	8.23	6.44	0.39	6.48	0.38	1.27	21.09*

* Best equation.

** The best of the best equations for the instruments studied.

Table 4 Calibration statistics for the best models obtained for predicting cutting energy (J) in intact green asparagus using MPLS regression for the three different instruments and the spectral ranges studied

Instrument	Spectral range (nm)	Number	Mathematic treatment	Factors	Range	Mean	SD	SEC	R^2	SECV	r^2	RPD	CV (%)
FNS-6500	500-2200	624	1,10,5,1	9	0.05-0.33	0.14	0.06	0.03	0.75	0.03	0.72	2.00	21.43**
	800-1650	636	1,5,5,1	8	0.05-0.33	0.14	0.06	0.03	0.72	0.03	0.69	2.00	21.43
	800-2200	632	1,10,5,1	6	0.05-0.33	0.14	0.06	0.03	0.72	0.03	0.69	2.00	21.43
	1100-1650	647	1,5,5,1	6	0.05-0.33	0.14	0.06	0.04	0.64	0.04	0.62	1.50	28.57
	1100-2200	628	1,5,5,1	7	0.05-0.33	0.14	0.06	0.03	0.74	0.03	0.68	2.00	21.43
Perten DA-7000	515-1650	633	2,5,5,1	8	0.05-0.34	0.14	0.06	0.03	0.74	0.03	0.71	2.00	21.43*
	800-1650	628	2,5,5,1	7	0.05-0.34	0.14	0.06	0.03	0.70	0.03	0.68	2.00	21.43
	1100-1650	618	2,10,5,1	11	0.05-0.33	0.14	0.06	0.03	0.70	0.03	0.68	2.00	21.43
Phazir 2400	1600-2400	618	1,10,5,1	6	0.05-0.31	0.14	0.05	0.04	0.53	0.04	0.52	1.25	28.57*

* Best equation.

** The best of the best equations for the instruments studied.

Table 5 Validation statistics for the best models for maximum shear force (N) using MPLS and LOCAL algorithms for the three instruments studied

Instrument	Method	Mathematic treatment	Spectral range (nm)	Factors	SEP	SEP (c)	Bias	r^2	Slope
FNS-6500	MPLS	2,10,5,1	1100-1650	6	6.54	6.53	-0.66	0.45[a]	0.99
	LOCAL (k[b] = 280)	2,10,5,1	500-2200	15 (-3)	6.08	5.84	-1.76	0.56[a]	0.98*
	(k = 350)	1,10,5,1	800-1650	15 (-3)	6.24	6.09	-1.44	0.52[a]	1.03
	(k = 350)	1,10,5,1	800-2200	15 (-3)	6.33	6.15	-1.57	0.51[a]	1.00
	(k = 210)	2,10,5,1	1100-1650	15 (-3)	6.49	6.27	-1.75	0.49[a]	0.94
	(k = 280)	2,10,5,1	1100-2200	15 (-3)	6.54	6.36	-1.61	0.48[a]	0.94
Perten DA-7000	MPLS	1,5,5,1	515-1650	6	6.36	6.26	-1.26	0.49[a]	1.04
	LOCAL (k = 280)	1,10,5,1	515-1650	15 (-3)	6.04	5.79	-1.78	0.57[a]	1.09**
	(k = 350)	1,5,5,1	800-1650	15 (-3)	6.09	5.89	-1.63	0.56[a]	1.11
	(k = 350)	2,5,5,1	1100-1650	15 (-3)	6.32	6.13	-1.62	0.51[a]	1.03
Phazir 2400	MPLS	1,5,5,1	1600-2400	2	7.25	7.26	-0.51	0.32[a]	0.99
	LOCAL (k = 210)	1,10,5,1	1600-2400	15 (-3)	6.37	6.27	-1.26	0.50[a]	0.93*

* Best equation for LOCAL algorithm in the instruments studied.

** The best of the best equations for the instruments studied and the regression algorithms evaluated

[a] Values exceeding control limits described in Materials and Methods Section.

[b] Number of samples used in LOCAL algorithm.

Table 6 Validation statistics for the best models for cutting energy (J) using MPLS and LOCAL algorithms for the three instruments studied

Instrument	Method	Mathematic treatment	Spectral range (nm)	Factors	SEP	SEP (c)	Bias	r^2	Slope
FNS-6500	MPLS	1,10,5,1	500-2200	9	0.042	0.042[a]	0.001	0.60	1.01
	LOCAL (k[b] = 350)	1,10,5,1	500-2200	15 (-3)	0.042	0.041	-0.009	0.62	0.96
	(k = 350)	2,5,5,1	800-1650	15 (-3)	0.042	0.041	-0.008	0.62	0.99**
	(k = 350)	1,10,5,1	800-2200	15 (-3)	0.042	0.042	-0.009	0.61	0.94
	(k = 280)	2,5,5,1	1100-1650	15 (-3)	0.043	0.043	-0.008	0.59[a]	0.99
	(k = 350)	1,10,5,1	1100-2200	15 (-3)	0.042	0.042	-0.007	0.61	0.92
Perten DA-7000	MPLS	2,5,5,1	515-1650	8	0.044	0.044[a]	0.002	0.58[a]	1.07
	LOCAL (k = 280)	2,5,5,1	515-1650	15 (-3)	0.043	0.044	-0.002	0.60	1.15
	(k = 140)	2,5,5,1	800-1650	15 (-3)	0.044	0.043	-0.005	0.60	1.07*
	(k = 280)	2,5,5,1	1100-1650	15 (-3)	0.045	0.045	-0.002	0.58	1.16
Phazir 2400	MPLS	1,10,5,1	1600-2400	6	0.045	0.045	0.006	0.50[a]	1.13
	LOCAL (k = 210)	2,10,5,1	1600-2400	15 (-3)	0.044	0.044	-0.006	0.53[a]	0.88[a]*

* Best equation for LOCAL algorithm in the instruments studied.

** The best of the best equations for the instruments studied and the regression algorithms evaluated

[a] Values exceeding control limits described in Materials and Methods Section.

[b] Number of samples used in LOCAL algorithm.

Fig. 1. Best SEP(c) values for the prediction of texture parameters in intact asparagus using the LOCAL algorithm for the different selected sample values (k), the best mathematical treatments and spectral ranges for the three instruments studied