PREDICTION OF THE SOLUBLE SOLIDS CONTENT IN THREE FRUIT SPECIES USING NIRS APPROACH

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ABSTRACT – The fruit structure effect (passion fruit, tomato and apricot) was investigated on prediction performance of soluble solids content (SSC) using NIR spectroscopy. Relationships between spectral wavelengths and SSC data were evaluated through the application of chemometric techniques based on partial least squares (PLS). Good prediction performance was obtained for apricot with correlation coefficients of 0.93 and root mean square errors of prediction (RMSEP %) of 3.3%. For the passion fruit and tomato, the prediction models were not satisfactorily accurate due to the high RMSEP. Results showed that NIR technology can be used to evaluate apricot internal quality, however, it was not appropriate to evaluate internal quality in fruits with thick skin, (passion fruit), and/or heterogeneous internal structure (tomato)

1. INTRODUCTION

Near Infrared Spectroscopy (NIRS) is becoming an attractive analytical technique for measuring quality parameters in food, especially because it allows non-destructive analysis of food products, requires little or no sample preparation and is both flexible and versatile, i.e., it is applicable to multiproduct and multicomponent analysis (Roberts *et al*., 2004). The NIR spectra are the result of the interaction of radiation with the sample, and their physical and chemical properties are reflected in it. The interactions occur with molecular groups associated with quality attributes such as the C–H group in sugars and acids and the O–H group in the water. Most of the NIR absorption bands associated with these groups is overtones or combination bands of the fundamental absorption bands in the near infrared region, which are themselves due to vibrational and rotational transitions. Scattering from microstructures can indirectly indicate physical parameters (Nicolai *et al*., 2007).

Previous research has demonstrated the potential of NIR spectroscopy for assessing soluble solid content (SSC), and/or other physiological properties in intact fruits such as in prune (Slaughter, *et al*., 2003), stonefruit (Golic and Walsh, 2006) and apricot (Bureau *et al*., 2009). However, this successful use of NIR spectroscopy was restricted to fruits with homogeneous pulp and thin skin. Guthrie, *et al*., (2006) obtained unsatisfactory results for melon fruit, similarly Guthrie and Walsh (1997) were not able to predict soluble solids content in pineapple. Lammertyn, *et al*., (2000) pointed out that penetration of NIR radiation into fruit tissue is limited. For example, in apple, the penetration depth is up to 4 mm in the 700–900 nm range and between 2 and 3 mm in the 900–1900 nm range. In fact, in a later study, Nicolai and co-workers (2007) concluded that depending on the uniformity of the fruit, the determination of quality attributes is difficult. The objective of the work was to assess the near-infrared spectroscopy, as a non-destructive method, to predict soluble solids, in three structurally different intact fruits: passion fruit (thick skin), tomato (heterogeneous internal structure) and apricot (homogeneous pulp and thin skin).

2. MATERIALS AND METHODS

2.1. Selection of passion fruit, tomato and apricot

A total of 61 yellow passion fruits (*Passiflora edulis f. flavicarpa*), in two different ripening stages (green–yellow and yellow) were harvested in 2011 in southern Brazil. For tomato, a total of 150 fruits of cultivar 'Levovil', in five different ripening stages (green, green–orange, orange–green, orange, red) were harvested in 2008 from an experimental greenhouse of INRA (Institut de la Recherche Agronomique) located in Southern France. 116 apricot fruits from three cultivars, named 'Bergeron', 'Iranien' and 'A4034' were harvested at two different stages of ripening: yellow (unripe) and orange (ripe) in INRA experimental orchards (Amarine and Gotheron), in South of France, in 2010. Non-destructive measurements were performed on the day of picking for each fruit and conventional, destructive, measurements were carried out a few days later on frozen materials.

2.2. Near-infrared diffuse reflectance measurements (FT-NIR)

Spectra were collected for all samples in reflectance mode (log $1R^{-1}$) using a multi-purpose analyser (MPA) spectrometer (Bruker Optics). The instrument was equipped with an integrating sphere to provide diffuse reflectance measurements and a TE-InGaAs detector. The MPA was fully software-controlled (OPUS software Version 5.0, Bruker Optics). The NIR spectrum for each sample was obtained from an average of 32 scans. NIR spectra were acquired between 800 and 2700 nm at 2 nm spectral resolution and a background of 32 scans. The time required to achieve a spectral measurement was 30 s. Intact tomato and apricot fruits were placed on an automated 30-position sample wheel, each position corresponding to an 18 mm diameter hole. The spectra for passion fruit were obtained in Brazil, an identical spectrometer was used (Bruker Optics) but without sample wheel. Fruits were placed at each-calyx axis set to the horizontal position. On each fruit, two opposite spectra were captured and the average of the two spectra was used (for the development of the models).

2.3. Determination of soluble solids content

Soluble solids content (SSC) was determined with a digital refractometer (PR-101 ATAGO, Norfolk, VA) with temperature compensation. SSC was expressed in °Brix.

2.4. Multivariate calibration

PCA (principal component analysis) was initially performed using all available samples (n = 61 for passion fruit; n = 150 for tomato and n = 116 for apricot) in order to evaluate the variability among the samples, to eliminate the aberrant spectra due to acquisition problems and to separate groups for calibration and internal validation. It is recommended for all practical applications (Nicolai *et al*., 2007). In order to generate the prediction models for the quality traits of interest, the samples were grouped into two sets to have 80% samples for calibration and 20% for internal validation (Table 1). MatLab software package (version 6.5, Mathworks USA.) and Origin 6.1® (OriginLab Inc., Northampton, USA) were used for chemometric treatment of data. In this study, different pretreatments, including mean centering, multiplicative scatter correction (MSC), first-derivative and smoothing, were applied. Quantification models for SSC were developed using PLS regression. To evaluate the results, root mean square error of cross-validation (RMSECV), root mean square error of prediction (RMSEP), the percentage of error of prediction (RMSEP%) and correlation coefficient of validation (R^2).

3. RESULTS

3.1. Characterization of the chemical and spectral data

The samples showed a large variability of SSC for fruits of the three species used in this trial. These results confirm that selected fruits were in different ripening stages. Statistical analysis for the calibration and validation sample sets, i.e., data ranges, means, standard deviations (SD) and number of samples for SSC are shown on Table 1.

Table 1 – SSC range, mean and standard deviation (SD) of the passion fruit, tomato and apricot in both calibration and validation sample sets

Fruit	Sample set	Range	Mean	Standard Deviation	Number of samples
Passion fruit	Calibration set	9.0 – 16.0	13.3	±1.8	49
	Validation set	12.1 – 14.2	14.2	±1.3	12
Tomato	Calibration set	3.7 - 6.4	4.8	±0.49	118
	Validation set	3.9 - 6.1	4.7	±0.54	32
Apricot	Calibration set	11.3 - 20.4	15.2	±2.3	92
	Validation set	11.6 - 20.1	15.3	±2.1	24

The general shapes of the spectra for the three fruit types were quite similar, though the spectra for the passion fruit showed weak absorption intensity and a slight displacement, possibly due to the thickness of the skin (Figure 1). The main absorption peaks coincided for all three fruits. The peak at 1190 nm corresponds to the second and third C–H overtone regions and 1500 nm overlaps with the first O–H overtone region associated with organic compounds (Roberts *et al*., 2004). In general, the absorbance patterns seen here can be loosely related to the functional groups associated with water and sugars. Indeed, most fruits contain 80–90% of water and show a rising sugar content throughout ripening. The spectra obtained here for apricot and tomato can be compared to other studies concerning apricot (Bureau *et al*., 2009) and tomato (Sirisomboon *et al*., 2012).

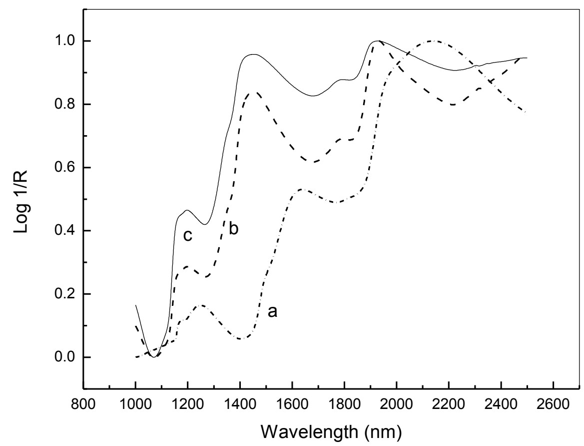

Figure 1 - Typical normalized NIR spectra (mean) performed on intact fruits of passion fruit (a), tomato (b) and apricot (c).

3.2. Prediction of soluble solids content

For fruits from the three different plant species used in this trial, different calibration models were calculated. The spectra pre-processing and the number of factors were both taken into consideration to determine the best models. The best PLS model developed for the passion fruit used pre-processing multiple scatter correction (MSC) and 5 latent variables (LVs) which provided the lowest cross validation error of 1.62 °Brix. When the model was applied to predict the 12 internal validation samples, a low correlation (R^2 = 0.63) and a high error of prediction (RMSEP% = 9.8%) were found. For tomatoes, results were similar to the results found for passion fruits. The lowest cross validation error (0.13 °Brix) was observed for models using 10 LVs and MSC pre-processing. When the model was used to predict the 32 internal validation samples, the prediction error was 8.85% and the correlation coefficient was 0.52. However, in apricot a good correlation was found. A R^2 = 0.93 and a low RMSEP 3.3% were observed, when the model was used to predict the 24 internal validation samples The same ratio was observed by Camps and Christen (2009). The lowest cross validation error (0.69 °Brix) was observed for models using 6 LVs and MSC pre-processing followed by smoothing.

3.3. NIR prediction results

The three species used in this trial have distinct physical (Figure 2) and biochemical (Table 1) characteristics. A broad range of values was recorded in this work for SSC in all of the three fruits. This finding is likely due to the fact that sampling was, as experimentally designed, carried out during different ripening stages, and it is well known that during ripening, sugars accumulate and acidity decreases, the later, as a result of the consumption of the predominant acids during fruit respiration.

Values of the SSC this work were within the range found in literature for passion fruit (Jiménez *et al*., 2011), tomato (Scibisz *et al*., 2011) and apricot (Bureau *et al*., 2009; Camps and Christen, 2009).

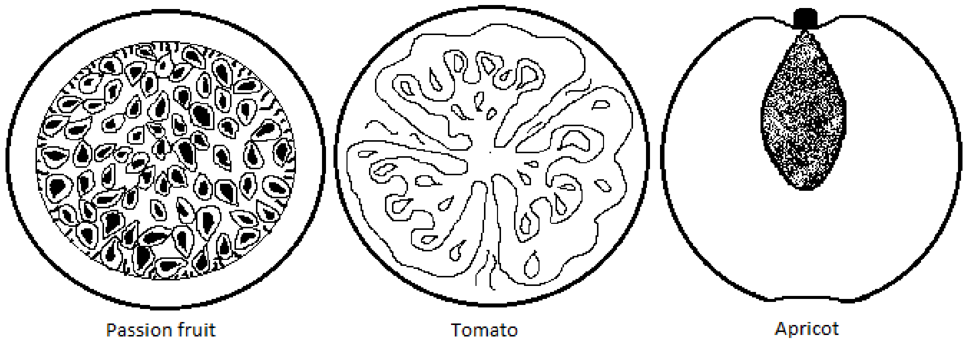

Figure 2 - Schematic representation of the fruit anatomy of the three species used in this trial. Equatorial sections are presented for passion fruit and tomato, and a transverse section for apricot.

Apricot is a stone fruit that consists of three parts: a thin skin, a fleshy mesocarp which encloses the seeds. The thickness and shape of the mesocarp vary according to different cultivars (Romani and Jennings, 1971). These characteristics seemed to favor the NIR prediction. Excellent results were found, showing that NIR technology can be effectively used for the quantification of the soluble solid for apricot. Measuring SSC have been reported also using reflectance mode, has shown excellent correlation for various fruits such as prune, plums and peaches (Louw and Theron, 2010; Pérez-Marín *et al*., 2009). All of these fruit share with apricot similar anatomical features such as thin skin and homogeneous pericarp.

The lowest correlation for the parameter SSC was found for passion fruit. Passion fruit contains similar soluble solids content when compared to apricot. However, the thick skin in passion fruit acts as a barrier and prevents the penetration of the infrared radiation to the pulp. The passion fruit is a fleshy, berry type fruit, with a thin pericarp (peel) that can be lignified. The passion fruit mesocarp thickness ranges from 0.5 to 4.0 cm, and the endocarp (pulp) contains seeds with fleshy aril (Vasconcellos *et al*., 2001). Indeed, Guthrie *et al*. (2006) determined the total soluble solids in intact melon and observed a correlation coefficient lower than the correlation coefficient found for other fruits, being the difference attributed to the heterogeneity of SSC distribution within the fruit and the poor penetration of light through the irregular fruit skin. Flores *et al*. (2008) evaluated SSC in cut and intact watermelons and melons using a NIR diode array spectrometer. The results of SSC prediction for cut watermelons and melons were much better than those of intact watermelons and melons (cut watermelons: R^2 = 0.92, RMESCV = 0.49; intact watermelons: R^2 = 0.81, RMSECV = 0.93; cut melons: R^2 = 0.94, RMSECV = 0.60, intact melons: R^2 = 0.87, RMSECV = 0.98). For passion fruit, the thick skin prevents the use of NIR to predict the composition of the internal pulp.

The tomato is a fleshy berry, with at least two locular cavities. The locular cavities contain the seeds, within a more or less abundant gel. They are enclosed by a parenchyma that forms a sub-epidermal layer of 0.2–1 cm, radial septa that separate the locules, and a collumella. The pericarp is protected to the outside by an epidermis covered with a waxy cuticle, presenting many hairs, stomata and lenticels (Hobson and Davies, 1971). The composition of these different tissues is not homogeneous. Cheng *et al*., (2011), in particular, showed that sugar concentrations in the placenta and close to the calix were consistently low relative to the outer pericarp, collumella, and locular cavity. The prediction of models for non-destructive measurement by spectroscopic methods has generally been poor (Walsh *et al*., 2004). Chen (2008) determined soluble solids content in two tomato varieties ('DRK 453' and 'Trust') in five different stages of maturity and found values remarkably low (R^2 = 0.03 and RMSEP 0.15 °Brix). However in these last two cases, prediction heavily relied on the internal correlation in the sample set, as a given variety has a defined genetic program that coordinates color evolution and sugar accumulation during maturation.

4. CONCLUSION

The analysis of the best models shows that the physical features of the fruit directly affect the results. The low correlation values for passion fruit were attributed to the low penetration of infrared radiation due the thick skin of the fruit. For tomatoes, internal characteristics (heterogeneity) and high water contents led to weak correlations. On the other hand, good and robust prediction results were observed for apricot, which is a fruit with thin skin and homogeneous pulp.

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