MEMS-NIRS TECHNOLOGY FOR FAST AUTHENTICATION OF GREEN ASPARAGUS GROWN UNDER ORGANIC AND CONVENTIONAL PRODUCTION SYSTEMS

María-Teresa Sánchez[a,*], Ana Garrido-Varo[b], José Emilio Guerrero[b], Dolores Pérez-Marín[b,*]

[a] Department of Bromathology and Food Technology, University of Cordoba, Campus of Rabanales, 14071 Córdoba, Spain

[b]Department of Animal Production, University of Cordoba, Campus of Rabanales, 14071 Córdoba, Spain

* Corresponding authors. Tel.: +34 957 212576; fax: +34 957 212000. E-mail addresses: teresa.sanchez@uco.es (M.T.S.); dcperez@uco.es (D.P.-M.)

ABSTRACT

This study sought to evaluate the ability of near-infrared reflectance spectroscopy (NIRS) to classify intact green asparagus as a function of growing method (organic *vs*. conventional) during postharvest refrigerated storage, and as a function of harvest month and postharvest cold storage duration. It also sought to identify the portion of the spear best suited for this purpose. A total of 300 green asparagus spears (*Asparagus Officinali*s L., cv 'Grande'), were sampled after 7, 14, 21 and 28 days of refrigerated storage (2ºC, 95% RH) and at commercial harvest time. Three commercially-available spectrophotometers were evaluated for this purpose: a scanning monochromator (scanning range 400-2500 nm), a diode-array Vis/NIR spectrophotometer (range 400-1700 nm) and a handheld MEMS spectrophotometer (range 1600-2400 nm). Models constructed using partial least squares 2-discriminant analysis (PLS2-DA) correctly classified 91% of samples by growing method using the diode array instrument, between 86% and 91% using the scanning monochromator and between 82% and 84% using the handheld spectrometer. The tip and the middle portion of the spear proved to be the most suitable for this purpose. Using similar models, the diode array instrument correctly classified 100% of samples by harvest month, compared with between 97% and 98% using the scanning monochromator and between 87% and 96% using the handheld instrument. Models also correctly classified between 66% and 97% of samples by postharvest storage time, depending on the instrument used. The results indicate good performance of the prediction models, particularly for predicting harvest month and growing method, determination of the latter being of considerable importance for the authentication of organic asparagus at industrial level.

Keywords: MEMS-NIR spectroscopy; Green asparagus; Organic agriculture; Harvest month; Shelf-life; Discriminant analysis.

1. Introduction

Over the last ten years, organic farming has become the fastest-growing sector in developed countries, resulting in a constantly-increasing consumer demand for organic produce (Magkos et al, 2003; Zepeda and Li, 2007).

The popularity of organic foods is due largely to the perception that produce grown without the use of artificial insecticides, herbicides and fertilizers will be of greater nutritional value and sensory quality than conventionally-grown produce (Demirkol and Cagri-Mehmetoglu, 2008).

Although the commercial promotion of organic foods is based on the idea that they are more nutritive and/or of better sensory quality than their conventional counterparts, the evidence adduced in support of these claims is by no means irrefutable; research has yielded conflicting results, which have made it difficult to reach a general consensus (Bourn and Prescott, 2002; Zhao et al., 2006; Zepeda and Li, 2007; Dangour et al., 2009). Moreover, the consumer preference for organic fruit and vegetables is not borne out by the findings of sensory evaluation panels (Bonti-Ankomah and Yiridoe, 2006; Zhao et al., 2007). However, despite this controversy and even though organic produce may not in fact be any better – in terms of nutritional or sensory quality – than conventionally-grown produce, consumers may have other reasons (e.g. food safety, environmental concerns) for their preference (Bourn and Presscot, 2002). Organic asparagus, for example, has significantly higher sugar content than conventionally-produced asparagus, and consumers may prefer its slightly sweeter taste (Lorlowhakarn et al., 2008).

The introduction of effective analytical techniques for identifying the origin and measuring the quality of raw materials and finished products remains something of a challenge for the food industry (Śmiechowska, 2007), which requires – among other things – non-destructive methods that are sufficiently accurate not only to identify potential quality differences between organic and conventional produce, but also to authenticate the organic origin of a given fruit or vegetable (Bourn and Prescott, 2002; Bonti-Ankomah and Yiridoe, 2006; Zhao et al., 2007).

Near-infrared reflectance spectroscopy (NIRS) is a promising analytical technique, likely to meet many of the industry's requirements with regard to the authentication/certification of raw materials and finished products, the measurement of physical/chemical, nutritional and sensory quality, and the estimation of postharvest shelf-life (Saranwong and Kawano, 2007; Sánchez and Pérez-Marín, 2011).

The value of NIRS technology for authenticating food products and determining their quality and shelf-life lies in the fact that every substance has a unique and characteristic NIR spectrum, much as fingerprints distinguish humans; it consists of a composite mosaic of radiation, scatter, specular and diffuse reflectance and absorption of radiation due to specific chemical bonds. If two samples of a material have very similar spectra, it may be assumed that they have very similar chemical and physical composition (i.e. scatter and surface reflectance). Differences between spectra, by contrast, indicate that the samples are physically and/or chemically different (Workman and Shenk, 2004). However, to extract unique, relevant physical and chemical information about each sample, mathematical algorithms are required for spectral-signal pretreatment (Bertrand, 2000).

In asparagus, NIRS technology has hitherto been used mainly for texture evaluation (Pérez Marín et al., 2002; Flores-Rojas et al., 2009). Although it might initially seem illogical to investigate texture using spectroscopic techniques traditionally used for chemical rather than structural measurements, a number of authors (Xie et al., 2003; Hsieh and Lee, 2005; Lu and Peng, 2006; Oey et al., 2007) have advocated the use of NIRS technology for measuring physical properties (hardness, firmness, particle size) closely linked to product texture and postharvest shelf life.

NIRS technology has been successfully used for authenticating green asparagus varieties (Pérez Marín et al., 2001), and for constructing models to estimate harvesting date and spear portion analyzed in white asparagus (Jarén et al., 2006). Sánchez et al. (2009) used NIR spectroscopy to construct models for the shelf-life discrimination of green asparagus stored in a cool room under controlled atmosphere.

The present study sought to evaluate the reliability and accuracy of MEMS-NIRS technology for authentication of the origin of green asparagus (organic *vs*. conventional), for identifying the portion of the spear analyzed, harvest time and postharvest cold storage duration. Three commercially-available spectrophotometers were evaluated (a MEMS-based spectrometer, a scanning monochromator and a diode-array spectrophotometer) in order to determine which was best suited for quality assurance and field/postharvest traceability in green asparagus.

2. Materials and methods

2.1. Vegetable material

In 2008, a total of 300 green asparagus spears (*Asparagus Officinali*s L., cultivar '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 between April and either June (conventionally-grown spears) or May (organically-grown spears). Spears were kept in refrigerated storage (2ºC, 95% R.H.) with their ends in water throughout the trial period, and samples were drawn for analysis at 7, 14, 21 and 28 days; fresh untreated samples (0 days) were used as controls.

Fresh and stored asparagus spears were cut into three parts for analysis: tip (0-6 cm, measured from the apex of the spear), middle portion (6-12 cm) and base (12-18 cm). After cutting spears into three portions, the total number of available samples was 900 (N = 540 conventionally-grown and N = 360 organically-grown).

2.2. Spectrum collection

Spectra were collected on all samples in reflectance mode (Log 1/R) using three NIR-instruments: (1) a scanning monochromator (FNS-6500, FOSS NIRSystems, Silver Spring, MD, USA); (2) a diode-array VIS–NIR spectrophotometer (Perten DA-7000, 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 (SM) 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 so that the desired asparagus location was centered on, and in direct contact with, the probe. Two measurements were made: 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.

NIR spectra of intact spears were also captured using a Perten DA-7000 parallel diode-array Vis–NIR spectrophotometer. 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). Samples were analyzed in up-view mode, in which the instrument is inverted with respect to its usual configuration; samples were placed directly on a round quartz window (diameter 127 mm); the surface as reduced to 50 * 6 mm in order to adapt to sample measurements. The spectrophotometer scanned at 5 nm intervals, across a range encompassing the entire visible (400–780 nm) and near IR

(780–1700 nm) wavelength ranges. Three separate spectral measurements were made on each zone of the spear analyzed, rotating the sample through 120º after the first measurement. The three spectra were averaged to provide a mean spectrum for each zone.

The Phazir 2400 is an integrated near-infrared handheld analyzer that incorporates all the essential components to deliver on-site applications. These include a MEMS-based DTS NIR spectrophotometer and a tungsten light source for illuminating the sample in the near-infrared region. The reflected light is collected and measured by a single InGaAs photodetector, and the instrument has no moving parts. The spectrophotometer scans at 8 nm intervals (pixel resolution 8 nm, optical resolution 12 nm), across a range of near IR wavelengths (1600–2400 nm). Two spectral measurements were made with this instrument, the first at a random location in the centre 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.

2.3. Definition of the calibration and validation sets

The design of models to classify asparagus by growing method, in order to evaluate the viability of using NIRS technology for authenticating green asparagus spears comprised 2 classification groups: organically-grown and conventionally-grown. Samples sets initially comprised 540 conventional asparagus samples and 360 organic asparagus samples, for each NIR spectrophotometer tested. The difference in number of samples was due to the early ending (May) of the harvesting season for organic asparagus. Models were also designed with class-balanced sets, by including only spears harvested in April and May under both growing methods; thus, 360 samples of each class were used for each of the spectrophotometers tested.

Using the handheld MEMS instrument, which allows spectra to be collected *in situ,* models were constructed to classify spears by growing method, taking into account the portion of the spear sampled, with a view to determining which portion is best suited for determining the growing method used. Sample sets for conventionally-grown asparagus comprised 180 samples taken from the tip, 180 samples drawn from the middle portion of the spear, and 180 from the base of the spear; for organically-grown asparagus, sample sets comprised 120 samples from the tip, 120 from the middle portion and 120 from the base. Class-unbalanced models were designed, comprising conventionally-grown spears harvested in April, May and June, and organically-grown spears harvested in April and May, as well as class-balanced models comprising only spears harvested in April and May under both growing methods.

The third of the discriminant models was designed to classify spears as a function of harvesting month, distinguishing between April and May for each growing method. Classification groups for each month comprised 180 samples for each growing method and instrument tested.

The design of models to classify asparagus by postharvest storage time with a view to estimating shelf-life was based on five classification groups: 0, 7, 14, 21 and 28 days' storage. Since the harvesting of organically-grown asparagus ended earlier than that of conventionally-grown asparagus, different number of samples were involved. Accordingly, two types of model were designed: (1) a class-balanced model in which each storage-day group contained 72 samples for each growing method and each NIRS instrument tested, i.e. eliminating conventionally-grown samples harvested in June; and (2) a class-unbalanced model in which groups of conventionally-grown asparagus comprised 108 samples, and those of organically-grown asparagus 72 samples for each of the three instruments tested.

For structuring the calibration set, an initial principal component analysis (PCA) was performed to calculate the centre of the population and the distance of samples (spectra) from that centre 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). After elimination of outlier spectra, samples to be used for calibration and external validation sets were selected solely on the basis of spectral data, following Shenk and Westerhaus (1991), using the CENTER algorithm included in the WinISI II software package version 1.50 (Infrasoft International, Port Matilda, PA, USA). After elimination of outlier spectra, and having ordered the sample set by spectral distances (from smallest to greatest distance from the center), a structured selection of the external validation set (20% of the samples for each classification group, i.e., 1 out of every 5 samples in the overall set), solely on the basis of spectral data, was performed following Shenk and Westerhaus (1991).

2.4. Construction of NIR classification models

Discriminant models were constructed to classify asparagus by growing method, harvest month and postharvest storage time, using PLS Discriminant Analysis (PLS-DA) for supervised classification (Naes et al., 2002). Specifically, the PLS2 algorithm was applied, using the "Discriminant Equations" option in the WINISI v. 1.50 software package (ISI, 2000).

All models were constructed using four cross-validation groups (i.e. the calibration set is partitioned into four groups; each group is then predicted using a calibration developed on the other samples), in the wavelength ranges: 1) 500-2200, for the FNS-6500; 2) 515-1650 nm, for the Perten DA-7000 and 3) 1600-2400 nm, for the Phazir 2400. To eliminate signal noise in the scanning monochromator and the diode array instrument at the beginning and end of the spectrum, the wavelength ranges between 400-500 and 2200-2500 nm in the former and 400-515 nm and 1650-1700 nm in the latter were discarded. A combined Standard Normal Variate (SNV) and Detrending (DT) method was used for scatter correction (Barnes et al., 1989). First and second-derivative treatments were tested: 1,5,5,1; 1,10,5,1; 2,5,5,1 and 2,10,5,1, 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, 1995).

The precision of the models obtained was evaluated using the percentage of correctly-classified samples. The best-fitting equations, as selected by statistical criteria, were subsequently validated, a procedure determining the predictive ability of a discriminant model based on a sample set which has not been used in the training procedures, taking into account the percentage of correctly-classified samples for the validation set.

3. Results and discussion

3.1. Classification by growing method

Since organic asparagus production concluded at the end of May, two sets comprising different sample numbers were analyzed: 1) conventionally-grown asparagus harvested in April, May and June, and organically-grown asparagus harvested in April and May (class-unbalanced set); and 2) equal numbers of conventionally- and organically-grown asparagus harvested in April and May (class-balanced set).

The results obtained for the best classification models for predicting growth method, using the PLS2-DA algorithm and the three NIRS instruments tested, are shown in Table 2, both for unbalanced and balanced sets. The percentage of correctly-classified samples ranged between 82.08% and 91.32% in class-unbalanced sets and between 83.71% and 91.20 % in balanced sets, differences between the values for the two sets being negligible.

In general terms, the most accurate models were obtained using D_1 log(1/R) for FNS-6500 and Phazir 2400, and D_2 log(1/R) for the Perten DA-7000.

The Perten DA-7000 instrument correctly classified 91% of spears by growth method, regardless of set size, compared with 91.32% of spears in the class-unbalanced set and 85.92% in the class-balanced set using the FNS-6500 and with 82.08% and 83.71%, respectively, for the Phazir 2400. These minimal differences in classification rates regardless of set size have also been reported by Pérez-Marín et al. (2006), who note that PLS2 is less sensitive to the use of class-unbalanced sets.

In short, although all models adequately classified intact green asparagus by growing method – indicating that NIR spectra enable discrimination between conventionally- and organically-grown produce – marginally better results were obtained using the Perten DA-7000 diode-array VIS–NIR spectrophotometer.

D_2 log(1/R) spectra for intact spears grown under organic and conventional systems, obtained using Perten DA-7000 instrument, are shown in Figure 1; areas of maximum difference, which are useful for discrimination purposes, are also indicated.

Absorption peaks at 615 nm, 670 nm, 860 nm, 915 nm, 1110 nm and 1355 nm appear to be especially relevant for the classification of asparagus by conventional vs. organic method. Due to the considerable overlap between the two average spectra, the wavelength range between 1315 nm and 1460 nm – mainly related to cellulose content (Maaloly and Jaillais, 2006) – was enlarged (Figure 1).

Models were validated using samples not included in the training sets. The percentage of correctly classified samples in class-unbalanced sets was between 90.65% and 92.93% using the Perten DA-7000, between 86.11% and 86.92% with the FNS-

6500, and between 74.65% and 93.40% with the Phazir 2400. For class-balanced sets, correct classification rates ranged from 87.50% to 92.96% for the Perten DA-7000; from 87.50% to 89.19% for the FNS-6500, and from 76.06% to 80.00% for the Phazir 2400.

Similar findings were reported by Lorlowhakarn et al. (2008) in a study using traditional analysis techniques to classify asparagus by growing method; these authors found that organically-grown asparagus contained significantly higher levels of iron, carbohydrates and total sugars than conventionally-grown asparagus, although protein levels were lower.

A further aim of the present study was to determine whether the portion of the spear from which the spectrum was collected (tip, middle portion, base) in any way enhanced the discriminant ability of the models. Hernández et al. (1993) and Garrido et al. (2001) reported that the middle portion of the spear yielded the most representative results for spear fiber content during harvesting. Here, spectral data were collected using the handheld MEMS instrument, which can be used for *in situ* spear measurement.

Results obtained using models for classifying spear portion (tip, middle, base) as a function of growing method are shown in Table 3.

For class-unbalanced models, the Phazir instrument correctly classified 88.14% of middle-portion samples by growing method, compared with 86.75% for tip samples and 85.04% for base samples, using D_1 log(1/R) for all models. Validation of class-unbalanced models yielded correct classification rates of between 80.00% and 91.66% for tip samples, between 87.37% and 89.01% for middle-portion samples, and between 79.16 and 80.55% for base samples.

Using class-balanced models, 88.17% of tip samples were correctly classified by growing method, compared with 87.83% for middle-portion samples and 83.96% for base samples, using D_1 log(1/R) in all cases. At validation, 79.16% of organic-asparagus base samples were correctly classified by growing method, compared with 95.83% of organic asparagus tip samples.

These results indicate that the tip and the middle portion of the spear are the most useful sampling areas for classifying spears by growing method.

3.2. Classification by harvest month

The results obtained for the best classification models for predicting harvest month (April *vs.* May) for both growing methods, using the all three NIRS instruments tested, are shown in Table 4.

Analysis of the results suggests that the most accurate discriminant models were obtained using D_1 log(1/R) for the FNS-6500 and Phazir 2400 spectrophotometers, and D_2 log(1/R) for the Perten DA-7000 instrument, for both conventionally- and organically-grown asparagus.

The Perten DA-7000 correctly classified 99.65% of organically-grown spears and 100% of conventionally-grown spears by harvest month, compared with 97.21% and 97.84%, respectively, for the FNS-6500 and 87.32% and 96.06% for the Phazir 2400.

Jarén et al., (2006) used a monochromator operating in the spectral region between 800 and 1700 nm to predict harvest date in intact white asparagus harvested in March, April and May; 75.4% of March samples were correctly classified, compared with 68.2% of April samples and 68.4% of May samples; these results were poorer than those obtained here with all three instruments tested (Table 4).

External validation of models for classifying spears as a function of harvest month yielded the following results: using the Perten DA-7000, between 97.22% and

100% of samples were correctly classified, compared with between 97.14% and 100% for the FNS-6500, and between 85.30% and 100% for the Phazir 2400.

Generally speaking, all three instruments proved suitable for predicting harvest month in green asparagus, although slightly better results were obtained using the Perten DA-7000 diode-array VIS–NIR spectrophotometer. These results confirm findings reported by Bhowmik et al. (2002) for the destructive measurement of texture in green asparagus between March and October; these authors found a larger number of tough spears in March, April and October as a consequence of slow growth due to cold weather. Lipton (1990) also concluded that asparagus is more fibrous when it grows in cool than in warm weather.

3.3. Classification by postharvest storage time

Results for the best classification models obtained, using PLS2-DA, for predicting postharvest storage time for organically- and conventionally-grown spears kept under refrigeration with their ends in water, are shown in Table 5.

The best discriminant models were obtained with D_2 log(1/R) for the FNS-6500 and Perten DA-7000 instruments, and with D_1 log(1/R) (conventional growing, balanced and unbalanced sets) and D_2 log(1/R) (organic growing) for the Phazir 2400.

The Perten DA-7000 instrument correctly classified 95.34% of organically-grown spears by storage duration, compared with 95.31% of conventionally-grown spears in the class-balanced set and 97.17% in the unbalanced set; the FNS-6500 correctly classified 75.90% of organically-grown spears, compared with 67.78% and 72.50% of conventionally-grown spears in the balanced and unbalanced sets, respectively; the Phazir 2400 correctly classified 75.09% of organically-grown spears, 65.87% of conventionally-grown spears in the balanced set and 79.71% in the unbalanced set.

These results confirm that all three instruments are suitable for predicting shelf-life in green asparagus; the scanning monochromator and the MEMS-based displayed very similar discriminant abilities, while the Perten DA-7000 spectrophotometer yielded marginally better results.

The results obtained here for the diode-array spectrophotometer are better than those reported by Sánchez et al. (2009) when comparing the same scanning monochromator used and a different diode array instrument with the same spectral range for predicting postharvest storage time in green asparagus stores under refrigerated conditions in three different atmosphere regimes: air (21 kPa O_2 + 0.03 kPa CO_2), controlled atmosphere 1 (5 kPa O_2 + 5 kPa CO_2) and controlled atmosphere 2 (10 kPa O_2 + 10 kPa CO_2); these authors found that the diode-array spectrophotometer correctly classified only 75% of samples stored in the air regime.

The mean spectra for each class (storage time) using the Perten DA-7000 instrument, together with the spectral signal pretreatment that yielded the best result in each case, grouped by growing method, are shown in Figure 2.

Absorption peaks at 610 nm, 645 nm, 680 nm, 905 nm, 935 nm, 1090 nm, 1125 nm, and in the region between 1235-1375 nm appeared to have more weight in the classification of organically- and conventionally-grown spears by postharvest storage time. This indicates that the discrimination of asparagus by storage time in the NIR region of the spectrum is related to water content and O-H combinations, suggesting that differences caused by water loss and fiber profiles might contribute to variations as a function of storage time. NIR spectra are clearly sensitive to chemical changes in neutral and acid detergent fiber and in sugar and organic acid contents over the storage period (Garrido et al., 2001; Bhowmik et al., 2002).

At subsequent external validation of models constructed to classify organic spears by postharvest storage time, between 92.86% and 100% of samples were correctly classified using the Perten DA-7000 instrument, while percentages were slight lower for the FNS-6500 (between 86.67% and 100%) and the Phazir 2400 (between 57.14% and 86.67%). For conventionally-grown spears in class-balanced sets, the Perten DA-7000 spectrophotometer correctly classified between 90.91% and 100% of spears; the FNS-6500 between 47.62% and 90.91%; and the Phazir 2400 between 47.62% and 80.95%. For conventionally-grown spears in class-unbalanced sets, percentages ranged from 93.33% to 100% for the Perten DA-7000; from 64.29% to 93.33% for the FNS-6500; and from 69.23% to 93.33% for the Phazir 2400.

4. Conclusions

The results obtained indicate that NIRS technology using a MEMS handheld instrument can be incorporated as a pre and postharvest sensor technology for use in the horticultural industry to authenticate the organic *vs.* conventional origin of intact green asparagus, with an accuracy of over 82%, although slightly better discriminant models were constructed using the diode array spectrophotometer, which can only be used for on-line determinations in the packing house. The tip and middle portion of the spear proved to be the most suitable sampling areas for determining the organic or conventional origin of green asparagus. The results also suggest that NIRS technology can be used for providing information about asparagus quality, i.e. harvest month and postharvest storage time, parameters that influence spear texture and final consumer acceptability.

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Table 1

Basic technical features of three spectrophotometers: scanning monochromator (FNS-6500), diode array (Perten DA-7000) and MEMS (Phazir-2400).

Properties	**Instrument**		
	FNS-6500	Perten DA-7000	Phazir-2400
Detector type	Silicon, 400–1100 nm. Lead sulphide, 1100–2500 nm	Silicon, 400-950 nm. Indium-gallium-arsenide, 950-1700 nm	Indium-gallium-arsenide, 1600-2400 nm
Wavelength range (nm)	400-2500	400-1700	1600-2400
Spectral data rate	1.8 scans/second	30 scans/second	1-2 scans/second
Dispersion	Pre	Post	Post
Light source	Full spectrum	Full spectrum	Full spectrum
Analysis mode	Interactance-Reflectance	Reflectance	Interactance-Reflectance

Table 2

Percentage of asparagus spears correctly classified by growing method. PLS-DA.

Qualitative groups	Unbalanced models						Balanced models					
	FNS-6500 A: 91.32 % B: 0.32 C: 20 D: 1,10,5,1		Perten DA-7000 A: 91.14% B: 0.32 C: 30 D: 2,10,5,1		Phazir 2400 A: 82.08% B: 0.38 C: 27 D: 1,5,5,1		FNS-6500 A: 85.92 % B: 0.35 C: 22 D: 1,10,5,1		Perten DA-7000 A: 91.20 % B: 0.32 C: 29 D: 2,5,5,1		Phazir 2400 A: 83.71% B: 0.37 C: 28 D: 1,5,5,1	
Growing method	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set
Organic	89.55%	86.11%	89.05%	92.93%	75.09%	74.65%	84.67%	87.50%	90.81%	92.96%	86.12%	76.06%
Conventional	92.51%	86.92%	92.52%	90.65%	86.73%	93.40%	87.19%	89.19%	91.58%	87.50%	81.29%	80.00%

A, Percentage of correctly classified training samples after cross validation; B, Model SECV; C, number of factors; D, math treatment.

Table 3

Percentage of spears correctly classified by sampling area and growing method. PLS-DA. Phazir 2400. Spectral range: 1600-2400 nm.

Qualitative groups	**Unbalanced models**						**Balanced models**					
	Tip		Middle		Base		Tip		Middle		Base	
	A: 86.75% B: 0.37 C: 28 D: 1,10,5,1		A: 88.14% B: 0.36 C: 28 D: 1,10,5,1		A: 85.04% B: 0.40 C: 27 D: 1,10,5,1		A: 88.17% B: 0.37 C: 20 D: 1,10,5,1		A: 87.83% B: 0.38 C: 23 D: 1,10,5,1		A: 83.96% B: 0.40 C: 25 D: 1,5,5,1	
Growing method	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set
Organic	82.11%	91.66%	86.17%	87.37%	95.83%	79.16%	87.37%	95.83%	86.17%	91.66%	84.95%	79.16%
Conventional	89.93%	80.00%	89.44%	89.01%	95.65%	80.55%	89.01%	95.65%	89.47%	83.33%	82.98%	87.50%

A, Percentage of correctly classified training samples after cross validation; B, Model SECV; C, number of factors; D, math treatment.

Table 4

Percentage of spears correctly classified by harvest month. PLS-DA.

Qualitative groups	**FNS-6500**				**Perten DA-7000**				**Phazir 2400**			
	Organic A: 97.21% B: 0.23 C: 14 D: 1,10,5,1		Conventional A: 97.84% B: 0.24 C: 26 D: 1,10,5,1		Organic A: 99.65% B: 0.22 C: 11 D: 2,5,5,1		Conventional A: 100% B: 0.19 C: 22 D: 2,5,5,1		Organic A: 87.32% B: 0.37 C: 27 D: 1,10,5,1		Conventional A: 96.06% B: 0.27 C: 23 D: 1,5,5,1	
Harvest month	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set	Training set	Validation set
April	97.90%	100%	97.84%	97.14%	100%	100%	100%	97.22%	85.19%	85.30%	94.96%	97.14%
May	96.53%	97.22%	97.84%	97.14%	99.30%	100%	100%	100%	89.36%	94.40%	97.14%	100%

A, Percentage of correctly classified training samples after cross validation; B, Model SECV; C, number of factors; D, math treatment.

Table 5. Percentage of spears correctly classified by storage time. PLS-DA.

Qualitative Groups	FNS-6500					
	Organic		Conventional[1]		Conventional[2]	
	A: 75.90%		A: 67.78%		A: 72.50%	
	B: 0.34		B: 0.36		B: 0.35	
	C: 24		C: 25		C: 27	
	D: 2,5,5,1		D: 2,5,5,1		D: 2,5,5,1	
Storage time (days)	Training set	Validation set	Training set	Validation set	Training set	Validation set
Day 0	85.71%	100%	82.14%	90.91%	82.14%	85.71%
Day 7	73.21%	92.86%	63.53%	81.82%	64.91%	66.67%
Day 14	67.86%	86.67%	47.62%	59.09%	57.14%	64.29%
Day 21	72.22%	92.86%	60.98%	47.62%	78.18%	64.29%
Day 28	80.36%	86.67%	84.52%	68.18%	80.36%	93.33%

Qualitative Groups	Perten DA-7000					
	Organic		Conventional[1]		Conventional[2]	
	A: 95.34%		A:95.31%		A: 97.17%	
	B: 0.23		B:0.24		B: 0.24	
	C: 30		C:30		C: 25	
	D: 2,5,5,1		D:2,5,5,1		D: 2,5,5,1	
Storage time (days)	Training set	Validation set	Training set	Validation set	Training set	Validation set
Day 0	96.49%	100%	98.84%	90.91%	100%	100%
Day 7	92.86%	100%	94.19%	100%	96.43%	100%
Day 14	96.43%	93.33%	92.86%	95.45%	96.49%	100%
Day 21	98.15%	100%	95.35%	100%	92.86%	93.33%
Day 28	92.86%	92.86%	95.24%	100%	100%	100%

Qualitative Groups	Phazir-2400					
	Organic		Conventional[1]		Conventional[2]	
	A: 75.09%		A: 65.87%		A: 79.71%	
	B: 0.33		B: 0.34		B: 0.31	
	C: 28		C: 29		C: 30	
	D: 2,5,5,1		D: 1,5,5,1		D: 1,10,5,1	
Storage time (days)	Training set	Validation set	Training set	Validation set	Training set	Validation set
Day 0	71.93%	73.33%	75.00%	72.73%	71.70%	71.43%
Day 7	77.19%	80.00%	56.63%	61.90%	80.70%	93.33%
Day 14	72.22%	57.14%	53.01%	47.62%	76.79%	69.23%
Day 21	73.21%	85.71%	75.29%	68.18%	78.57%	93.33%
Day 28	80.70%	86.67%	69.05%	80.95%	90.74%	85.71%

Conventional[1]= Balanced population; Conventional[2]= Unbalanced population; A, Percentage of correctly classified training samples after cross validation; B, Model SECV; C, number of factors; D, math treatment.

Fig. 1. D_2 Log(1/R) spectra for green asparagus grown organically and conventionally. Perten DA-7000 spectrophotometer.

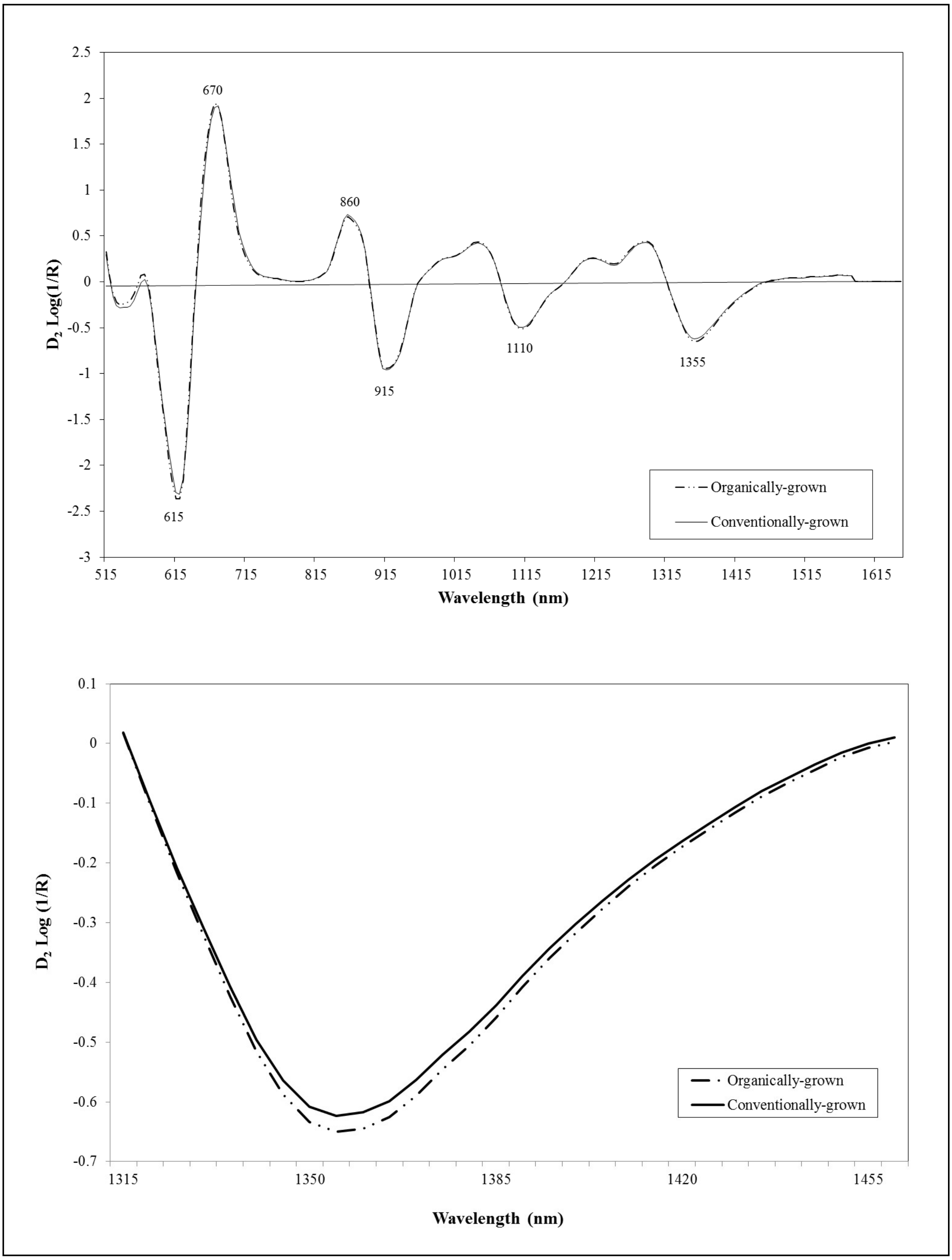

Fig. 2. D_2 Log(1/R) spectra for postharvest behavior of green asparagus grown organically and conventionally. Perten DA-7000 spectrophotometer.