Running Title: Orange ripening and at harvest monitoring by NIRS

Application of NIRS for non-destructive measurement of quality parameters in intact oranges during on-tree ripening and at harvest

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Abstract

External and internal quality parameters were measured in oranges (*Citrus sinensis*, (L.) Osbeck cv. 'Powell Summer Navel') during on-tree ripening and at harvest using NIR spectroscopy. The performance of two NIRS instruments was evaluated: a handheld micro-electro-mechanical system (MEMS) spectrometer working in the 1,600–2,400 nm range; and a diode-array Vis–NIR spectrometer working in the 380–1,700 nm range. Spectra and analytical data were used to construct MPLS prediction models for quantifying weight, size (equatorial and axial diameters), color (L*, a*, b*, C*, h*, color index), texture (firmness, maximum penetration force), yield (pericarp thickness, juice weight, juice content) and chemical parameters (soluble solid content, pH, titratable acidity, maturity index). Both instruments yielded promising results for on-tree and at-harvest quality measurements, but models constructed using the diode-array instrument provided greater predictive capacity, particularly for fruit size (equatorial and axial diameters) and total soluble solids content. Subsequent evaluation of the LOCAL algorithm revealed that it increased the predictive capacity of models constructed for all the main parameters tested. These results confirm that non-invasive NIRS technology can be used to simultaneously evaluate external and internal quality parameters in intact oranges both during on-tree ripening and at harvest, thus making it easier for farmers to monitor the ripening process and also to optimize harvest timing in order to meet the demands of the citrus-fruit industry.

Keywords Near-IR spectroscopy, Portable sensors, MEMS technology, Orange, Quality parameters, On-tree, At harvest.

Introduction

Nowadays, the fruit industry has to do everything possible to ensure the effective management of food quality and safety. As a result, traceability has become a key issue (Zhang et al. 2011a, b).

Traceability in oranges starts with on-tree visual inspection by the farmer, based solely on fruit surface color, with a view to ascertaining ripeness status and optimizing the harvest date (Agustí 2003). However, this method is not particularly reliable, since fruit color may be influenced by a range of factors, and especially by water availability; as a result, fruit may be harvested before it is commercially ripe. Periods of drought, however short, not only give rise to smaller oranges but also bring forward external coloring whilst delaying internal ripening (Pérez-Pérez et al. 2008).

Within the orange handling and processing industry, the next check takes place after harvest, when a small number of samples from incoming batches – indeed, a negligible number in terms of overall throughput – are subjected to quality control, using destructive analytical methods to measure two flavor parameters: soluble solid content (SSC) and titratable acidity (TA). The ratio of one to the other, known as the ripeness index (SSC/TA), is the main indicator of fruit ripeness and juiciness (Zude et al. 2008; Liu et al. 2010). Often, however, to save both costs and time, fruit quality assessment tends to be based solely on soluble solid content (Zude et al. 2008).

There is therefore a considerable need – both in the production sector and in the citrus-fruit industry – for techniques enabling the rapid, non-destructive analysis of individual fruits, with a view to helping the farmer make harvesting decisions and at the same time enabling the processing industry to ensure consumer satisfaction.

Near-infrared reflectance spectroscopy (NIRS) is ideally suited to the requirements of both farmers and the fruit industry: it is not only non-destructive, rapid

and accurate, but also economical, flexible and versatile; sample presentation is simple and data (spectra) are collected very rapidly. Moreover, recent advances in instrumentation have enabled measurements to be made *in situ,* both on the tree and on the production line, enabling various external and internal fruit quality parameters to be measured simultaneously (Pérez-Marín et al. 2009, 2010, 2011).

Although a number of papers address the application of NIRS to quality control in fruit (e.g. Nicolaï et al. 2007; Saranwong and Kawano 2007; Sánchez and Pérez-Marín 2011), few studies have focused specifically on the use of this technology with whole intact oranges, perhaps due to the complexities involved. The parameters most commonly measured to date are soluble solids content, firmness and titratable acidity (Miller and Zude-Sasse 2004; Lu et al. 2006; Cayuela 2008; Cayuela and Weilland 2010; Liu et al. 2010). However, no previously-published research has dealt with the prediction of quality parameters in unharvested oranges.

NIR spectroscopy is particularly well-suited to the monitoring of the on-tree ripening process, in that it enables changes in the various quality parameters to be charted simultaneously and non-destructively, thus ensuring that oranges are harvested at the optimum stage of ripening, depending on the industrial use to which they are subsequently to be put.

This study sought to assess the suitability of NIRS technology for predicting major external and internal quality parameters in intact oranges (weight, equatorial and axial diameters, color, firmness, maximum penetration force, pericarp thickness, juice weight, juice content, soluble solids content, pH, titratable acidity, and maturity index) during on-tree ripening and at harvest, comparing the quality of the prediction models obtained using two NIRS instruments: a hand-held MEMS-based device ideal for on-

tree measurement of intact fruits; and a diode-array device well suited for at-line monitoring of incoming oranges by the citrus-fruit industry.

Materials and Methods

Orange Sampling

The initial sample set comprised 192 oranges (*Citrus sinensis*, (L.) Osbeck cv. 'Powell Summer Navel') grown on a commercial plantation near the village of La Campana (Seville, Spain) under four different irrigation regimes.

Each experimental plot comprised 3 rows of four trees, with four repetitions for each irrigation regime; oranges were monitored on the two central trees in each plot. Thus ripening was monitored on 8 trees for each of the 4 irrigation regimes, giving a total of 32 trees.

A total of 6 oranges were labeled on each of the 32 trees: one for each of the four possible orientations (north, south, east and west) and one for each of two heights on the tree (1.25 and 1.75 m), thus giving a total of 192 oranges. However, in the course of the study, one ripe orange dropped off the tree, and was thus excluded. The final sample set thus comprised 191 oranges.

Oranges were harvested on three different dates in 2010: 9 March (48 oranges), 16 March (48 oranges) and finally 22 March, by which time commercial ripeness had been attained (95 oranges).

For the first harvesting date, oranges were selected using a pre-arranged strategy: two oranges were picked from the first tree and one from the second for each repetition of each irrigation regime. For the second date, the reverse process was used, i.e. one orange from the first tree and two from the second, etc.; for the third harvesting date, all the labeled oranges remaining were harvested.

Harvested oranges were kept in refrigerated storage at 5ºC and 90% RH until the following day, when laboratory testing was performed. Prior to each test, oranges were allowed to reach room temperature. All tests were performed at 20ºC.

NIR Spectrum Acquisition

Spectra were collected on all fruits in reflectance mode (log 1/R) using: (1) a handheld MEMS spectrophotometer (Phazir 2400, Polychromix, Inc., Wilmington, MA, USA), and (2) a diode-array Vis–NIR spectrophotometer (Corona 45 VIS/NIR, Carl Zeiss, Inc., Thornwood, NY, USA).

The Phazir 2400 is an integrated near-infrared handheld analyzer working in reflectance mode that incorporates all the essential components to deliver on-tree applications. The instrument scans at 8 nm intervals (pixel resolution 8 nm, optical resolution 12 nm), across the range of NIR wavelengths (1,600-2,400 nm). Using this instrument, four spectral on-tree measurements were made on each orange. The first was made on the equator, and the fruit was then turned through 90º for each successive measurement. The four spectra were averaged to provide a mean spectrum for each fruit.

After harvesting, spectral measurements were made with the portable Zeiss Corona non-contact diode-array spectrophotometer (model Corona 45 VIS/NIR) working in reflectance mode and equipped with the turnstep module (revolving plate) and a ring support yielding a window 11 cm in diameter, on which oranges were arranged with the stem-calyx axis horizontal. The spectrophotometer scanned at 2 nm intervals, across a range encompassing the entire visible (380-780 nm) and near-IR (780-1,700 nm) wavelength ranges. Four separate spectral measurements were made on each orange, rotating the sample through 90º after each measurement. The four spectra were averaged to provide a mean spectrum for each fruit.

Measurement of Physical/Chemical Quality Parameters

External quality parameters

Oranges were individually weighed on an electronic balance (0-1.000 ± 0.01 g; model P1000 N, Metter-Toledo, GmbH, Greifensee, Switzerland).

Equatorial and axial diameters were then measured using a digital precision calibrator (0-300 ± 0.01 mm; Comecta, Barcelona, Spain).

Skin or external color values (L*, a*, b*) were individually measured at the equator, turning the fruit through 90º between measurements, using a Minolta Chroma Meter CR-400 (Minolta Corporation, Ramsay, NJ, USA). Chroma (C*), hue angle (h*) and color index were calculated as (a*^2+b*^2)^(1/2), $\tan^{-1}$ (b*/a*) and (1000a*/L*b*), respectively. The illuminant C and the 2-degree standard observer were used for all measurements in this study. The four measurements obtained per fruit for each of the color parameters tested were averaged.

Internal quality parameters

Firmness was measured as the maximum force required to penetrate the oranges to a puncturing depth of 10 mm. The maximum force required to pierce the fruit after a total penetration of 15 mm was also established. In both cases, a 6-mm cylindrical tip was used. Oranges were arranged with the stem-calyx axis horizontal; the first measurement was made at a point on the equator, and the second after turning the orange through 180º. Texture measurements were made using a Universal Instron Texturometer (Model 3343, single-column, Instron Corporation, Norwood, MA, USA), with a head speed of 0.0016 m/s (100 mm/min) and a 1,000 N load cell.

Fruits were then halved through the equatorial plane, and pericarp thickness was measured at two points on one of the halves using the same digital calibrator. Fruits were then individually pressed using a domestic juicer, and the juice obtained was

weighed on an electronic balance (0–210 ± 0.001 g; model C-600-SX, Cobos, Barcelona, Spain); the juice weight/fruit weight ratio was also calculated.

Soluble solids content (SSC), pH and titratable acidity (TA) were measured following Obenland et al. (2008). The maturity index (SSC/TA ratio) was also calculated.

Quantitative Calibrations: Sets and Data Processing

Prior to carrying out NIRS calibrations, the structure and spectral variability of the sample population were determined following Shenk and Westerhaus (1991a b; 1995a), using the CENTER algorithm included in the WinISI II software package, version 1.50 (Infrasoft International, Port Matilda, PA, USA). The CENTER algorithm was applied in the spectral regions 380-1,690 nm (Corona 45 VIS/NIR) and 1,600-2,400 nm (Phazir 2400). The Standard Normal Variate (SNV) and Detrending (DT) methods were applied for scatter correction (Barnes et al. 1989), together with the mathematical derivation treatment '1,4,4,1', 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; ISI 2000).

Having ordered the initial sample set by spectral distance from the center of the population, 3 spectra were identified as outliers using the Phazir 2400 instrument, and 2 using the Corona 45 VIS/NIR spectrophotometer (Shenk and Westerhaus 1991a b; 1995a). The final sample set thus comprised 188 samples for the Phazir 2400 and 189 for the Corona 45 VIS/NIR. From these sets, one in every 4 samples was removed to form the validation set (N = 63 samples for the Corona 45 VIS/NIR; N = 62 for the Phazir 2400), leaving a calibration set comprising 126 samples.

Data were subjected to chemometric treatment using the WinISI II software package (ISI 2000).

Construction and validation of prediction models by MPLS regression

Calibration models were obtained for predicting external and internal quality parameters in intact oranges using MPLS as regression method (Shenk and Westerhaus 1995a); four cross-validation steps were included in the process in order to avoid overfitting (Shenk and Westerhaus 1995a).

For each analytical parameter, different mathematical treatments were evaluated for scatter correction, including SNV and DT methods (Barnes et al. 1989). Furthermore, four derivate mathematical treatments were tested in the development of NIRS calibrations: 1,5,5,1; 2,5,5,1; 1,10,5,1 and 2,10,5,1 (Shenk and Westerhaus 1995b).

Here, for calibration of fruit quality parameters, the following spectral regions were tested: (1) for the Phazir 2400: 1,600–2,400 nm; and (2) for the Corona 45 VIS/NIR: 500–1,690 nm and 1,100-1,690 nm. To eliminate spectral noise at the beginning and end of the spectrum, the regions between 380 and 500 nm and between 1,690-1,700 nm were discarded when using the Corona 45 VIS/NIR.

The statistics used to select the best equations were: standard error of calibration (SEC), coefficient of determination for calibration (R^2), standard error of cross-validation (SECV), coefficient of determination for cross-validation (r^2), RPD or ratio of the standard deviation of the original data (SD) to SECV, RER or ratio of the range of the original data to SECV, and the coefficient of variation (CV) or ratio of the SECV to the mean value of the reference data for the calibration set. These latter three statistics enable SECV to be standardized, facilitating the comparison of the results obtained with sets of different means (Williams 2001).

The best-fitting equations obtained for the calibration set, as selected by statistical criteria, were subsequently evaluated by external validation following the protocol outlined by Shenk et al. (2001).

Construction of prediction models for major quality parameters in intact oranges using the LOCAL algorithm

The LOCAL algorithm was used to obtain models for predicting major quality-related parameters (weight, equatorial diameter, a*, firmness, maximum penetration force, pericarp thickness, juice weight, soluble solids content and titratable acidity). Previous research have demonstrated the potential of this algorithm for measuring some of these parameters in agro-food products (Sánchez et al. 2011, 2012).

The LOCAL algorithm operates by searching and selecting samples in large databases that have spectra similar to that of the sample being analyzed (Shenk et al. 1997). The selected samples are then used to compute a specific (LOCAL) calibration equation, based on PLS regression, for predicting the constituents of an unknown sample. Selection of the calibration samples is controlled by the value of the coefficient of correlation between the spectrum of the unknown sample and those comprising the spectral database (Shenk et al. 1997); the samples with the highest correlation are selected. A minimum correlation cutoff is available to ensure that the selected samples are highly correlated (Barton II et al. 2000).

In the present study and for the main quality parameters analyzed (Kahn et al. 2007), an optimization design for the LOCAL algorithm was set up by varying the number of calibration samples (k) from 70 to 100 in steps of 10 and the number of terms (l) from 13 to 15 in steps of 1. This yielded a factorial design of 4 x 3 = 12 runs. Finally, the number of PLS factors discarded was set at the first three, while the minimum number of samples used for each calibration set was set at 15.

For LOCAL equation development, the spectral regions and signal pretreatments indicated in Section 2.4.1 were used. The accuracy of prediction was evaluated by comparing results for the standard error of prediction (SEP), the coefficient of regression for external validation (r^2), the bias and the SEP(c) with those obtained for the MPLS prediction.

Results and Discussion

Descriptive Data for NIR Calibrations and Validations

Values for range, mean, standard deviation and coefficient of variation for each of the parameters analyzed using the calibration and validation sets after application of the CENTER algorithm are shown in Table 1. Structured selection using only spectral information treatment algorithms such as CENTER proved adequate, since the calibration and validation sets displayed similar values for mean, range and standard deviation for all study parameters, and ranges for the validation set lay within the range recorded for the calibration set.

With the exception of pH and the color-related parameters, all study parameters covered a wide range of values. This was particularly true of: firmness (CV = 66.09%), titratable acidity (CV = 26.01%), maturity index (CV = 26.00%), maximum penetration force (CV = 25.23%), juice weight (CV =24.57%), fruit weight (21.99%) and pericarp thickness (21.65%).

Williams (2001) and Pérez-Marín et al. (2005) highlight the importance of both sample set size and sample distribution within the calibration set, noting that sample sets for calibration should ideally ensure uniform distribution of composition across the range of the study parameter in question.

Prediction of External Quality Parameters using MPLS Regression and NIR Spectra

The best calibration for each instrument and external quality parameter (weight, axial and equatorial diameter, color), using the combination of signal pretreatments yielding the best results in each case, are shown in Table 2, which also summarizes results for the external validation of those models.

Models obtained using the Corona 45 VIS/NIR instrument displayed greater predictive ability for all study parameters. For each instrument, models were also obtained for the whole set of external quality parameters, over the complete wavelength range (500-1,690 nm).

With the exception of parameters b* and color index, where separation was only possible into low, medium and high values, the calibration models constructed yielded acceptable precision within the limits established by Shenk and Westerhaus (1996).

The calibration model displaying the greatest predictive capacity for the weight parameter was obtained with the diode-array instrument in the spectral region 500-1,690 nm, using D2 log (1/R) (r^2 = 0.79; SECV = 27.94 g; RPD = 2.15; RER = 10.24; CV = 9.25%), which enabled acceptable quantification of intact orange weight values. Using the Phazir 2400 in the spectral range 1,600-2,400 nm, the best model (r^2 = 0.47; SECV = 42.30 g; RPD = 1.37; RER = 5.90; CV = 14.01%) only enabled fruit to be classified as high or low weight (Shenk and Westerhaus 1996).

Few published studies have addressed the use of NIR spectroscopy for predicting fruit weight. Pérez-Marín et al. (2009) tested a diode-array instrument (Perten DA-7000) and the same MEMS-base device used here (Phazir-2400) for predicting weight in intact nectarines both on the tree and in the laboratory, reporting better results with the diode-array instrument (RPD = 5.47; CV = 4.51%) over a spectral range similar to that used here, than with the MEMS device (RPD = 1.40; CV = 17.30%). The authors attributed the difference in predictive capacity to the measurement area

involved: whereas the Perten DA-700 perfoms a scan of the whole sample, the handheld MEMS instrument measures only a small area of the fruit, due to the small probe diameter (around 2 mm). In a later study, Cayuela and Weiland (2010) used two NIRS spectrophotometers in reflectance mode – a diode array device (Labspec VIS/NIR, 500-2,300 nm) and an acousto-optic tunable filter (AOTF) instrument (Luminar 5030, 1,100-2,300 nm) – to predict the weight of intact oranges in the laboratory; they also reported better results with the diode-array instrument, with values (RPD = 2.94; CV = 5.82%), slightly better than those obtained here.

Application of the calibration to the external validation sets yielded SEP(c) values of 36.54 g and 50.22 g, with a coefficient of determination of 0.67 and 0.38 and a bias of 6.68 g and 7.31 g, for the diode-array and MEMS instruments, respectively (Table 2).

Using the monitoring procedure outlined by Shenk et al. (2001), the prediction-statistic values obtained here either fell short of the limits recommended for routine application (coefficient of determination, MEMS device), or exceeded those limits (SEP(c), diode-array instrument).

Models constructed for predicting equatorial diameter using the Corona 45 VIS/NIR were more accurate and precise (r^2 = 0.70; SECV = 3.51 mm; RPD = 1.84; RER = 9.02; CV = 4.25%) than those obtained with the Phazir 2400 (r^2 = 0.59; SECV = 4.11 mm; RPD = 1.57; RER = 7.46; CV = 4.97%). D2 log (1/R) was used in both cases, and the diode-array instrument was used in the spectral region 500-1,690 nm. The model constructed for predicting axial diameter using the Corona 45 VIS/NIR instrument displayed adequate predictive capacity (r^2 = 0.77; SECV = 3.53 mm; RPD = 2.10; RER = 9.97; CV = 4.03%;), whereas the Phazir 2400 was only able to

discriminate between high, medium and low values (r^2 = 0.51; SECV = 5.25 mm; RPD = 1.42; RER = 6.90; CV = 6.01%).

Slightly better results have been reported by Pérez-Marín et al. (2009) when using a diode-array instrument for predicting equatorial diameter in nectarines (RPD = 2.22; CV = 5.95%); the authors suggest this is because the measurement area is greater than in the MEMS instrument.

Validation statistics for the prediction of these parameters in intact oranges on-tree and at harvest are also shown in Table 2. In terms of the validation protocol proposed by Shenk et al. (2001) for the routine implementation of NIRS prediction models, the only models yielding sufficiently accurate predictions of equatorial and axial diameter were those obtained with the Corona 45 VIS/NIR spectrophotometer.

Better results were obtained for the prediction of color-related parameters (L*, a*, b*, C*, h* and color index) using the diode-array instrument, since it works in the spectral region 500-1,690 nm, which includes much of the visible spectrum; this NIRS spectrophotometer is additionally able to detect color differences barely apparent to the human eye. The calibration models obtained displayed acceptable predictive capacity for all color-related parameters (r^2 = 0.66-0.73; SECV = 0.32-1.27; RPD = 1.72-1.92; RER = 8.32-9.74; CV = 1.03-6.08%) (Shenk and Westerhaus 1996). Models constructed using the MEMS device exhibited poorer predictive capacity, largely because its spectral working region (1,600-2,400 nm) does not include the visible spectrum. Even so, models were able to discriminate between high and low values for all color-related parameters (r^2 = 0.43-0.65; SECV = 0.38-1.66; RPD = 1.33-1.69; RER = 6.67-9.26; CV = 1.04-7.26%).

Values obtained for the statistics used to assess the external validation of color-prediction models indicate that these models cannot be used routinely, in that they fail

to fulfill the requirements outlined by Shenk et al. (2001). Even so, the simultaneous measurement of various colour parameters along with other external and internal quality parameters is clearly of interest to the citrus industry.

Prediction of Internal Physical Quality Parameters using MPLS Regression and NIR Spectra

Models obtained using the Corona 45 VIS/NIR spectrophotometer displayed greater predictive capacity than those constructed with the MEMS-based device for all except texture-related parameters (firmness and maximum penetration force), for which slightly better results were obtained using the Phazir 2400 (Table 3). This may be due to the measurement area involved, since the Corona 45 VIS/NIR performs a scan of the whole sample, while the Phazir 2400 measures only a small area of the fruit (around 2 mm at each measurement). A better fit was noted between the reference data for these two parameters and the NIR spectra captured using the MEMS instrument.

Using the diode-array spectrophotometer, the best models for firmness and fruit weight were obtained using the whole wavelength range of the instrument (500-1,690 nm), whilst for maximum penetration force, pericarp thickness and juice content, the best models were obtained in the 1,100-1,690 nm range.

Of the two texture measurements, maximum penetration force displayed greater correlation with the NIR spectral data obtained.

Neither of the instruments used, regardless of the math treatments applied, yielded viable models for the routine prediction of firmness, coefficient of determination values (r^2) never exceeding 0.42, which would only enable discrimination between high and low firmness values (Shenk and Westerhaus 1996). These results highlight the difficulty in correlating destructive measurements made to a puncturing depth of 10 mm and non-destructive NIR measurements, particularly for thick-peel

fruits such as this orange variety; as Peirs et al. (2002) have noted, NIR light will only penetrate usefully down to a depth of between 1 and 5 mm, depending on the wavelength, the instrument and the fruit ripeness stage.

Perhaps because of the challenges involved, very few studies have addressed the measurement of firmness in oranges using NIRS technology. Cayuela and Weiland (2010) measured firmness in orange pulp (i.e. fruit without pericarp), a process thus requiring previous sample preparation; the models obtained displayed sufficient predictive capacity to distinguish between high, medium and low values for this parameter (r^2 = 0.66; RPD = 1.85). However, their results cannot be compared with those of the present study, since they were using peeled rather than intact fruit.

The models obtained using both instruments displayed greater predictive capacity for maximum penetration force than for firmness, yielding values close to those provided by the destructive reference method; similar values were obtained with both instruments, as indicated by the descriptive statistics (r^2 = 0.76-0.79; SECV = 4.14-4.40 N; RPD = 2.03-2.19; RER = 10.69-11.18; CV = 10.47-10.89%), for the diode-array and MEMS-based instruments, respectively. The best results were obtained in both cases using D1 log (1/R).

It should be stressed that the quality of the predictions obtained for firmness (both instruments) and maximum penetration force (Phazir 2400) using MPLS regression might well be considered unacceptable, exceeding the confidence limits recommended, particularly in view of the low r^2 values obtained (Table 3).

The best model for predicting pericarp thickness was again obtained with the diode-array instrument, using D2 log (1/R) and the spectral region 1100-1690 nm (r^2 = 0.80; SECV = 0.46 mm; RPD = 2.25; RER = 10.61; CV = 9.19%). The model provided

acceptable quantification for this parameter, which is of particular interest to the citrus-fruit industry because it is linked to fruit yield.

It is worth noting in this respect that NIRS analysis was carried out on intact oranges; the greater light intensity provided by the Corona 45 VIS/NIR spectrophotometer may ensure greater penetration of light into the fruit, thus improving thickness estimates (Paz et al. 2008 2009; Pérez-Marín et al. 2009 2010).

The best models for predicting juice weight and juice content – the latter calculated from the ratio of juice weight to fruit weight – were obtained with the Corona 45 VIS/NIR instrument, using the spectral range 500-1,690 nm and the D2 log (1/R) mathematical treatment for juice weight (r^2 = 0.71; SECV = 15.39 g; RPD = 1.85; RER = 9.13; CV = 11.37%), and the range 1,100-1,690 nm with D2 log (1/R) treatment for juice content (r^2 = 0.52; SECV = 2.86%; RPD = 1.44; RER = 7.15; CV = 6.38%). These two parameters are essential ripeness indicators for the orange-processing industry.

The models constructed using data obtained with the MEMS-based instrument only enabled fruit to be classified by high or low juice weight and juice content (Table 3).

In a laboratory study of similar parameters using two NIRS instruments, Cayuela and Weiland (2010) found that the diode-array instrument displayed greater predictive capacity than an AOTF instrument for both juice volume (RPD = 2.94; CV = 16.22%) and juice volume/fruit weight ratio (RPD = 1.61; CV= 8.11%); their results were slightly better than those observed here, and the number of samples was also far larger (n = 396).

The robustness of NIRS predictions for these parameters, while better with the Corona 45 VIS/NIR instrument, cannot be considered acceptable for routine purpose (Table 3).

Prediction of Internal Chemical Quality Parameters using MPLS Regression and NIR Spectra

Models constructed using data obtained with the Corona 45 VIS/NIR spectrophotometer displayed greater predictive capacity than those provided by the Phazir 2400 for all the chemical parameters tested (Table 4).

The diode-array spectrophotometer adequately predicted fruit soluble solids content (SSC) regardless of the mathematical treatment applied (Shenk and Westerhaus 1996), although the best model was obtained using D2 log (1/R) over the whole spectral range of the device (r^2 = 0.80; SECV = 0.58%; RPD = 2.19; RER = 9.37; CV = 4.78%). The best model using the MEMS instrument (r^2 = 0.62; SECV = 0.79%; RPD = 1.61; RER = 6.94; CV = 6.47%) was also obtained with the D2 log (1/R) treatment.

The predictive capacity of the SSC model constructed using the Corona 45 VIS/NIR instrument was similar to that reported for intact oranges by Cayuela (2008) (RPD = 2.65; CV = 4.37%) and by Cayuela and Weiland (2010) (RPD = 2.13; CV= 6.12%), and slightly lower than that observed by Liu et al. (2010) using a diode-array instrument with range similar to those used here (RPD = 2.84; CV = 3.42%).

To test robustness, the models constructed using the two spectrophotometers were applied to the external validation set (Table 1). The SSC prediction model constructed using the Phazir 2400 instrument met the validation requirements recommended by Shenk et al. (2001), confirming sufficiently accurate prediction, whilst with the Corona 45 VIS/NIRS spectrophotometer, the value obtained for SEP(c) exceeded the recommended confidence limit (Table 4).

The results obtained with calibration models constructed for pH and titratable acidity confirmed the limited viability of NIRS technology for estimating acidity-related parameters, perhaps because in this case oranges were harvested at commercial

maturity, and thus exhibited considerable uniformity and minimal variation. Due to the very narrow range for pH and titratable acidity, and the resulting low SD, NIRS prediction models could not be constructed using the MPLS algorithm (González-Caballero et al. 2010). Williams (2001) notes that, from a practical point of view, if the SD is very low for a population of reasonable size (60 samples or more), this may indicate that the variance is so low that analysis is not necessary, except for quality control purposes. However, and despite the low range in reference values, there is still a need for regular frequent analyses to ensure that specifications are being met.

Models constructed using the Corona 45 VIS/NIR were able to distinguish between high and low pH values (Shenk and Westerhaus 1996). Cayuela (2008) and Cayuela and Weiland (2010) have drawn attention to the difficulty in predicting pH in oranges using NIRS technology, noting that results obtained so far continue to prove unacceptable.

The predictive capacity of models for measuring titratable acidity was found to be equally unsatisfactory (Table 4). Similar results have been reported by a number of authors attempting to measure acidity in oranges using NIRS technology: Cayuela (2008) obtained models displaying very limited predictive capacity (RPD = 1.35; CV = 15.36%), although the results were slightly better than those recorded here, perhaps because the training set used exhibited a wider range of acidity values and thus a larger standard deviation than those obtained in the present study. Cayuela and Weiland (2010) later constructed models to predict titratable acidity in oranges using a diode-array instrument, with a broader range of values, again achieving slightly greater predictive capacity than that recorded here (RPD = 1.69; CV= 17.58%).

The MPLS models predicted pH and titratable acidity in validation-set samples with low values for r^2 (0.10-0.32 for pH and 0.04-0.22 for titratable acidity), in neither

case meeting the recommendations of Shenk et al. (2001). These models are thus not suitable for routine applications.

Models for predicting the maturity index (i.e. SSC/TA ratio) were influenced, using both spectrophotometers, by the poor predictive capacity of the models obtained for titratable acidity. The Corona 45 VIS/NIR diode-array instrument yielded slightly better results, comparable to those reported in the literature (Cayuela and Weiland 2010).

At validation (Table 4), r^2 values were found to be lower than the control limit suggested by Shenk et al. (2001), confirming the non-robustness of the model for predicting maturity index in intact oranges.

Prediction of Main Quality Parameters using MPLS versus LOCAL Algorithms

This study applied a non-linear regression strategy based on the LOCAL algorithm, in order to determine whether it improved the robustness of models for predicting major quality parameters in intact oranges obtained using linear regression (MPLS).

Values for SEP, SEP(c), bias and r^2 obtained using the best mathematical treatment for each parameter and for all 12 runs (3 values for l and 4 values for k) are shown in Table 5, which also indicates the combination of k and l yielding the lowest SEP for each parameter and instrument.

When applying the LOCAL algorithm to predict the external validation set, between 70 and 90 samples were used for all parameters except equatorial diameter and pericarp thickness with the Phazir 2400 instrument, for which 100 samples were used.

Comparison of the performance of the two algorithms for predicting the main external quality parameters (weight, equatorial diameter and colour (a*)) in intact oranges using both spectrophotometers (Table 5) shows that models constructed using the LOCAL algorithm and data obtained using the diode-array instrument displayed

improved predictive capacity (r^2 > 0.7) with regard to those constructed using MPLS regression. The LOCAL algorithm also improved the performance of MEMS-based models for predicting weight and equatorial diameter, although these were still unsuitable for routine application.

Application of the LOCAL algorithm also enhanced the predictive performance of models for the two texture-related parameters, increasing the coefficient of determination for firmness prediction by 21% for the diode-array instrument and 66% for the MEMS instrument. Similar results were obtained for maximum penetration force, for which application of LOCAL yielded good predictive capacity using the Corona 45 VIS-NIR.

Sánchez et al. (2011) have also reported that use of the LOCAL algorithm rather than MPLS regression enhances the performance of models for predicting texture-related parameters in intact fruits.

Application of LOCAL improved the capacity of models for predicting the four parameters of greatest interest to the juice industry (pericarp thickness, juice weight, SSC and TA), slightly better results being achieved with the diode-array spectrophotometer.

Results obtained for the two physical parameters studied suggest that, using the Corona 45 VIS-NIR, application of the LOCAL algorithm would enable the processing industry to distinguish between thick, medium and fine peel, and between high, medium and low juice weights (r^2 = 0.68 for both parameters), whereas using the Phazir 2400, discrimination would be possible only between thick and thin peels and between high or low juice weights (r^2 = 0.46 for pericarp thickness; r^2 = 0.41 for juice weight).

Models constructed using LOCAL for predicting SSC displayed good predictive capacity using the diode-array instrument (r^2 = 0.74) and sufficient capacity (r^2 = 0.68)

to distinguish between high, medium and low values using the MEMS instrument. The LOCAL algorithm also enhanced, albeit slightly, the predictive capacity of models for TA, although this is still likely to be deemed unacceptable in view of the low r^2 values obtained.

Sánchez et al. (2012) report that use of LOCAL rather than MPLS enhanced the performance of models for predicting all quality parameters in strawberries, the most noticeable improvement being recorded for maximum penetration force. It is significant that improvements were also achieved for parameters such as firmness, titratable acidity and pH, all considered tricky to predict using NIRS applications (González-Caballero et al. 2010; Pérez-Marín et al. 2010).

Conclusions

These results confirm that NIRS technology is a viable option for the simultaneous and non-destructive measurement of a large number of internal and external quality parameters in intact oranges, both on the tree and on arrival at processing plants or wholesale distribution centers. Models obtained using the diode-array instrument (Corona 45 VIS/NIR) displayed greater predictive capacity than those constructed using the latest-generation, hand-held compact MEMS device (Phazir 2400). However, the latter displayed acceptable predictive capacity for NIRS prediction of certain internal and external quality parameters, and is also particularly suited to the on-tree monitoring and evaluation of individual oranges; it is therefore a promising tool in fruit ripening protocols aimed at optimizing the harvesting date depending on whether the fruit is to be processed for juice or consumed fresh. The LOCAL algorithm proved to be considerably more effective than MPLS regression for improving the prediction of the main quality parameters in intact oranges, especially when using the MEMS instrument. To our knowledge, this is the first attempt to implement NIR spectroscopy on-tree for

this purpose. Over the coming years, however, recalibration may be required, especially for acidity and texture related parameters, increasing the number of samples in the calibration set.

Acknowledgement

This research was funded by the Andalusian Regional Government under the Research Excellence Program (Project No. P09-AGR-5129 "MEMS and NIRS-image sensors for the in situ nondestructive analysis of food and feed". The authors are grateful to Mr. Antonio López and Mrs. Mª Carmen Fernández of the Animal Production Department (ETSIAM-UCO) for technical assistance.

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Table 1 Statistical analysis of calibration and validation sets: data range, mean and standard deviation (SD) and coefficient of variation (CV)

Parameter	Set	Range	Mean	SD	CV (%)
Weight (g)	Calibration	170.00-598.30	306.24	67.34	21.99
	Validation	196.40-561.25	324.40	79.70	24.57
Equatorial diameter (mm)	Calibration	69.24-108.34	83.02	6.98	8.41
	Validation	70.71-107.18	84.46	7.58	8.97
Axial diameter (mm)	Calibration	69.69-107.20	87.29	7.74	8.87
	Validation	74.46-106.35	88.07	7.97	9.05
L*	Calibration	64.06-79.52	68.75	1.70	2.47
	Validation	65.23-71.19	68.70	1.22	1.78
a*	Calibration	20.93-30.88	25.74	1.94	7.53
	Validation	22.09-30.55	26.09	1.68	6.45
b*	Calibration	63.01-78.14	71.86	2.43	3.39
	Validation	66.07-75.95	71.80	1.99	2.78
C*	Calibration	68.34-81.98	76.36	2.32	3.04
	Validation	71.60-79.90	76.42	1.82	2.38
h*	Calibration	66.59-73.52	70.28	1.56	2.22
	Validation	67.09-72.93	70.08	1.34	1.91
Color index	Calibration	3.76-6.75	5.23	0.55	10.52
	Validation	4.34-6.36	5.29	0.46	8.75
Firmness (N)	Calibration	5.34-75.17	21.44	14.17	66.09
	Validation	5.60-62.18	20.08	14.14	70.39
Maximum penetration force (N)	Calibration	21.59-75.93	40.94	10.33	25.23
	Validation	23.73-62.58	38.69	9.04	23.06
Pericarp thickness (mm)	Calibration	2.69-8.35	5.06	1.10	21.65
	Validation	3.36-7.48	4.90	0.90	18.38
Juice weight (g)	Calibration	73.62-282.96	137.05	33.67	24.57
	Validation	86.09-236.91	146.18	30.67	20.98
Juice content (%)	Calibration	23.99-61.68	44.84	5.09	11.35
	Validation	34.38-53.15	44.83	4.87	10.87
Soluble solids content (%)	Calibration	9.35-14.8	12.13	1.28	10.53
	Validation	9.50-13.30	11.95	1.22	10.24
pH	Calibration	3.17-4.14	3.64	0.21	5.73
	Validation	3.25-4.02	3.63	0.19	5.12
Titratable acidity (% citric acid)	Calibration	0.36-1.05	0.59	0.15	26.01
	Validation	0.38-0.91	0.59	0.13	21.74
Maturity index	Calibration	12.02-40.03	22.00	5.72	26.00
	Validation	12.71-34.08	21.04	4.58	21.75

Table 2 MPLS regression statistics for NIR-based models for predicting external quality parameters in intact oranges

Parameter	Instrument	Spectral range (nm)	Mathematic treatment	Calibration						Validation			
				N[a]	SECV	r^2	RPD	RER	CV	N[b]	r^2	SEP(c)	Bias
Weight (g)	Corona	500-1690	2,5,5,1	121	27.94	0.79	2.15	10.24	9.25**	63	0.67	36.54*	6.68
	Phazir	1600-2400	1,5,5,1	123	42.30	0.47	1.37	5.90	14.01	62	0.38*	50.22	7.31
Equatorial diameter (mm)	Corona	500-1690	2,5,5,1	124	3.51	0.70	1.84	9.02	4.25**	63	0.75	3.62	0.61
	Phazir	1600-2400	2,10,5,1	125	4.11	0.59	1.57	7.46	4.97	62	0.49*	5.03*	0.65
Axial diameter (mm)	Corona	500-1690	1,10,5,1	120	3.53	0.77	2.10	9.97	4.03**	63	0.72	3.95	0.55
	Phazir	1600-2400	2,10,5,1	121	5.25	0.51	1.42	6.90	6.01	62	0.51*	5.18	0.63
L*	Corona	500-1690	2,5,5,1	118	0.71	0.71	1.87	9.39	1.03**	63	0.59*	0.91*	0.01
	Phazir	1600-2400	1,10,5,1	115	0.72	0.65	1.69	9.26	1.04	62	0.43*	0.99*	-0.19
a*	Corona	500-1690	1,5,5,1	124	0.98	0.73	1.92	9.74	3.78**	63	0.66	1.04*	-0.20
	Phazir	1600-2400	2,5,5,1	120	1.22	0.55	1.49	7.63	4.76	62	0.39*	1.54*	0.09
b*	Corona	500- 1690	2,5,5,1	121	1.27	0.68	1.75	8.32	1.76**	63	0.51*	1.48*	0.01
	Phazir	1600-2400	2,10,5,1	121	1.66	0.43	1.33	6.67	2.30	62	0.15*	1.87*	0.20
C*	Corona	500-1690	2,5,5,1	122	1.15	0.72	1.87	9.46	1.51**	63	0.51*	1.37*	-0.05
	Phazir	1600-2400	2,10,5,1	121	1.45	0.54	1.48	7.52	1.90	62	0.26*	1.66*	0.23
h*	Corona	500-1690	2,10,5,1	124	0.81	0.72	1.89	8.46	1.15**	63	0.61	0.98*	0.09
	Phazir	1600-2400	1,10,5,1	119	0.99	0.56	1.50	7.03	1.40	62	0.21*	1.39*	0.12
Color index	Corona	500-1690	2,10,5,1	125	0.32	0.66	1.72	9.40	6.08**	63	0.60	0.36*	-0.06
	Phazir	1600-2400	1,5,5,1	120	0.38	0.46	1.34	6.96	7.26	62	0.23*	0.43	0.06

[a] Number of samples in the calibration set.

[b] Number of samples in the validation set.

* Values exceeding control limits recommended by Shenk et al. 2001.

** Best model.

Table 3 MPLS regression statistics for NIR-based models for predicting internal physical quality parameters in intact oranges

Parameter	Instrument	Spectral range (nm)	Mathematic treatment	Calibration						Validation			
				N[a]	SECV	r^2	RPD	RER	CV	N[b]	r^2	SEP(c)	Bias
Firmness (N)	Corona	500-1690	2,5,5,1	122	10.55	0.33	1.20	5.88	51.56	63	0.33*	11.60*	1.35
	Phazir	1600-2400	2,10,5,1	113	10.03	0.42	1.30	5.46	48.43**	62	0.30*	15.05*	-1.98
Maximum penetration force (N)	Corona	1100-1690	1,10,5,1	115	4.14	0.76	2.03	10.69	10.47	63	0.68	5.16*	0.47
	Phazir	1600-2400	1,10,5,1	112	4.40	0.79	2.19	11.18	10.89**	62	0.43*	6.91*	-0.03
Pericarp thickness (mm)	Corona	1100-1690	2,10,5,1	122	0.46	0.80	2.25	10.61	9.19**	63	0.58*	0.64*	-0.14
	Phazir	1600-2400	2,5,5,1	121	0.66	0.58	1.54	7.07	13.18	62	0.43*	0.76	-0.08
Juice weight (g)	Corona	500-1690	2,5,5,1	117	15.39	0.71	1.85	9.13	11.37**	63	0.58*	18.45*	1.79
	Phazir	1600-2400	2,10,5,1	122	22.62	0.33	1.21	6.35	16.87	62	0.28*	23.81	4.68
Juice content (%)	Corona	1100-1690	2,5,5,1	117	2.86	0.52	1.44	7.15	6.38**	63	0.26*	4.24*	-0.14
	Phazir	1600-2400	1,5,5,1	123	3.78	0.33	1.22	7.73	8.38	62	0.21*	4.73*	-0.59

[a] Number of samples in the calibration set.

[b] Number of samples in the validation set.

* Values exceeding control limits recommended by Shenk et al. 2001.

** Best model.

Table 4 MPLS regression statistics for NIR-based models for predicting internal chemical quality parameters in intact oranges.

Parameter	Instrument	Spectral range (nm)	Mathematic treatment	Calibration						Validation			
				N[a]	SECV	r^2	RPD	RER	CV	N[b]	r^2	SEP(c)	Bias
Soluble solids content (%)	Corona	500-1690	2,10,5,1	122	0.58	0.80	2.19	9.37	4.78**	63	0.71	0.67*	-0.01
	Phazir	1600-2400	2,10,5,1	126	0.79	0.62	1.61	6.94	6.47	62	0.61	0.77	-0.10
pH	Corona	500-1690	2,10,5,1	122	0.15	0.45	1.34	6.34	4.21**	63	0.32*	0.15	0.01
	Phazir	1600-2400	1,10,5,1	126	0.20	0.12	1.07	4.97	5.36	62	0.10*	0.19	-0.01
Titratable acidity (% citric acid)	Corona	500-1690	1,5,5,1	125	0.12	0.36	1.24	5.58	20.77**	63	0.22*	0.12	0.02
	Phazir	1600-2400	1,5,5,1	124	0.14	0.09	1.05	4.06	23.78	62	0.04*	0.13	0.02
Maturity index (SSC/TA)	Corona	500-1690	1,5,5, 1	122	4.25	0.35	1.24	5.48	19.68**	63	0.24*	4.05	-0.79
	Phazir	1600-2400	2,5,5,1	124	4.52	0.32	1.21	5.15	20.76	62	0.16*	4.56	-0.26

[a] Number of samples in the calibration set.

[b] Number of samples in the validation set.

* Values exceeding control limits recommended by Shenk et al. 2001.

** Best model.

Table 5 Validation statistics for the best models for predicting main quality parameters in intact oranges using MPLS and LOCAL algorithms

Parameter	Instrument	Regression method	Spectral range (nm)	Mathematic treatment	Factors	SEP	SEP(c)	Bias	r^2
Weight (g)	Corona	MPLS	500-1690	2,5,5,1	5	36.84	36.54*	6.68	0.67
		LOCAL (k^a = 80)**	1100-1690	1,5,5,1	15 (-3)	44.94	44.15*	10.05	0.74
	Phazir	MPLS	1600-2400	1,5,5,1	2	50.32	50.22	7.31	0.38*
		LOCAL (k = 80)	1600-2400	2,10,5,1	15 (-3)	62.61	61.52*	13.99	0.42*
Equatorial diameter (mm)	Corona	MPLS	500-1690	2,5,5,1	2	3.64	3.62	0.61	0.75
		LOCAL (k = 90)**	1100-1690	1,5,5,1	15 (-3)	3.65	3.65	0.46	0.78
	Phazir	MPLS	1600-2400	2,10,5,1	2	5.03	5.03*	0.65	0.49*
		LOCAL (k = 100)	1600-2400	2,10,5,1	13 (-3)	5.40	5.32*	1.13	0.52*
a*	Corona	MPLS	500-1690	1,5,5,1	9	1.05	1.04*	-0.20	0.66
		LOCAL (k = 90)**	500-1690	1,5,5,1	14 (-3)	0.91	0.91	-0.15	0.74
	Phazir	MPLS	1600-2400	2,5,5,1	15	1.53	1.54*	0.09	0.39*
		LOCAL (k = 90)	1600-2400	2,5,5,1	13 (-3)	1.41	1.40*	0.25	0.29*
Firmness (N)	Corona	MPLS	500-1690	2,5,5,1	4	11.59	11.60*	1.35	0.33*
		LOCAL (k = 70)	500-1690	2,10,5,1	14 (-3)	10.99	10.96	-1.63	0.40*
	Phazir	MPLS	1600-2400	2,10,5,1	12	15.05	15.05*	-1.98	0.30*
		LOCAL (k = 90)**	1600-2400	2,5,5,1	14 (-3)	10.58	10.66	0.20	0.50*
Maximum penetration force (N)	Corona	MPLS	1100-1690	1,10,5,1	6	5.14	5.16*	0.47	0.68
		LOCAL (k = 90)**	500-1690	2,10,5,1	15 (-3)	4.64	4.65	-0.52	0.74
	Phazir	MPLS	1600-2400	1,10,5,1	13	6.85	6.91*	-0.03	0.43*
		LOCAL (k = 90)	1600-2400	1,5,5,1	14 (-3)	5.45	5.44*	-0.79	0.63
Pericarp thickness (mm)	Corona	MPLS	1100-1690	2,10,5,1	10	0.65	0.64*	-0.14	0.58*
		LOCAL (k = 80)**	1100-1690	1,5,5,1	14 (-3)	0.58	0.57*	-0.15	0.68
	Phazir	MPLS	1600-2400	2,5,5,1	2	1.76	0.76	-0.08	0.43*
		LOCAL (k = 100)	1600-2400	2,5,5,1	13 (-3)	0.77	0.75	-0.19	0.46*
Juice weight (g)	Corona	MPLS	500-1690	2,5,5,1	3	18.39	18.45*	1.79	0.58*
		LOCAL (k = 80)**	1100-1690	1,5,5,1	14 (-3)	18.26	18.30*	1.95	0.68
	Phazir	MPLS	1600-2400	2,10,5,1	4	24.07	23.81	4.68	0.28*
		LOCAL (k = 80)	1600-2400	1,5,5,1	14 (-3)	25.56	24.79	7.00	0.41*
Soluble solids content (%)	Corona	MPLS	500-1690	2,10,5,1	5	0.67	0.67*	-0.01	0.71
		LOCAL (k = 70)**	500-1690	1,5,5,1	13 (-3)	0.62	0.63*	-0.01	0.74
	Phazir	MPLS	1600-2400	2,10,5,1	5	0.77	0.77	-0.10	0.61
		LOCAL (k = 90)	1600-2400	1,5,5,1	14 (-3)	0.70	0.69	-0.14	0.68
Titratable acidity (% citric acid)	Corona	MPLS	500-1690	1,5,5,1	6	0.12	0.12	0.02	0.22*
		LOCAL (k = 80)**	1100-1690	2,5,5,1	15 (-3)	0.11	0.11	0.02	0.27*
	Phazir	MPLS	1600-2400	1,5,5,1	1	0.13	0.13	0.02	0.04*
		LOCAL (k = 80)	1600-2400	1,10,5,1	15 (-3)	0.12	0.12	0.01	0.15*

[a] Number of samples used in LOCAL algorithm.

* Values exceeding control limits recommended by Shenk et al. 2001.

** Best model.