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Short communication

Determination of soluble solid content in market tomatoes using near-infrared spectroscopy

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ABSTRACT

Tomatoes are widely consumed worldwide, and the soluble solid content (SSC) is one of the most important quality parameters for the commercialization of fresh tomatoes, mainly in the salad group. In this regard, partial least square models for intact tomatoes SSC were developed using a portable F-750 Vis-near-infrared (NIR) with Zeiss MMS1-NIR spectrometer in an interactance geometry. Thus, tomatoes from five regions (states of Goiás, Bahia, Santa Catarina, Minas Gerais, and São Paulo) were collected weekly from November 2018 to November 2019, with a total sample number of 2.085, divided into three populations, two for calibration and one for prediction. The best partial least squares regression prediction model was obtained using the Vis-NIR spectral region of 840–1050 nm with Orthogonal Signal Correction (OSC) pre-treatment applied. The calibration population standard deviation (SD) was 0.52%, and for the prediction population, the SD was 0.56%. Low root mean square error cross-calibration of 0.32%, and root mean square error prediction of 0.32% were achieved. The models were able to discriminate low from high values and vice versa.

1. Introduction

Tomato (*Solanum lycopersicum* L.) is a climacteric fruit, which means that after harvesting, the functions of living tissues, besides ethylene production, are still affected, which makes the fruit palatable and also develops senescence and subsequent fruit ripening (Arah et al., 2015). During this phase, the sugars may still accumulate because of the metabolism of stored carbohydrates, lipids, and proteins (Kays & Paull, 2004). According to Kader (2008), sugars, acids, phenols, and minerals are the main constituents of tomato taste with sugars, quantitatively, making the largest contribution, because the flavor results from the complex interaction of taste and aroma.

Therefore, it is important to manage a good postharvest quality to handle the concentration of ethylene and timing of ethylene synthesis such that the fruit reaches the consumer at the optimal eating quality (Beckles, 2012). The postharvest quality of the fruit maintenance is based on pre-harvest factors (Arah et al., 2015). For example, tomato fruit that are diseased and infected by pests, inappropriately irrigated and fertilized, or generally of poor quality before harvesting, can never be improved in quality by any postharvest treatment methods (Harvey, 1978). In tomato crops, postharvest losses can be either quantitative or qualitative, though the qualitative losses – deterioration in the harvested fruit, premature softening, irregular color development, off-flavor development and mechanical injury (bruised fruit) – harm parameters,

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such as consumer acceptability, nutrient status of fruit, and financial income to producers (Arah et al., 2015).

Although the consumer is influenced by the visual appearance in the initial purchase, the subsequent purchases will be influenced by the eating quality of the previous purchase. The amount and types of sugars stored in tomatoes will affect the taste and overall fruit quality, influencing consequent consumption, therefore, the determination of SSC is important to the quality of tomatoes designed for the fresh market. These sugars and their influence on the taste and aroma of tomato fruit can be measured in many ways: total soluble solids (TSS), the TSS-to-titratable acid ratio, and the total sweetness index (TSI). The TSS is a refractometric index that indicates the proportion (%) of dissolved solids in a solution. It is the sum of sugars (sucrose and hexoses; 65%), acids (citrate and malate; 13%), and other minor components (phenols, amino acids, soluble pectins, ascorbic acid, and minerals) in the tomato fruit pulp (Balibrea et al., 2006; Kader, 2008).

Being a widely produced and consumed crop, high-quality tomatoes are demanded and should have a good appearance in color, shape, texture and acceptable internal qualities such as soluble solid content (SSC), acidity, and important factors of flavor and aroma (Huang, 2018a). In general, SSC determination is performed easily and rapidly with the use of refractometers (IAL, 1985). However, this method is destructive and leads to losses of the sampled fruit, in addition to not allowing the characterization of the fruit to ensure individual quality (Nikbakht et al., 2011). In this context, near-infrared (NIR) spectroscopy has been used as an alternative method to determine SSC in intact fruit because of its fast and non-destructive nature (Saad et al., 2014).

Recently, studies have reported the possibility of using NIR spectroscopy for the determination of SSC, TA, carotenoid compounds, and DM in salad tomatoes (Radzevičius et al., 2016; Saad et al., 2016; Acharya et al., 2017; Huang et al., 2018; Feng et al., 2019; Ibáñez et al., 2019). Despite many studies in this area, most of them did not use tomatoes produced in different growing regions as well as in different seasons. For a model to be considered robust, it needs to be developed with different growing regions, seasons, cultivars and heterogeneous samples considering the within-tree variability (tree age, crop load, spur age, position within the tree, and light effects), within-orchard variability (location of tree and light effects), orchard variability (soil characteristics, nutrition, and weather conditions), and fruit age and seasonal variability (Peirs et al., 2003; Nicolai et al., 2007, 2014). Therefore, considering the large variation existing in relation to the growing regions and the seasons of production, the objective of this study was to develop robust models to predict SSC in tomatoes using portable Vis-NIR spectroscopy.

2. Material and methods

2.1. Plant material

The batches with tomato salad fruit (*Solanum lycopersicum* L.) at pink, light red, and red ripeness levels and with the water content around 95%, were acquired weekly from November 2018 to November 2019 at a commercial maturity stage at the Centrais de Abastecimento de Goiás (CEASA-GO) and identified according to their origin and year of collection. Therefore, the fruit were classified according to their origins, as follows: Goiás – GO (n = 1706, collection years 2018 and 2019), São Paulo - SP (n = 65, year of collection 2018), Minas Gerais (MG) (n = 280, year of collection 2019), Bahia – BA (n = 10, year of collection 2018), and Santa Catarina – SC (n = 24, year of collection 2019), which were combined to create a calibration set (Pop-1 + Pop-2) and a prediction set (Pop-3).

To develop the calibration models, the dataset was divided into populations based on the year of collection and origin, i.e., population 1 (2018 data and samples from Goiás, São Paulo, and Bahia), population 2 (2/3 of 2019 data and samples from Goiás, Minas Gerais, and Santa Catarina), population 1 + 2 (sum of 2018 data and 2/3 of 2019 data) for calibration, and population 3 (1/3 of 2019 data and samples from Goiás, Minas Gerais, and Santa Catarina) for external validation (Table 1).

2.2. Vis-NIR spectra acquisition

After temperature stabilization (~20 °C), Vis-NIR spectra were collected at three distinct points on the epidermis of the fruit, exactly in the equatorial region that corresponds to the central line of the fruit using a portable F-750 instrument (Felix Instruments, Camas, WA, USA), employed with a Carl Zeiss MMS1-NIR spectrometer in an interactance geometry, with wavelengths ranging from 310 to 1100 nm, with a pixel resolution of approximately 3 nm (spectral sample size), an optical resolution of 8–13 nm (depending on wavelength), with a Xenon tungsten lamp as light source and lens with fused silica, coated to enhance NIR.

2.3. Reference analysis

The same epidermal region used to collect the Vis-NIR spectra was used to determine the SSC. For this purpose, cylinders approximately 3 cm in diameter and 1 cm in depth were removed and macerated in a porcelain mortar until a homogeneous liquid was obtained. The liquid was filtered through hydrophilic gauze, and SSC was determined using a digital refractometer (Digital Brix/RI-Chek; Reichet Analytical Instruments, USA), according to the AOAC method no. 932.12 (AOAC, 1997). The SSC values were grouped according to the origin of the fruit batch (Table 1).

2.4. Principal component analysis (PCA) and PLSR

The Unscrambler software (version 10.4, CAMO, Oslo, Norway) was used for chemometric analyses, including PCA and PLSR. For the PCA, the full-cross-validation method was used, as well as to determine the best number of factors used in the PLSR models. The Vis-NIR spectra were preprocessed using the first and the second derivatives of Savitzky–Golay (Savitzky & Golay, 1964), with a second polynomial order, using a nine point (4 + 4), 15 point (7 + 7), 13 point (6 + 6), and 21 point (10 + 10) smoothing window for the first and the second derivatives, as well as the pre-processing multiplicative scatter correction (MSC) and orthogonal signal correction (OSC).

The best wavelength intervals were selected according to the loading of the best model developed with the wavelength interval between 396 and 1131 nm and the second derivative of Savitsky-Golay with 13 points with 1 factor. Thus, the following combinations of selected intervals were reached: 837–921 nm, 927–933 nm, 942–954 nm, 960–966 nm, 972–987 nm, 993–1005 nm, 1026 nm, and 1032–1035 nm, in addition to spectral ranges 396–1131 nm and 840–1050 nm (Fig. 1).

Table 1
Soluble solid content relation of the analyzed populations.

Population	Localities	SOLUBLE SOLID CONTENT (%)				N
		Mean	SD	Maximum	Minimum	
POP1	(GO[a] + SP[b] + BA[c])	4,5	0,47	6,1	3,4	283
POP2	(GO + MG[d] + SC[e])	4,5	0,53	6,8	3,2	1202
POP1+2	(GO + SP + BA + MG + SC)	4,5	0,52	6,8	3,2	1485
POP3	(GO + MG + SC)	4,5	0,56	6,8	3,2	601

[a] Goiás.
[b] São Paulo.
[c] Bahia.
[d] Minas Gerais.
[e] Santa Catarina.

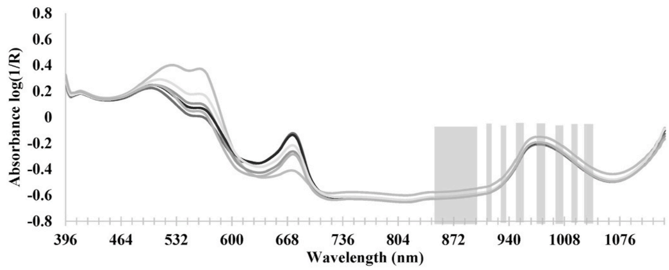

Fig. 1. Selected wavelength used in the model development with partial least squares regression (PLSR).

2.5. PLSR model selection

The performance of the models was evaluated using the coefficients of determination of the calibration set (R^2c) and cross-validation (R^2cv), by the root mean square error of calibration (RMSEC), root mean square of error of cross-validation (RMSECV), and the ratio between the standard deviation (SD) of the calibration population and the RMSEC (SDRcv). For the prediction, the following parameters were considered: coefficient of determination (R^2p), bias, root square of the mean quadratic error of prediction (RMSEP), and the ratio between the SD of the prediction population and the bias-corrected RMSEP (SDRp). The relationship among RMSEP, bias, and SEP was evaluated using the equation: $RMSEP^2 = SEP^2 + bias^2$ (Golic & Walsh, 2006). The use of SDR statistics allowed the comparison of model performance across the population with different SDs, as shown by the equation for calibration: SDRcv = D.P./RMSECV, in which D.P. is the SD of the calibration, and the equation for prediction: SDRp = D.Pp/RMSEP, in which D.Pp is the standard deviation of the prediction (Golic & Walsh, 2006).

3. Results and discussion

3.1. SSC

There was a significant difference ($p < 0.05$) between the SSC means of the tomatoes obtained in different growing regions (Table 2). Nevertheless, these differences were of minor importance in relation to the sensory aspect because the consumer will only perceive the variations in SSC of approximately 1.0% (Harker et al., 2002).

Overall, the tomatoes from the states of Bahia and Santa Catarina had the highest SSC (4.8%) when compared to that of the other states where the SSC ranged from 4.4% to 4.2% (Table 2). It was also possible to observe large variation in these contents (3.1–6.8%), but the SSC values were similar to those commonly reported in salad tomatoes produced in Brazil, i.e., contents ranging from 4.5% (Ferreira et al., 2010) to 6.5% (Feltrin et al., 2002). The same was observed by other authors such as Radzevičius et al. (2016) who found values from 3,4 to 4,9%, Saad et al. (2016) with values from 4,8 to 6,4% and Ibáñez et al. (2019), who found values close to 5.65%.

Table 2
Analysis of Variance (ANOVA) of the soluble solid content mean from the tomato fruit identified according to their state of origin: São Paulo (SP), Goiás (GO), Minas Gerais (MG), Santa Catarina (SC), and Bahia (BA).

State	Means
SP	4.29^{a} [a]
GO	4.43^{a}
MG	4.48^{ab}
SC	4.82^{bc}
BA	4.85^{c}
CV^2 (%) 11.49	

[a] Means in the column followed by the same letter do not differ from each other by Tukey test at 5%; 2 – Coefficient of variation.

3.2. Vis-NIR spectra

The Vis-NIR spectra of the different populations are shown in Fig. 2. It was possible to observe spectral differences based on the origin of the fruit because tomatoes from the states of Goiás, São Paulo, Minas Gerais, and Santa Catarina had lower absorbances than the spectra of the fruit from the state of Bahia, which presented higher absorbance in the region of 500–570 nm, indicating a higher presence of red pigments, probably from carotenoids, such as lycopene, which is characteristic of tomato fruit (Gómez et al., 2006).

However, the fruit from Bahia had lower absorbance in the region of 660–684 nm, corresponding to chlorophyll (Subedi & Walsh, 2020). Hence, the Vis-NIR spectra of the tomatoes from the states of Goiás, São Paulo, Minas Gerais, and Santa Catarina can mostly be associated with tomatoes at less developed maturity stage in relation to the fruit from the state of Bahia because these fruit exhibited a lower absorbance in the region corresponding to lycopene content. As tomatoes from Bahia showed a lower absorbance in the region of 660–684 nm, which corresponds to chlorophyll (675–678 nm), it is understood that these tomatoes might have higher lycopene content than the others because chlorophyll has been degraded in the synthesis of new carotenoids, and during the alteration between the carotenoids while fruit ripening in the immature stage, there is a higher lutein content, and these carotenoids change to β-carotene or lycopene (Bianchetti & Dias, 2016).

In the NIR region, higher absorbances were observed in the range of 900–1030 nm, with a peak at 978 nm (Fig. 2). According to Feng et al. (2019), this peak is caused by the presence of water because of its relation to the O–H absorption band range (740 nm, 840 nm, 960 nm, and 1440 nm) (Subedi & Walsh, 2020). On the contrary, in the region of 1170 nm, the increase in absorbance is associated with C–H stretching of second overtone bonds, related to carbohydrates present in fruit (Talari et al., 2016).

Thus, the Vis-NIR spectra are characteristic of ripe fruit because ripe salad tomatoes have water contents ranging from 92% to 97% (Terrão & De Mendonça, 2009) and SSC between 4% and 9% (Minami & Mello, 2017). Additionally, immature tomatoes have peaks between 675 and 678 nm because of the presence of chlorophyll (Tiwari et al., 2013), but in the samples used in this study, these peaks showed low absorbance when compared to those related to the presence of carotenoid compounds (Fig. 2).

For the development of the models, both the Vis-NIR spectra without preprocessing (Fig. 2) and with preprocessing were used. The spectra were pre-processed with first (Fig. 3) and second derivatives of Savitzky-Golay (Fig. 4), MSC (Fig. 5) to correct the Vis-NIR spectra to make them as close as possible to a reference spectrum (Windig et al., 2008), and the OSC (Fig. 6) to minimize the variability that is not related to the analyzed variables (Blanco et al., 2001). When using these preprocessing

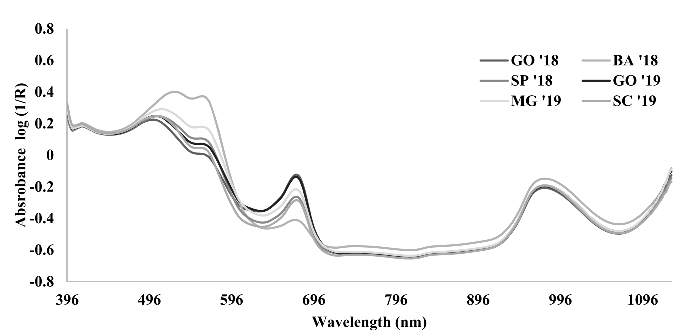

Fig. 2. Absorbance Vis-NIR spectra from intact tomatoes according to different origin and year.

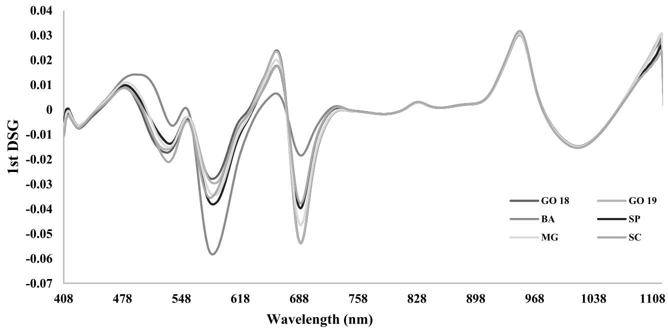

Fig. 3. –NIR spectra of intact tomatoes after preprocessing with the first derivative in a range of 396–1131 nm.

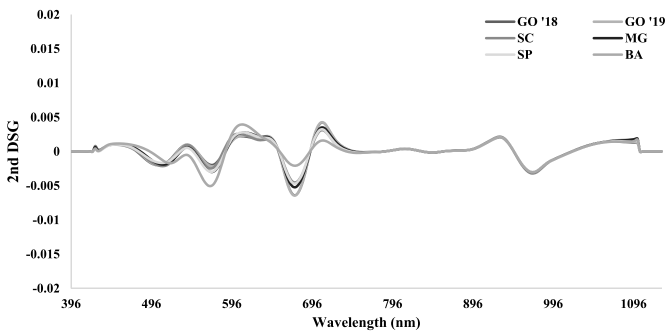

Fig. 4. NIR spectra of intact tomatoes after preprocessing with the second derivative in a range of 396–1131 nm.

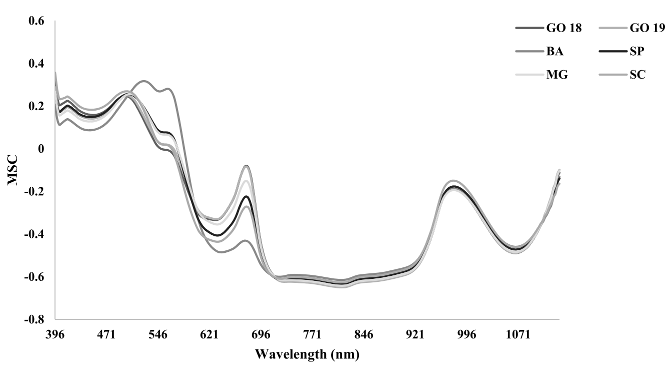

Fig. 5. NIR spectra of intact tomatoes after preprocessing with MSC in a range of 396–1131 nm.

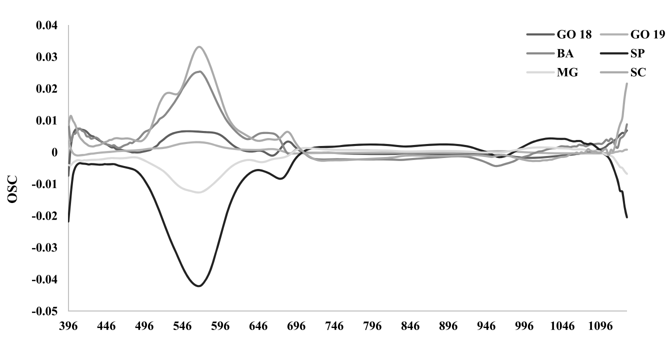

Fig. 6. NIR spectra of intact tomatoes after preprocessing with OSC in a range of 396–1131 nm.

methods, problems such as baseline and scattering lights can be corrected (Saad et al., 2014).

3.3. Chemometrics analyses

3.3.1. PCA

There was no clustering formation of Vis-NIR spectra regarding the origin of salad tomatoes in 2018 (Fig. 7A). The same occurred for the samples from 2019; again, there was no spectral clustering between the fruit from the different origins (Fig. 7B). When 2/3 of the 2019 samples was added to the 2018 samples, no clusters were observed (Fig. 7C). Thus, the origin and the year of the collection did not interfere with the discrimination of tomatoes. Despite having distinct origins, tomatoes grown for fresh consumption had similar SSC values, because the cultivars of the sub-groups generally had common agronomic attributes, for example, the production of SSC required for the commercialization of fresh fruit (3.5 %–4.5%).

3.3.2. PLSR

As the samples did not present differences between the growing regions using PCA, the populations were separated into calibration and prediction sets according to the seasons (2018 and 2019). Therefore, the calibration set consisted of the 2018 samples (population 1) plus 2/3 of the 2019 samples (population 2); on the other hand, the prediction set consisted of the remaining 1/3 of the 2019 samples (population 3). Table 3 shows the results of the developed models.

The models were developed using PLSR with the full wavelength window of 396–1131 nm (data not shown), but the best performances were obtained when the spectral range of 840–1050 nm was used, which could be caused by absorption peaks for water and carbohydrates in the 740 nm, 840 nm, 960 nm, and 1440 nm (Subedi & Walsh, 2020). Therefore, low values of RMSECV (0.32%) and high R^2cv (0.63%) were reported for the calibration model (Table 3). The RMSECV was low and resembled the values reported by Beghi et al. (2018), who found an RMSEC of 0.38% in fresh tomatoes, without specifying the cultivars used in the study. For the prediction set, the best model exhibited an RMSEP = 0.32%, R^2p = 0.67%, and SDR = 1.73 (Table 3). According to Nicolai et al. (2007), when SDR values are between 1.5 and 2.0, it implies a model with the capacity to discriminate low from high values and vice versa.

The low SDR obtained in this study was caused by the low SD of the attribute of interest in the calibration and validation sets, which could be a limitation because a low range in the population will necessarily be associated with a low RMSEC and a low R^2 (Acharya et al., 2017). For example, a low SDR was found by Walsh et al. (2004) because of a population SD of 0.3%. In the present study, the population SD was higher (0.56%) and the SDR value (1.73) was higher than that obtained by Walsh et al. (2004) (SDR = 1.5%) for SSC prediction using interactance shortwave near-infrared (SWNIR) in intact tomatoes.

The results obtained in this study are similar to those of other studies that used interactance to determine SSC in tomatoes, such as Walsh et al. (2004) who obtained lower values of SEP (0.20%) and lower values of R^2 (0.59) and Tiwari et al. (2013), Zhang et al. (2021), using a system based on the integrating sphere system in an interactance mode found a RMSEP of 0,21% and RPD of 1,72. Comparisons with other studies are important, but variations, such as in optical geometry, type of spectrophotometer, and other factors, including fruit maturation point, growth conditions, and cultivar, can influence prediction results (Huang et al., 2018).

When external validation was performed, it was noted that the RMSEP and R^2p values were increased, which is fundamental in the development of calibration models, because most studies use prediction populations originating from the same sample set as the calibration set (Nicolai et al., 2007). The incorporation of heterogeneous samples in the model is also quite important because fruit and vegetables are matrices subject to within-orchard variability in plant age, position in the

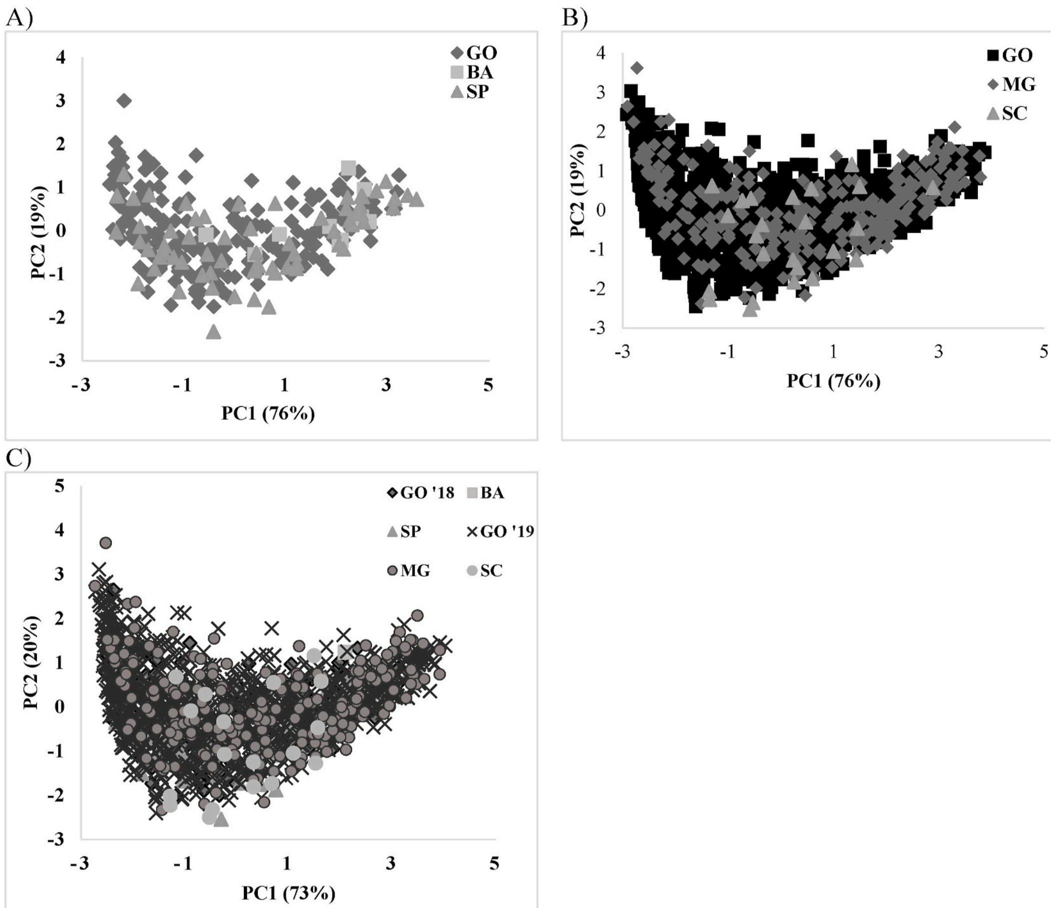

Fig. 7. Principal component analysis for the NIR spectra of intact tomatoes in absorbance from samples of 2018 (A), 2019 (B), and the samples from 2018 plus 2/3 of 2019 (C).

Table 3
Partial least squares regression results for the calibration and the prediction models for soluble solid content (%).

Population	Pre-processing	Wavelength (nm)	P, C[a].	CALIBRATION					PREDICTION				
				R^2 [b]	R^2_{cv} [c]	RMESEC[d]	RMSECV[e]	SDR[f] (SD/RMSECV)	Population	R^2 [g]	RMSEP[h]	SEP[i]	SDR[j] (SD/SEP)
2018 + (2/3) 2019	OSC	840–1050	11	0.6513	0.6318	0.3079	0.3166	1.6475	(1/3) 2019	0.6665	0.3227	0.3223	1.7316
2018 + (2/3) 2019	OSC	SELEC[k].	10	0.6476	0.6339	0.3095	0.3157	1.6523	(1/3) 2019	0.6612	0.3252	0.3249	1.7178
2018 + (2/3) 2019	ABS	840–1050	12	0.6219	0.6015	0.3206	0.3294	1.5835	(1/3) 2019	0.6453	0.3327	0.3324	1.6790
2018 + (2/3) 2019	OSC	402–798	9	0,3053	0,2900	0,4346	0,4397	1,1864	(1/3) 2019	0,3303	0,4575	0,4568	1,2220

[a] Principal components.
[b] Calibration coefficient.
[c] Cross-validation coefficients.
[d] Root mean square error calibration.
[e] Root mean square error cross-validation.
[f] Ratio (calibration standard deviation/RMSECV).
[g] Prediction coefficient.
[h] Root mean square error prediction.
[i] RMSEP corrected by bias.
[j] Ratio (prediction standard deviation/SEP).
[k] Wavelength.

orchard, and light effects, as well as soil characteristics, nutrition, and climatic conditions (Peirs et al., 2003). Therefore, the models presented in Table 3 were constructed by incorporating samples from different regions and times, which improved the robustness of the developed model, making it less sensitive to the variations that salad tomato fruit can present.

4. Conclusions

A portable Vis-NIR spectrometer can be used to predict SSC in salad tomatoes, and the developed model was able to discriminate low from high values and vice versa. This study demonstrated that it is possible to use the models as a tool to quantify SSC on-site in the field and to ensure the quality desired by consumers. However, it is important to improve the models and add variabilities, such as different seasons and cultivars, and a large number of samples.

Author contributions

Annelisa Arruda de Brito: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Project administration **Fernanda Campos**: Investigation, Data Curation **Abadia dos Reis Nascimento**: Resources, Funding acquisition. **Gilmarcos de Carvalho Corrêa:** Resources, Funding acquisition. **Flávio Alves da Silva**: Writing - Review & Editing **Gustavo Henrique de Almeida Teixeira:** Conceptualization, Methodology, Writing - Review & Editing **Luis Carlos Cunha Júnior**: Conceptualization, Methodology, Software, Validation, Formal analysis, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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