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Abstract: Two commercial portable spectrometers were compared for orange quality non-destructive predictions by developing Partial Least Squares calibration models, reflectance mode spectra acquisition being used in both. One of them was a Vis/NIR spectrometer in which the radiation reflected by the fruit is collected and conducted by optic fiber to the three detectors (350-2500 nm) of the instrument. The other is an AOTF-NIR with a reflectance post dispersive optical configuration and InGaAs (1100-2300 nm) detector. Four orange varieties were included in calibrations. The parameters studied were soluble solids content, acidity, titratable acidity, maturity index, flesh firmness, juice volume, fruit weight, rind weight, juice volume to fruit weight ratio, fruit colour index and juice colour index. The results indicate a good performance of the predictive models, particularly for the direct NIR prediction of soluble solids content, and maturity index, the prediction of this last parameter being notable for its relevance and novelty. The RPD ratios for these parameters were in the range from 1.67 to 2.21 with the Labspec, which showed better predictive performance, and from 1.03 to 2.33 with the Luminar.

Cover letter

Ttitle: Intact orange quality prediction with two portable NIR spectrometers

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Explanation of the manuscript's significance

In this work**,** two commercial portable spectrometers of Vis/NIR and NIR were compared for orange non-destructive quality prediction by developing Partial Least Squares calibration models. Four orange varieties were included in calibrations. The parameters studied were soluble solids content, acidity, titratable acidity, maturity index defined by the soluble solids content to titratable acidity ratio, flesh firmness, juice volume, fruit weight, rind weight, juice volume to fruit weight ratio, fruit colour index and juice colour index. The results indicate a good performance of the predictive models, particularly for the direct NIR prediction of the maturity index, soluble solids content, fruit weight and rind weight.

The most noteworthy aspects of work are direct NIR predicting maturity index, what is reported as suitable methodology to avoid the difficulty of accurately NIR-predicting titratable acidity.

Intact orange quality prediction with two portable NIR spectrometers

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Abstract

Two commercial portable spectrometers were compared for orange quality non-destructive predictions by developing Partial Least Squares calibration models, reflectance mode spectra acquisition being used in both. ~~of~~One of them was a Vis/NIR spectrometer in which the radiation reflected by the fruit is collected and conducted by optic fiber to the three detectors (350-2500 nm) of the instrument. The other is~~and~~ an AOTF-NIR with a reflectance post dispersive optical configuration and InGaAs (1100-2300 nm) detector. ~~were compared for orange non-destructive quality prediction by developing Partial Least Squares calibration models.~~ Four orange varieties were included in calibrations. The parameters studied were soluble solids content, acidity, titratable acidity, ~~soluble solids content to titratable acidity ratio~~maturity index, flesh firmness, juice volume, fruit weight, rind weight, juice volume to fruit weight ratio, fruit colour index and juice colour index. The results indicate a good performance of the predictive models, particularly for the direct NIR prediction of ~~fruit weight, rind weight, juice volume,~~ soluble solids content, ~~acidity~~ and ~~the ratio soluble solids content to titratable acidity directly predicted~~maturity index, the prediction of this last parameter being notable for its relevance and novelty. The RPD ratios for these parameters were in

the range from 1.64~~7~~ to ~~4.76~~2.21 with the Labspec, which showed better predictive performance, and from 1.03 to 2.33 with the Luminar.

Key words: acidity, fruit weight, ~~hardness~~firmness, juiciness, maturity index, NIR, orange~~s~~, soluble solid content.

INTRODUCTION

~~Citrus fruit is fast becoming a stable food product in the daily diet of many people. The genus Citrus includes several important fruits such as oranges, mandarins, limes, lemons and grapefruits, orange and mandarins being the most consumed species. Spain leads the world in fresh orange and mandarin exports (Ladaniya, 2008).~~

Consumers purchase citrus fruits on the basis of quality~~, it being~~as a combination of characteristics and attributes ~~are~~ significant for acceptability.

Citrus are non-climateric fruit, hence the ripening process stops once separated from the tree and, consequently, fruits can only be harvested and marketed once adequate maturity has been reached (Watkins, 2008). Moreover, the content of sugars and acids in citrus fruit is fairly stable before and after harvest, sugars-to-acid balance being the key to acceptability in these commodities. The content of sugars is generally measured by refractometry as soluble solids content (SSC), sugars representing the main part in it, and acids content is commonly measured as titratable acidity (TA). The ratio of soluble solids content to titratable acidity (SSC/TA) is widely used as maturity criterion for non-climateric fruits (Fellars, 1991), for the reasons indicated above, and particularly used as maturity index in citrus.

Organic acids in citrus fruit rank in the 10% range in their contribution to the SSC. Total acidity prediction by Near Infrared Spectroscopy (NIR) has been considered

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difficult to achieve, due to the relatively low levels of organic acids in fruits (McGlone et al., 2003; Guthrie et al., 2005~~; McGlone et al., 2003~~). Several authors have reported various levels of success in predicting titratable acidity (TA) of pineapple (Shiina et al., 1993), plum (Onda et al., 1994), apple (Sohn et al., 2000), mango (Schmilovitch et al., 2000).~~intact~~ Imperial mandarin (Guthrie et al., 2005) and~~,~~ Satsuma mandarin (Hernández et al., 2006), ~~pineapple (Shiina et al., 1993), plum (Onda et al., 1994), apple (Sohn et al., 2000) and mango (Schmilovitch et al., 2000).~~ .

Citrus fruit are anisotropic objects, showing different physical and chemical properties when measured in different directions. Hence, equatorial measurement are reasonable since at least in citrus, SSC are greatest in the distal apex of fruit decreasing towards the proximal, the opposite happening with A and TA as reported by Peiris et al. (1999).

Colour is considered as one of the most important external factors of fruit quality (Francis, 1995), since the fruit's appearance greatly influences the consumer. The change of colour in citrus is a consequence of the maturation process, although it is also highly dependent on the existence of cool temperatures at night, not always present under tropical and subtropical growth conditions, which is the reason why a green citrus fruit may or may not be physiologically mature (Olmo et al., 2000).

Fruit softening is often used as criterion for selecting the most suitable harvest date for several commodities (Taylor et al., 1995; Lehman-Salada, 1996). The most common method to determine the firmness of a fruit is destructive and measures its resistance to

penetration (Lehman-Salada, 1996; Ahumada and Cantwell, 1996; Mercado-Silva et al., 1998). Other methods based on fruit resistance to compression do not necessarily destroy the fruit, but they do require ~~it to be~~its harvest~~ed~~ (Polderdijk et al., 1993; Brovelli et al., 1998). Other methods, in addition to being non-destructive, can be used directly on the tree, such us the use of the hand densitometer (García et al., 1998) or those based on the transmission of acoustic waves through the fruit (Muramatsu et al., 1996). In citrus fruit, the relationship between the degradation of the cellular wall and the loss of firmness that accompanies fruit maturation has also been observed (Goto and Araki, 1983). Other important attributes of the internal quality of fruits, along with those mentioned above, are texture and rind thickness. In the same way, juiciness is another important fruit attribute, which can eventually be reduced in citrus by factors affecting the content of the juice sacs, such as freezing or excess of nitrogen fertilization during summer and early autumn (Flint, 1991).

Excepting fruit colour, all of them are impossible to be known by the fruit appearance by the consumer, whose decision to choose fruit of a desired quality is not supported by sufficient objective information (Poole et al., 2006).

There is a need for techniques for a swift, non-destructive determination of fruit internal quality, to ensure that all fruit meet a minimum level of acceptance. ~~A s~~Simplification of the analysis ~~is an important reason for this objective. A further reason is that the conventional destructive methods of analysis are based upon a limited number of fruit samples, whereas non destructive techniques makes it possible~~and the possibility to monitor practically all the fruit in real time are important reasons for this objective. Conversely, improving the environmental sustainability of human activities is a current

challenge ~~to~~that should be emphasized~~.~~. ~~achievement of which can contribute to the~~ ~~n~~Non-destructive analytical techniques can contribute, since it does not require chemical reagents or solvents and no waste is generated.

The most suitable technology depends on ~~what is~~ the main quality parameter ~~required~~ to be measured. Among several techniques, NIR has great potential for non-destructive determination of internal and maturity attributes (Abbot, 1999).

The measurement modes most frequent for intact fruit SSC and TA prediction are reflectance, transmittance and interactance. Although it has been reported predictive outcomes slightly higher using transmittance regarding reflectance and interactance with intact mandarin (McGlone et al., 2003), good results using reflectance mode have been reported with mandarin (Guthrie et al., 2005; Hernández et al., 2006) and orange (Cayuela, 2008). Reflectance is the easiest mode to obtain measurements, since no contact with the fruit is required and light levels are relatively high (Mowat and Poole, 1997). In the transmission mode, the measurements are expected to be more influenced by fruit size, the amount of light penetrating the fruit often being very small, thus making it difficult to obtain accurate transmission measurements at grading line speeds (Kawano et al., 1993).

~~NIR technology has been used to determine the soluble solids content (SSC) non-destructively in fruit such as apples (Iyo and Kawano, 2001; Hernández et al., 2003; Zude et al, 2006), citrus (Tsuchikawa et al., 2003; Guthrie et al., 2005), peaches (Slaughter, 1992; Peiris et al., 1997), cherries (Lu, 2001) and melons (Dull et al., 1989; Dull et al. 1992; Ito et al., 2002; Guthrie et al., 2006), among others. Nicolaï et al. (2007) offered a review on non-destructive measurement of fruit and vegetable quality by NIR.~~

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The NIR spectra are the result of the interaction of radiation with the sample, and their physical and chemical properties are reflected in it. Fruit juiciness and fruit weight are fruit physical properties. Successful results of NIR calibrations for citrus juiciness prediction have been reported (Guthrie et al., 2005). The possibility of estimating fruit weight by NIR has rarely been reported, the exploration of this possibility being of great interest, since fruit weight could be added to other fruit quality parameters such as CSS, TA or fruit firmness as different outputs from a single NIR measure. In fact, some good outcomes have been found recently regarding NIR measuring nectarine fruit weight (Pérez et al. 2009).~~In fact, good results have recently been found in nectarine fruit weight NIR measuring (Pérez et al. 2009).~~ Previous research (Cayuela, unpublished data) also indicated that nectarine fruit weight can be predicted by NIR.

One of the advantages of NIR spectrometry is its portability when the parameter must be measured *in situ*. A few models of portable NIR spectrometers of several brands are available, but the applications to fruit monitoring are few. Furthermore, the technical and constructive characteristics of NIR spectrometers are very diverse, and research into their suitability for use in new applications is needed. Riquelme (2008) included in her doctoral thesis a full revision of the commercial models of on-line NIR instruments and the portable NIR spectrometers applicable to fruit.

In this work, the feasibility of non-destructive NIR prediction of quality parameters on orange fruit, comparing ~~with~~ two commercially representative portable spectrometers~~,~~ using predictive models constructed by Partial Least Squares (PLS), has been evaluated. The successful prediction of some parameters in this work analysed is reported for the first time.

MATERIALS AND METHODS

Fruit

Sanguinelli, Valencia, Salustiana and Navelate oranges were hand picked, at random, during the commercial harvest period, from a local experimental grove belonging to the College of Agricultural Engineering, University of Huelva, transported to the laboratory and used immediately or after storage at 4 ºC for up to one week. The orange varieties included in this study are taxonomically all them *Citrus sinensis* (L) Osb. The number of samples from each variety contributing to the set of calibration is indicated in Table 1. The oranges were harvested at five different dates from January to April 2009, and therefore, an ample diversity in the fruit quality parameters w~~ere~~as assured. Before testing, samples were taken out from the cooling and maintained at room temperature (23-25 ºC) for 18 h in order to allow for acclimatization to the experimental conditions. Fruit were cleaned with a cloth moistened in sterile water, then dried at the lab environment prior to measurement. Each fruit unit constituted the sample, and were numbered in the fruit peduncle area.

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Spectral acquisition

The spectral acquisition of every sample was performed using two portable spectrophotometers with different optical and constructive features: Labspec (Analytical Spectral Devices Inc., Boulder) and Luminar 5030 (Brimrose Corp., Maryland).

Labspec is a Visible/NIR spectrometer equipped with three detectors. The detector for the visible range (350-1000 nm) is a fixed reflective holographic diode array with a

sensitivity of 512 pixels. Wavelengths in the visible spectrum can carry information relating to some of the quality parameters analyzed, such as fruit color and color of the juice, and perhaps additional ones as the fruit size. ~~The portability of the equipment is assured by the weight of the spectrometer 8.5 kg.~~ The wavelength range of 1000-1800 nm is covered by a holographic fast scanner InGaAs detector cooled at -25ºC. The same aforementioned device coupled with a high order blocking filter operates for the 1800-2500 nm interval. The instrument is equipped with internal shutters and automatic offset correction, the scanning speed being 100 ms. The acquisition of spectra was performed using the high intensity contact probe accessory of the spectrometer, with light source diameter 20 mm ~~(Fig. 1)~~, and standard SMA 905 fiber optic connectors. The whole spectrum ~~(350-2500 nm)~~ was acquired, each spectral variable corresponding to 2 nm interval. The repeatability of the instrument, expressed as standard deviation on the average absorbance of 350 to 2500 nm of five measures of a white tile, is 6.00 10^{-4}. The orange spectra acquisition was carried out using Indico Pro software (Analytical Spectral Devices Inc., Boulder). The portability of the equipment is assured by the weight of the spectrometer 8.5 kg.

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Luminar 5030 is an AOTF (acousto-optic tunable filter) NIR spectrophotometer, equipped with a reflectance post dispersive optical configuration and InGaAs (1100-2300 nm) detector. The reference spectrum is automatically taken by the instrument, just as an UV-VIS spectrophotometer dual beam; the beam is divided before leaving and a small portion is sent to a second detector that makes the reference. The scanning speed in Luminar 5030 is 60 ms. The spectrometer is formed by the hand-held unit, shaped and used similarly to a ‘gun’, the diameter of the exit cone of the light source

being 8 mm ~~(Fig. 1)~~, and the computer unit; the spectrometer set, with a total weight of 5.26 Kg, offers a good portability, with 4h of autonomy using a set of batteries that allows *in situ* measuring on crop; this is an important advantage to note. The hand-held unit is equipped with a base for facultative use in the laboratory. The whole spectrum ~~(1100-2300 nm)~~ was acquired, each spectral variable corresponding to a 2 nm interval. The repeatability of the instrument, expressed as standard deviation on the average absorbance of 1100 to 2300 nm of five measures of a white tile, is 6.76 10-4. The signals were acquired with software Acquire (Brimrose Corp., Maryland).

~~Citrus fruit are anisotropic objects, showing different physical and chemical properties when measured in different directions. Equatorial measurement was selected because, at least in citrus, SSC are greatest in the distal apex of fruit, decreasing towards the proximal, the opposite happening with A and TA, as reported by Peiris et al. (1999).~~

The sample unit was the fruit, an averaged spectrum being obtained for each sample, resulting from a total 100 spectra corresponding to two measures of 50 spectra each, it for both spectrometers, taken at opposite equatorial locations~~,~~. ~~according to the reasons indicated above.~~

~~Figure 1~~

Reference analysis

The quality attributes of each fruit were evaluated by analysis of their physical and chemical parameters. Additionally, parameters calculated arithmetically were assessed.

Physical parameters

Fruit weight (FW, g) and rind weight (RW, g) were measured using electronic precision balance (0.001 g). RW was determined once the fruit was pealed by separating the rind from the flesh. For the measurement of intact fruit colour a spectral colour analyser (colorimeter PCE-RGB 1002) was used, determining the same in triplicate for the same fruit. This instrument has a RGB (red, green, blue) colour scale 0-1023. The Easy-RGB software (Logicol Colour Technology Co.) was used for the conversion into the L, a and b parameters of the Hunter scale. The results expressed by the colour index (FCI) were obtained from the mathematical formula [1].

$$CI = 1000a / Lb \qquad [1]$$

Flesh firmness (F, ~~Kg~~N) was quantified using a hand penetrometer (TR FT-327 Turoni S.r.l., Forcy, Italy) with a 7 mm diameter cylindrical plunger, twice on the peeled fruit at the equatorial circumference. The fruit were halved through the equatorial plane and juice extracted with a commercial juice extractor. Juice volume (JV, mL) was measured with a test tube. Juice volume to fruit weight ratio was calculated and expressed as a percentage (JV/FW, %). Juice colour was determined with the same colorimeter and units above indicated for fruit colour and expressed as juice colour index (JCI). The measurement was performed on a juice sample of each individual orange fruit in a Petri plate, this measurement being made through the glass at the bottom of the plate. This procedure was used to avoid the risk of any introduction in the juice of the colorimeter light source. ~~The SSC was measured on each fruit juice by a hand help digital refractometer (Atago Co, PAC-1 Brix Meter, Tokyo) and obtained from two replicates, expressed as Brix units.~~

Chemical parameters

The SSC was measured on each fruit juice by a hand-help digital refractometer (Atago Co, PAC-1 Brix-Meter, Tokyo) and obtained from two replicates, expressed as percentage.

The acidity (A, pH) was measured on the juice of each individual fruit from two replicates, using a digital pH-meter. The titratable acidity (TA) was analogously measured from two replicates by direct titration of a 10 mL juice sample added with 10 mL distilled water, neutralized with NaOH 0.1 N until pH 8.2 and expressed as citric acid (g/L).

Arithmetically calculated parameters

The maturity index reference (MI) ~~ratio soluble solids content to titratable acidity~~ was arithmetically obtained from the ratio between SSC and TA reference analysis values ~~(SSC_R/TA_R) and in turn, by .~~The arithmetical computation from SSC and TA obtained using the NIR predictive models developed in this work for both parameters (SSC_P/TA_P) was compared with the prediction outcomes from the model developed for MI directly predicting~~.~~

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Chemometrics and calibration procedure

Partial Least Squares ~~(Wold et al., 1983)~~ models were obtained with Unscrumbler 9.7 (CAMO Software AS, Norway). For the Labspec spectra, noise intervals 350-499 nm and 2301-2500 nm were removed. ~~Calibration tests were conducted for the Labspec to eliminate spectral noise at the beginning and end of spectrum, using 500 to 2300 nm wavelengths for this purpose.~~ In turn, tests were carried out for the same spectrometer excluding 600-750 nm, a range strongly affected by the skin pigment chlorophyll that absorbs red light, whose absorbance band corresponds to 680 nm ~~(McGlone et al.,~~

~~2003)~~. This band is not included in the Luminar's wavelengths range. Exclusion of the initial and final areas of spectrum to eliminate noise, in the case of Luminar was also considered unnecessary. ~~Faulty reference analytical data were identified and eliminated prior to calibration.~~

Before calibrations, the reflectance data were transformed to absorbance, mean normalized, and optionally treated by multiplicative scatter correction (MSC) using Unscrumbler 9.7. The influence of the pre-processing on the prediction of the calibration models was tested by different gap and smooth combinations for first and second gap-segment derivatives. Standard ~~N~~normal ~~V~~variate t~~T~~ransformation (SNV) was also tested. Full-cross internal validation (FCV) was used for building the models. Calibration tests were also conducted with different numbers of principal components in order to determine the number of PCs optimum and the results assessed in terms of standard error of cross validation (SECV). Exceptionally, where indicated in the tables, points clearly separated from the calibration sets in the scatter plots were identified as outliers and removed with Unscrumbler 9.7 using its specific application for this purpose.

Validation procedure

Two ~~E~~external validation exercises were carried out using the corresponding models for predicting the parameters~~ on completely independent samples.~~, One validation exercise was conducted using 1/5 ~~being reserved from the total reference analysed~~of the total number of samples for each parameter, the set for validation being formed by Unscrumbler's specific application, the first from every 5 samples taken with this purpose (V1). Other exercise was conducted for the set of samples 51 to 100,

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corresponding to Sanguinelli (V2), which was excluded from the corresponding calibrations that were developed previously for this purpose.

In assessing the soundness of the calibrations performance, the main considerations were the root mean square error of prediction (RMSEP) and the residual predictive deviation (RPD), described by Williams and Sobering (1996) as the ratio of the standard deviation of the reference data for the validation set to the SEP.

Paired samples T test for dependent samples were also conducted to verify the results from RPD and RMSEP analysis. Not established as statistic specifically for assessing PLS model performance, T test was applied here exclusively referred to the data pairs included in the external validation exercise. For this purpose, data pairs of the reference value and the resulting prediction corresponding to the external validation sets were compared. The paired T test is a parametric procedure, useful for testing whether the means of two groups are different, where the samples are drawn in pairs. The T test was carried out using SPSS Statistics software (SPSS Inc., Chicago). The compliance with the null hypothesis in this test (*P>0.05) indicates that the measure NIR provides at least the same accuracy as the reference method.

The prediction output from the calibration model for direct NIR MI measuring ~~the SSC/TA ratio~~ was compared both with ~~SSC_R/TA_R~~the reference values and with SSC_P/TA_P above described ~~above~~, also using the paired samples T test.

RESULTS

Fruit NIR spectrum

Typical diffuse absorbance spectra for intact oranges acquired by both instruments (Labspec and Luminar 5030) are shown in Fig ~~2~~1. The spectra from the two instruments

showed characteristics similar to those also previously described in oranges (Cayuela, 2008) or in Satsuma mandarin (Hernández et al., 2006) beyond differences regarding the wavelengths acquired.

High intensity peaks are noted, related to the strong water absorbance bands present from their first overtone at 1400 to 1500 nm and combination band at 1880-2100 nm with an interval of relative intensities of high absorption, approximately between 1400 and 2200 nm. Absorbance falls around the 1500 nm and rises again from approximately 1850 nm where oscillation exists probably due to carbohydrates. Overall, the pattern of the absorption curves is similar to that for other fruit such as peach (Peiris, 1997), kiwifruit (McGlone and Kawano, 1998), mangoes (Budiastra et al., 1998), apple (Lu et al., 2000) and cherries (Lu, 2001).

Figure ~~2~~1

Population characterization

The mean and standard deviation values of the populations of orange varieties used in the calibrations and the external validations for the parameters analysed are shown in Table 1. The ~~ratio SSC/TA~~ MI in the different varieties shows that Valencia oranges corresponded to a less advanced stage of maturation, Sanguinelli and Navelate being at approximately the same maturity stage and Salustiana showing, according to its ~~SSC/TA~~ MI ratio, the most advanced maturity of the four varieties. As can be seen, wide ranges of variation of all the parameters analysed were included in the populations.

The characteristics of the sample sets used for the validation exercises, conducted using obtained models for predicting each parameter in samples independent from the calibrations sets, are shown in Table 2. The contribution of each variety to the

validation sets were 50 Sanguinelli, 10 Valencia, 9 Salustiana and 10 Navelate samples, according to the proportion 1/5 regarding calibration sets.

Table 1

Table 2

Calibration development

The statistical coefficients of best calibration models with Labspec and Luminar 5030 for predicting orange quality parameters according to the treatment used for the two instruments tested, are included in Tables 3 and 4 respectively.

The range from 600 to750 nm could be affected by the skin pigment chlorophyll, as has been previously indicated. Calibration tests were conducted with the Labspec excluding this range, without any improvement when including it. This result probably reflects the fact that no green areas were present in the skin of any of the orange samples used in the calibrations. This test was unnecessary with the Luminar, since its spectral range does not include 600-750 nm.

The calibration ~~coefficients~~ statistics for V1 were relatively ~~similar~~close with both instruments for SSC, A, ~~SSC/TA~~MI, JV and JV/FW. Hence, with the Labspec the RMSECV were 0.60, 0.12, 1.81, 7.39 and 0.03, whereas for the Luminar it were 0.67, 0.15, 2.06, 7.97 and 0.03 respectively for these parameters (Table 3 and Table 4). Some differences were found between both spectrometers for FW, RW and F~~F~~, the Labspec showing RMSECV 19.89, 14.61 and 1.18, whereas for the Luminar it were 22.69, 17.07 and 1.27 ~~(Table 3 and Table 4).~~ All the cases, the lower values RMSECV from the Labspec implies a better predictive performance for these parameters. Calibration for FCI and JCI were attempted only with the Labspec, since it integrates Visible and NIR.

Generally, mean normalized data provided the best fits for most parameters analysed. In some cases, shown in Tables 3 and 4, in both or either spectrometers, MSC treatment alone or after mean normalization facilitated the best calibration coefficients.

Table 3

Table 4

Model external validation

The ~~statistical coefficients of the predictions carried out in~~outcomes from the external validation exercises V1 for each orange quality parameter with both spectrometers ~~-~~are shown in Table 3 and Table 4. The predictions ~~output~~ versus the analysed value of each parameter in th~~is~~e external validation exercise are shown in Fig ~~3~~2.

As can be seen from the validation plots, and according to the validation coefficients RMSEP and RPD shown in Table 3 and Table 4, prediction accuracy was similar for most fruit quality parameters with both spectrometers and slightly better with the Labspec for FW, RW and F~~F~~.

The validation exercise V2, corresponding to Sanguinelli, provided better performance for all the parameters analyzed with the Labspec. The statistical values are shown in Table 5. The best RPD with the same spectrometer in this exercise were reached for SSC and MI predictions.

Figure ~~3~~2

Table 5

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DISCUSSION

The ~~predictive calibration for SSC showed slightly better fit with the Labspec, although it was very close to that obtained with the Luminar 5030, in which the~~ external

validation exercise V1 carried out for SSC showed analogous accuracy with both spectrometers, as can be deduced from the RPD ratios. ~~gave a more accurate prediction . Acidity, Titratable Acidity and the SSC/TA ratio predictive calibrations were also very close between both spectrometers.~~

The values RMSEP in the ~~predictive models~~ validations V1 and V2 for SSC 0.74 and 0.87 (Labspec) or 0.68 and 1.12 (Luminar) were ~~slightly~~ higher to those previously reported by Cayuela (2008) ~~also~~ for Valencia Late orange and using reflectance (570–1850 nm) with a non portable Vis-NIR spectrometer InfraXact (Foss), where RMSEP 0.55 is reported. In that work the direc NIR prediction of MI was not addressed.

For A, TA and MI the accuracy were similar in the V1 validation exercise for the Labspec (Table 3) and the Luminar (Table 4). The validation V2 conducted with a Sanguinelli fruit set (Table 5) showed lower RPD values for all these parameters and both spectrometers, excepting for MI with the Labspec. The RPD values were higher for the Labspec in this exercise, hence showing better performance.

~~Both predictive calibrations for acidity (pH) and titratable acidity in this study with both spectrometers achieve lower RMSEP values than the 0.33 for titratable acidity and 0.49 for pH reported previously with oranges (Cayuela, 2008), which could be attributed to the wider ranges of the values of these parameters included in the calibrations in this work.~~ For a Fantec-FQA, from the SEP and σ for pH and TA reported by Riquelme (2008) can be deducted RPD values 0.68 and 0.56 using internal software for mandarins and oranges, as well 0.79 and 0.37 for the same fruits using calibration developed by the author, these values being lower to those reported in this work.

Several other results have been reported with Satsuma mandarin (Hernández et al., 2006) also using reflectance and with Imperial mandarin using other optical modes

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(Guthrie et al., 2005; McGlone et al., 2003). However, a comparison is not recommended because oranges are larger in size, ~~and with~~having a different structure to mandarin fruit. Moreover, literature about using NIR spectroscopy to SSC and pH measuring in several fruit is very wide, as is referred in the introduction, thus the aim here is not to demonstrate this possibility and their industrial application.

The RPD coefficients from the external validations for SSC, A and TA were comprised in both spectrometers between ~~1.54~~0.80 and 2.33. For reference, RPD ranging from 0.12 to 0.56 were reported using a Fantec-FQA for the same parameters (Riquelme, 2008). Models constructed with both spectrometers were able to determine SSC and A in V1 with an accuracy approaching 95%, according to an arithmetic calculation of the difference between the values estimated by NIR and reference values (data not shown). The external validation V1 with the calibration for the ratio ~~SSC/TA~~MI showed RPD very similar values in both spectrometers, this being 1.67 with the Labspec and 1.64 with the Luminar. The exercise V2 showed for the same coefficient RPD with the Labspec 1.75, higher to the RPD 1.26 with the Luminar. Riquelme (2008) reported RPD 0.25 for the same parameter and also in oranges using a Fantec-FQA., but not much information scientific has been reported regarding citrus MI direct NIR prediction.

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The predictions obtained in the exercises V1 and V2 with the models for NIR measuring directly ~~Soluble Solids Content to Titratable Acidity ratio (SSC/TA)~~MI, were compared using paired sample test T both with ~~the ratio SSC/TA arithmetically obtained from SSC and TA~~ reference analysis values ~~(SSC_R/TA_R)~~ and with the arithmetical computation from SSC and TA independient NIR obtained (SSC_P/TA_P). No significant differences were found in V1 between ~~SSC/TA~~MI predictions and

~~SSC_R/TA_R~~references ~~(~~sig. 0.629) while on the contrary, there were significant differences between SSC_P/TA_P and ~~SSC_R/TA_R~~references (*P = 0.039). Similar result was found with V2 exercise (data not shown). Therefore, ~~the ratio SSC/TA arithmetically obtained from SSC and from TA values~~MI is easy and accurately ~~if it is~~ obtained from the reference analysis values ~~(SSC_R/TA_R)~~, but the arithmetical computation of MI would give worse results if these values are to be NIR obtained (SSC_P/TA_P), which will be the case when using a NIR spectrometer in routine analysis. The~~n~~refore, the use of models for MI direct NIR prediction is advantageous. As the SSC/TA ratio constitutes the most widely used ~~maturity index~~MI, the possibility of its NIR prediction in real time is of great interest, regardless of the SSC and TA values, which are also NIR measured at the same moment.

On the other hand, thise study ~~conducted~~ revealed that NIR prediction of ~~SSC/TA~~MI, ~~a~~ more interesting ~~maturity index~~ than titratable acidity by itself, were more accurate than TA NIR prediction, as revealed in the V1 exercise by the ~~statistical coefficients of the calibration and external validation exercises~~RPD for both parameters ~~SSC/TA~~MI and TA, included in Table 3 (Labspec) and Table 4 (Luminar), and in the V2 exercise (Table 5) for both spectrometers. From these results it appears that it is a methodology suitable for avoiding the difficulty of accurately NIR-predicting ~~titratable acidity~~TA, as described by various authors (Mc Glone et al., 2003; Guthrie at a., 2005), since it is possible to predict ~~SSC/TA~~MI ratio directly by NIR~~,~~. ~~which could be used as maturity index~~.

~~T~~The high accuracy of the predictive calibrations for fruit weight and rind weight in the V1 exercise must be highlighted since~~, for the first time,~~ it makes ~~it~~ possible to measure

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these parameters by NIR spectroscopy in citrus. Fruit weight NIR measuring is very scarcely mentioned in the literature, even for other fruit, as indicated in the introduction. This accuracy is referred to each weight measurement on single fruit, it being essential for the industry to ensure that all the fruit included in each bag or box has a minimum suitable size or weight. The RPD from the external validation reached with the Labspec for fruit weight and rind weight in the V1 exercise were 4.76 and 4.54, and with the Luminar, 3.03 and 3.23, values, all cases being higher than three, the value that ideally should be reached to ensure the goodness of a model (Williams and Sobering, 1996).

Regarding Juice volume ~~calibrations~~models in V1 validation, they were fairly accurate, coefficients being very close in both spectrometers, as shown in Tables 3 and 4. ~~The external validation for juice volume with b~~Both spectrometers showed RPD near to three in this exercise, revealing good performance. Although the volume of orange juice is not generally included in trade rules for citrus fruits, the accuracy level needed has not even been defined, nevertheless it is a very interesting quality parameter to be monitored in each single fruit, as Riquelme (2008) reported, since citrus can eventually suffer from juiciness defects.

The external validation V1 ~~with the calibration~~ for the ratio JV/FW with both the Labspec (Table 3) and the Luminar (Table 4) ~~RPD~~ showed RPD values higher to 1.5 and lower to 2, what are not optimal but reveals a good predictive potential of these models. ~~The statistical coefficients from the external validation exercises corresponding to each of these parameters with both spectrometers are shown in Table 3 and Table 4.~~

Fruit flesh firmness showed ~~the value~~RPD 1.85 in the V1 external validation with the Labspec. The ability of NIR estimating orange flesh firmness with sufficient accuracy is also of great interest, since it could be used as maturity index (Olmo, 2000), although more research is needed about the relationship between orange firmness and maturity stage to establish maturity indices based upon this parameter on specific varieties. The accuracy level reached in ~~the external validation~~V1~~,~~ with the Labspec for flesh firmness was 83.9%, and 79.0% with the Luminar, according to an arithmetic calculation of the difference between the values NIR estimated and reference values (data not shown). ~~This means that the difference between the model prediction and the reference analysis were, in both cases, approximately in the order of 20%.~~

The external validation V1 for FCI corresponding to the Labspec provided low and relatively good accuracy RMSEP values, with RPD 1.75. This last data indicate differences between model prediction and reference analysis of approximately 10%, on average.

The statistical coefficients of the external validation V1 for predicting JCI (RPD 1.31) revealed that model performance was far from good. However, the paired T test determined no significant differences between predictions and reference values. This fact could be related with some possible inconsistent reference values that may be attributed to the methodology used for measuring juice colour and, particularly, the inclusion of the Petri plate bottom in the juice colour measurement, needing to be improved.

However, considerable disagreement was found in the statistics between both validation exercises V1 and V2 conducted with both spectrometers for FW, F and JV. The RPD

values were clearly lower for these parameters in the exercise V2. The RPD reached for the JV/FW, FCI and JCI in the V2 exercise were also lower than in V1. This facts shows that the predictive potential of the technique for these parameters, when measuring a set of samples not considered in the calibrations, can be lower than expected.

~~Some~~ Most quality orange fruit parameters showed a RPD ratio lower than three, value considered as threshold for an optimal validation (Williams and Sobering, 1996). ~~These parameters were soluble solids content, acidity, titratable acidity, soluble solid content to titratable acidity ratio, flesh firmness, juice volume to fruit weight ratio, and additionally, with the Labspec colour index and juice colour index.~~ However, consideration of other criteria in the external validation exercises, such as paired test T for all parameters studied indicated no significant differences between the laboratory reference and the NIR determined values, which means that NIR was at least as accurate as the reference methodologies. The unique particularity was with colour index, presenting *P 0.055, which is the limit of significance, therefore reference and NIR measure were very near to be different in this parameter.

The ~~predictions for fruit weight, rind weight and flesh firmness showed slightly~~ better statistical coefficients from calibration and external validation using the Labspec~~. This fact~~ can be due to the contact probe used in spectra acquisition with the~~is Labspec~~spectrometer, presenting light source diameter (20 mm), larger than that of the Luminar 5030 (8 mm), and, therefore, being different the area of the fruit surface illuminated in both cases. This factor contributes to being able to explore a larger portion of the fruit in the case of the spectrometer Labspec.

~~CONCLUSIONS~~

~~The predictions of both SSC and TA and the SSC/TA relationship has been successful in the external validation by applying the corresponding calibrations developed using both spectrometers. The direct NIR prediction of SSC/TA ratio was advantageous regarding the arithmetical computation from the values of SSC and TA NIR obtained. The NIR prediction of SSC/TA was more accurate than TA NIR prediction. Therefore NIR directly predicting SSC/TA ratio can be a suitable methodology to avoid the difficulty of accurately NIR predicting titratable acidity.~~

~~The predictive calibrations for Fruit Weight and Rind Weight facilitated high accuracy with both spectrometers, which is the first time that measuring these parameters by NIR spectroscopy has been reported in citrus. Also, for Juice volume and JV/FW ratio calibrations were fairly accurate.~~

~~The use of NIR measurements of Fruit Colour Index together with the ratio SSC/TA and with the Flesh Firmness predictions may contribute to better defining the ripeness of citrus fruit regarding that obtained with these parameters separately.~~

~~The satisfactory result obtained in the validation of models integrating four orange varieties showed that it is possible to develop predictive models for orange quality parameters in general, and not only models specific for an orange variety.~~

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Figure captions

Figure 1. A) Labspec, contact probe. B) Luminar 5030, hand held unit

Figure 21. A) Labspec, B) Luminar 5030. Examples of absorbance spectra from the same five oranges

Figure ~~3~~2. External validation plots V1.
A) Labspec, B) Luminar 5030. RPD values at the lower right corner.

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Table 1

	Sanguinelli			Valencia			Salustiana			Navelate			Total		
	N	**σ**	$\overline{X}$	**N**	**σ**	$\overline{X}$	**N**	**σ**	$\overline{X}$	**N**	**σ**	$\overline{X}$	**N**	**σ**	$\overline{X}$
SSC	250	0.84	8.53	50	1.04	8.16	44	0.84	10.94	52	0.72	11.86	396	1.56	9.19
A	250	0.15	3.14	50	0.13	3.17	44	0.12	3.87	52	0.13	3.52	396	0.28	3.28
TA	250	0.19	0.78	50	0.21	1.48	44	0.09	0.70	52	0.16	1.06	396	3.12	9.38
MI	250	2.45	11.35	50	0.63	5.56	44	2.30	15.85	52	1.79	11.44	396	3.36	11.14
F	250	1.96	5.79	50	1.39	7.67	44	1.06	5.76	52	1.43	7.44	396	1.91	6.24
JV	250	7.25	31.88	50	9.40	48.58	44	6.29	76.80	52	7.87	74.27	396	19.80	44.55
FW	250	20.71	81.52	50	23.98	124.05	44	9.41	214.60	52	19.22	290.19	396	77.88	129.08
JV/FW	250	0.04	0.39	50	0.02	0.39	44	0.02	0.36	52	0.03	0.26	396	0.06	0.37
RW	250	14.16	43.62	50	14.70	72.09	44	6.62	128.15	52	17.59	209.72	396	59.29	78.42
FCI	250	8.62	21.05	50	8.40	15.07	44	6.08	26.48	52	3.54	18.51	396	8.35	20.56
JCI	250	88.35	62.97	50	24.52	-71.05	44	14.80	-35.62	52	30.18	-72.46	396	93.90	17.31

Table 1. Statistical data of the sets of samples and orange varieties.

SSC, soluble solids content (%); A, Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; F, flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); RW, rind weight (g); FCI, fruit colour index; JCI, juice colour index; σ, standard deviation; $\overline{X}$, mean.

Table 2

Parameter	Samples	Range	σ	$\overline{X}$
SSC	76	5.5-12.4	1.59	9.08
A	76	1.1-3.9	0.28	3.27
TA	75	0.6-2.6	0.29	0.91
MI	75	4.0-16.7	3.22	10.85
F	76	1.5-11.7	1.93	5.96
JV	74	18.0-88.0	20.58	45.00
FW	75	47.4-311.4	79.19	127.08
JV/FW	76	0.2-0.5	0.06	0.37
RW	76	18.5-228.5	60.0	76.5
FCI	72	8.7-31.0	4.64	20.54
JCI	76	-141.9-223.4	87.40	16.40

Table 2. Statistical data of the sets of samples used in V1.

SSC, soluble solids content (%); A, Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; F, flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); RW, rind weight (g); FCI, fruit colour index; JCI, juice colour index; σ, standard Deviation; $\overline{X}$, mean.

Table 3

		Calibration					Validation		
Parameter	**Treatment**	**PCs**	**Outl.**	**RMSECV**	**R**	**R_{CV}**	**RMSEP**	**RPD**	**T**
SSC	MN	10	0	0.60	0.92	0.91	0.74	2.13	0.719
A	MN, MSC	10	4	0.12	0.90	0.88	0.15	1.85	0.714
TA	MN	10	0	0.16	0.86	0.83	0.17	1.69	0.978
MI	MN	8	0	1.81	0.85	0.81	1.92	1.67	0.765
FW	MN, MSC	10	2	19.89	0.97	0.96	16.52	4.76	0.716
F	MN	7	3	1.18	0.76	0.72	1.05	1.85	0.356
JV	MN	9	3	7.39	0.92	0.91	7.05	2.94	0.511
JV/FW	MN, MSC	9	3	0.03	0.89	0.87	0.04	1.61	0.327
RW	MN	10	2	14.61	0.97	0.96	12.98	4.54	0.349
FCI	MN, MSC	8	0	3.45	0.90	0.87	2.65	1.75	0.055
JCI	MN, MSC	10	0	1.59	0.86	0.83	66.78	1.31	0.286

Table 3. Labspec. Statistics of calibrations and validations. Wavelength 500-2300 nm.

SSC, soluble solids content (%); Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; Flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); Rind weight (g); MN, mean normalisation; MSC, multiplicative scatter correction; Outl., outliers; RMSEC, root mean square error of calibration; R, coefficient of calibration; R_{CV}, coefficient of cross validation; RMSEP, root mean square error of prediction; RPD, residual predictive deviation; T, **p* value from paired samples test.

Table 4

		Calibration					Validation		
Parameter	**Treatment**	**PCs**	**Outl.**	**RMSECV**	**R**	**R_{CV}**	**RMSEP**	**RPD**	**T**
SSC	MN, MSC	10	0	0.67	0.91	0.89	0.68	2.33	0.273
A	MN, MSC	10	1	0.15	0.84	0.81	0.16	1.75	0.931
TA	MN	10	2	0.18	0.80	0.77	0.19	1.54	0.321
MI	MN, MSC	9	1	2.06	0.79	0.74	1.96	1.64	0.313
FW	none	9	3	22.69	0.96	0.95	26.26	3.03	0.414
F	MSC	10	0	1.27	0.71	0.66	1.39	1.39	0.280
JV	MN, MSC	9	2	7.97	0.91	0.91	8.00	2.56	0.977
JV/FW	MSC	9	1	0.03	0.83	0.80	0.04	1.67	0.148
RW	none	9	2	17.07	0.96	0.95	18.86	3.23	0.249

Table 4. Luminar 5030. Statistics of calibrations and validations. Wavelengths 1100-2300 nm.

SSC, soluble solids content (%); Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; F, flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); RW, Rind weight (g). MN, mean normalisation. MSC, multiplicative scatter correction; Outl., outliers; RMSEC, root mean square error of calibration; R, coefficient of calibration; R_{CV}, coefficient of cross validation; RMSEP, root mean square error of prediction; RPD, residual predictive deviation; T, *p value from paired samples test.

Table 5

	Labspec		Luminar 5030	
Parameter	**RMSEP**	**RPD**	**RMSEP**	**RPD**
SSC	0.87	2.21	1.12	1.03
A	0.13	1.05	0.40	0.80
TA	2.47	1.26	2.07	1.07
MI	1.54	1.75	2.57	1.26
FW	43.51	1.11	32.63	0.75
F	1.82	1.20	1.53	1.03
JV	8.38	1.10	12.13	0.84
JV/FW	0.04	1.18	0.05	1.10
RW	16.07	1.11	14.71	0.73
FCI	6.48	1.64		
JCI	55.69	0.67		

Table 5. **V**alidation V2. N = 50. Wavelength 500-2300 nm.

SSC, soluble solids content (%); A, Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; Flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); Rind weight (g); RMSEP, root mean square error of prediction; RPD, residual predictive deviation; N, number of samples of the validation set.

Figure 1

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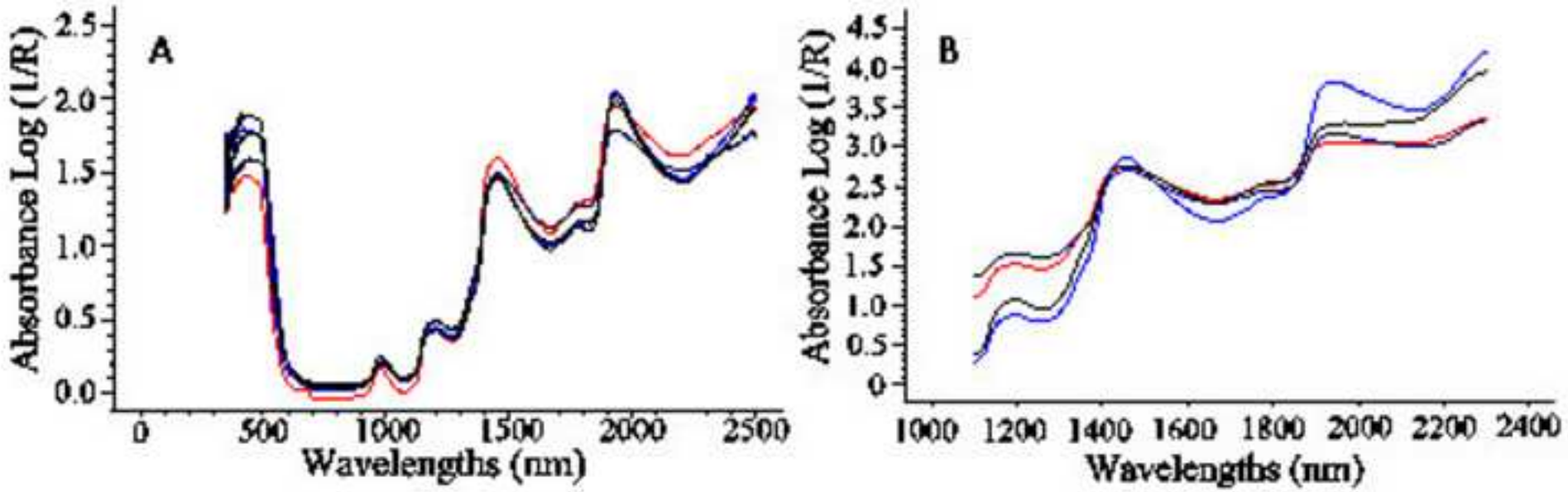
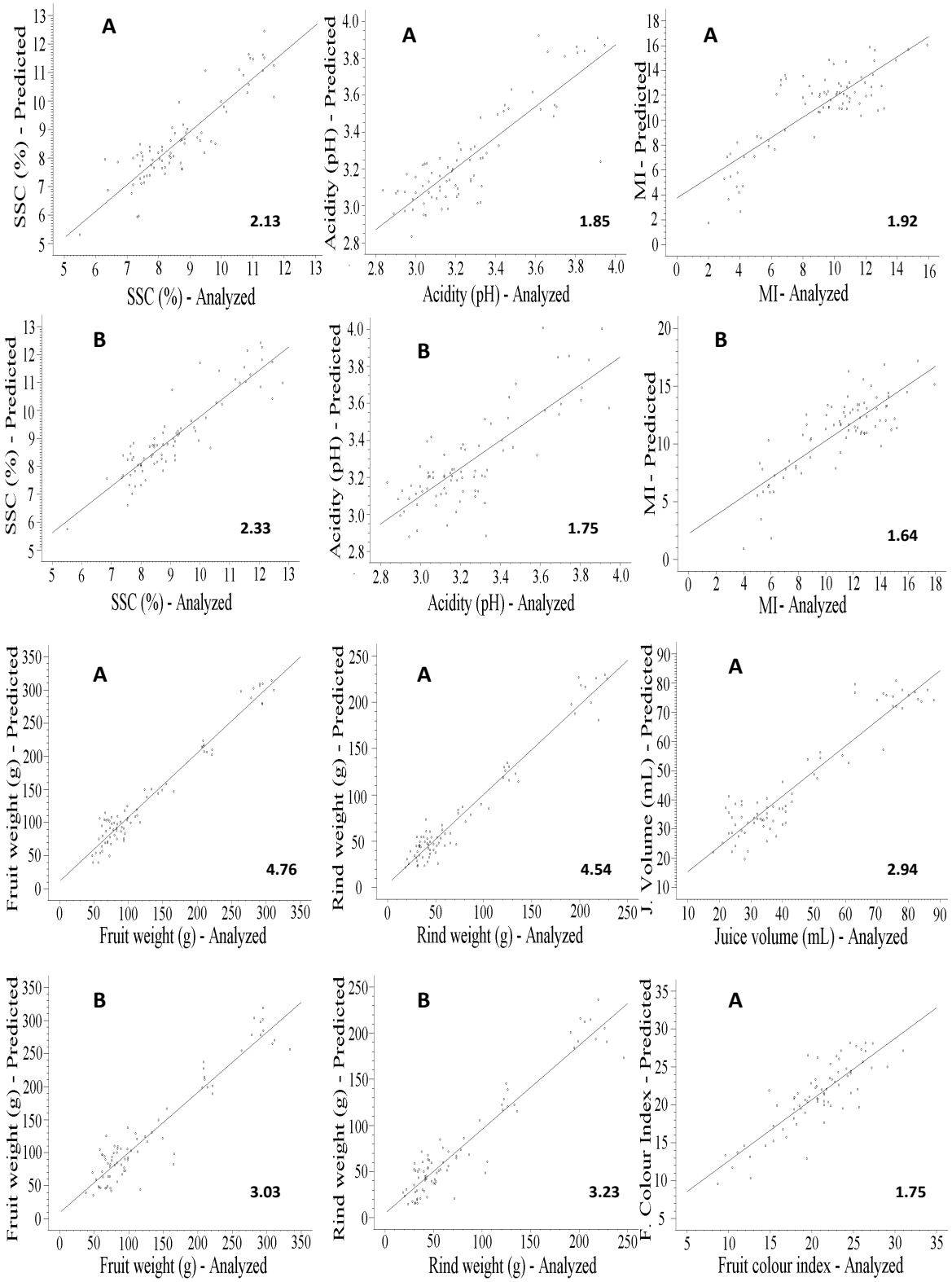


Figure 2


A
SSC (%) - Predicted
SSC (%) - Analyzed
2.13
A
Acidity (pH) - Predicted
Acidity (pH) - Analyzed
1.85
A
MI- Predicted
MI- Analyzed
1.92
B
SSC (%) - Predicted
SSC (%) - Analyzed
2.33
B
Acidity (pH) - Predicted
Acidity (pH) - Analyzed
1.75
B
MI - Predicted
MI- Analyzed
1.64
A
Fruit weight (g) - Predicted
Fruit weight (g) - Analyzed
4.76
A
Rind weight (g) - Predicted
Rind weight (g) - Analyzed
4.54
A
J. Volume (mL) - Predicted
Juice volume (mL) - Analyzed
2.94
B
Fruit weight (g) - Predicted
Fruit weight (g) - Analyzed
3.03
B
Rind weight (g) - Predicted
Rind weight (g) - Analyzed
3.23
A
F. Colour Index - Predicted
Fruit colour index - Analyzed
1.75