Comparing the analytical performances of Micro-NIR and FT-NIR spectrometers in the evaluation of acerola fruit quality, using PLS and SVM regression algorithms

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ABSTRACT

The main goal of this study was to investigate the analytical performances of a state-of-the-art device, one of the smallest dispersion NIR spectrometers on the market (MicroNIR 1700), making a critical comparison with a benchtop FT-NIR spectrometer in the evaluation of the prediction accuracy. In particular, the aim of this study was to estimate in a non-destructive manner, titratable acidity and ascorbic acid content in acerola fruit during ripening, in a view of direct applicability in field of this new miniaturised handheld device. Acerola (Malpighia emarginata DC.) is a super-fruit characterised by a considerable amount of ascorbic acid, ranging from 1.0% to 4.5%. However, during ripening, acerola colour changes and the fruit may lose as much as half of its ascorbic acid content. Because the variability of chemical parameters followed a non-strictly linear profile, two different regression algorithms were compared: PLS and SVM. Regression models obtained with Micro-NIR spectra give better results using SVM algorithm, for both ascorbic acid and titratable acidity estimation. FT-NIR data give comparable results using both SVM and PLS algorithms, with lower errors for SVM regression. The prediction ability of the two instruments was statistically compared using the Passing-Bablok regression algorithm; the outcomes are critically discussed together with the regression models, showing the suitability of the portable Micro-NIR for in field monitoring of chemical parameters of interest in acerola fruits.

1. Introduction

Acerola (*Malpighia emarginata* DC.) is a fruit native to Central America and Northern South America, with some of the largest plantings in Brazil. Acerola is considered a super-fruit due to its high concentration of vitamin C, ranging from 1.0% to 4.5% (w/w). Nevertheless, research on this fruit is very limited and, until now, only the authors studied the quality characteristics using non-destructive techniques [1,2]. Furthermore, its biochemical evolution is not completely known and its perishability is very rapid, preventing the export of the fresh fruit.

There are numerous studies highlighting the potential of near-infrared (NIR) spectroscopy applied to fruit and vegetables and promoting its use as a rapid and non-destructive analytical technique useful for determining internal and external characteristics, either quantitative or qualitative [3,4]. However, considerable attention has been given to the miniaturisation and portability of spectroscopic devices, but only in the last few years, small and precise handheld near-infrared scanning spectrometers became commercially available [5]. A survey of scientific papers published in the last decade shows a steady increase in the number of research and development studies being conducted using these types of portable spectrometer [6–8]. It is clear that the greatest advantage of these compact systems is the possibility of being implemented for new applications on-site and on-line at an industrial level but the potential of these instruments can only be realized if the reduction in size does not compromise the performance of the spectrometer [9]. Although most comparison studies reported that portable instruments had lower performance scores than laboratory instruments, the main conclusions were that their flexibility and possibility of field-use were major advantages that

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made the portable options the best solution in many practical situations. Most of the scientific studies carried out recently with handheld devices in the post-harvest field were actually performed under laboratory conditions, applying such devices onto intact harvested fruits [10].

Within this context, the fruit and vegetable industry demands simple equipment capable of performing real time in field analyses, to allow growers to reach the proper "on tree ripening" and to establish the most suitable harvest dates, shelf-life and storage conditions. Fruit quality standard was enhanced in the last recent years, although consumers were not always satisfied about the quality of the fruits available in the marked. Reaching the proper harvest time on the tree will allow maximising fruit quality, so the possibility to have a handheld NIR device directly in field could ensure the best possible crop quality, required by an increasingly more demanding market, while avoiding wastes and losses [11].

The processing of spectral data obtained with the NIR devices requires a multivariate statistical approach for extracting useful information from the acquired signals, because wavelength-dependent scattering effects, instrumental noise, ambient effects, and other sources of variability may affect the spectra. In order to relate the spectra (independent variables) to specific fruit quality parameters (dependent variables) a regression method is required [12]. Consequently, many studies are focused on finding the calibration models, testing and comparing several different pre-processing techniques, and optimising regression methods [10].

In the present study, two different regression algorithms are compared: Partial Least Squares (PLS) and Support Vector Machines (SVM). The first one is widely used for regression models because of its simplicity to use, speed, relative good performance and easy accessibility, while a possible large advantage of SVM is its ability to model nonlinear relations [12]. In the field of chemistry and, more specifically, chemometrics, only a few applications of SVM for regression tasks have been published [13,14].

The main goal of this study was to investigate the analytical performances of a state-of-the-art device, a miniature dispersion NIR spectrometer (weight < 60 g), evaluating the prediction accuracy in a view of direct applicability in field. So far, very few studies described the use of this novel device in analytical food characterization [6] and the present study performs, for the first time, a critical comparison between the miniaturised device and a benchtop FT-NIR spectrometer. In particular, the aim of this study was to estimate, in a non-destructive manner, titratable acidity and ascorbic acid content in acerola fruit during ripening, with two spectrometers. For these purposes, the spectra modelling was carried out using not only a method (PLS) particularly suitable for linear models but also a non-linear one; SVM, which could be more appropriate for the evaluation of the ripening process, with the monitored indices reaching a plateau at the physiological maturity [15]. The outcomes are critically discussed.

2. Material and methods

2.1. Fruit samples

A total of 117 acerola fruit of the most commercialised cultivar 'Junko' were harvested in April 2014 in Petrolina (PE – Brazil) at the development stage of 1−25% of red skin colour and were analysed during fourteen days at room temperature (25 ± 2 ℃). Fruit ripening involves complex physiological and biochemical changes such as the conversion of chloroplasts to chromoplasts and synthesis of pigments such as carotenoids and anthocyanins, which cause the skin colour changes from green to yellow and, later, to red-purple [16]. No deep studies were carried out on acerola biochemical modification during ripening, so, like in previous studies on this fruit [17−19], the colour of the skin was chosen as a parameter for the evaluation of the ripeness level.

2.2. Near infrared spectrometers and spectral acquisition

Near infrared spectral acquisition was accomplished with two different NIR devices:

- a MicroNIR 1700, working in the range of 950−1650 nm (10,500−6000 cm^{-1}), an ultra-compact and low-cost device distributed by Viavi Solution – Milpitas, CA, United States;
- a Perkin Elmer Frontier FT-Spectrometer, working in the range of 12,000−4000 cm^{-1} (830−2500 nm), equipped with a Reflectance Accessory (NIRA).

The MicroNIR dimensions are 45 mm in diameter and 42 mm in height, weighting about 60 g, and it is equipped with a 128-pixel detector array, which records data with a nominal spectral resolution of 6.25 nm. The system is composed by two small tungsten light bulbs as the radiation source and a linear-variable filter (LVF) directly connected to a linear indium gallium arsenide (InGaAs) array detector.

In this study, the acquisition was carried out in the reflectance mode between 950 and 1650 nm; the integration time was 10 ms and each spectrum was the average of 50 scans, resulting in a measurement time of 0.50 s.

2.3. Reference analysis

Titratable acidity was determined by volumetric titration of 1 g of acerola juice, diluted in 50 mL of distilled water, with a standardised solution of NaOH 0.1 mol L^{-1}. Phenolphthalein was used as the colour indicator of the titration end point (light permanent pink, according to AOAC [20]). The results were expressed as percentage of malic acid. According to AOAC 1968 [21], the quantification of ascorbic acid was carried out by volumetric titration of 1 g of acerola juice, diluted in 100 mL of oxalic acid (0.5% v/v) water solution, with a water solution of DCPIP (2,6-dichlorophenolindophenol, 0.02% v/v) as the redox titrant and colour indicator. The results were expressed as mg of ascorbic acid per 100 g of acerola juice. All the reagents used in the titration procedures were of analytical grade and were purchased from Sigma Aldrich (Steinheim, Germany).

2.4. Data processing

The spectral data were modelled using two different regression algorithms, PLS and SVM. The first algorithm was used because of its simplicity, good performance and easy accessibility, while SVM is intended to model non-linear relations with high dimensional input vector.

First, the spectra of both devices were pre-processed applying the SNV (standard normal variate) algorithm for the baseline correction; 11 point of smoothing (2 polynomial order) were applied to reduce noise. The data were divided in two sets by way of the Kennard and Stone duplex algorithm [22,23] the first one used for the calibration (77 fruits) and the second one as a test set (40 fruits).

PLS regression was calculated with the SIMPLS algorithm [24] and a leave-one-out cross validation. SVM algorithm was applied, after column mean centering of the spectra, choosing the Ɛ-SVR (epsilon-support vector regression) algorithm [25], with the following parameters: radial basis function as kernel type, ɣ=0.01 and Ɛ=0.1. A PCA compression with 10 components was chosen to maximise the model stability and reduce the possibility to over-fit the data.

The accuracies of the models were compared using the RMSE (root mean square error) in calibration and in validation, as well as bias and R^2 (coefficient of determination). These indices allow evaluating the ability of the model in predicting new samples, intended as the reliability of the quality parameters estimation.

The comparison between the estimation abilities of the two instruments (Micro-NIR and FT-NIR) in prediction was performed thanks to

a joint test on slopes and intercepts of linear regression models (Micro-NIR vs. FT-NIR). The null hypothesis (H_0) is that the slope is not significantly different from 1 and that the intercept is not significantly different from 0, meaning that there are no significant differences between the two methods at a 95% confidence level. Since both of the analytical methods are affected by a non-negligible experimental error, linear regression models cannot be built by means of the ordinary least squares algorithm, the application of which requires the x variable to be exempt from error. For this reason, method comparison was afforded by Passing–Bablok regression [26], a suitable non-parametric method that does not impose a priori that one of the methods is chosen as the reference. This approach was used to highlight statistically significant differences not only between the two instruments but also between the instrumental estimation and the chemical determinations. The test was conducted on the sample test set for both the quality parameters considered in this study and for predictions made by both PLS and SVM algorithms.

All the data processing was carried out on Matlab® environment, version 2015a (The MathWorks, Inc) and applying algorithms from the PLS Toolbox, version 8.1.1 (Eigenvector Research, Inc).

3. Results and discussion

3.1. Chemical data

The determinations of ascorbic acid and titratable acidity in 117 acerola fruits are presented in Fig. 1; the mean value with its uncertainty (standard deviation – SD) for ascorbic acid content was 2844 ± 449 mg 100 g^{-1}, while titratable acidity was 2.29 ± 0.27 g of malic acid 100 g^{-1}. To better understand the variability of these data, a repeatability test (five replicates) on a standard solution with concentration similar to the samples analysed was carried out. For the two chemical analyses, the test gave the following results: 1526 ± 27 mg of ascorbic acid 100 g^{-1} and $1.93 \pm 0.04\%$ of malic acid, respectively. Considering these results, it can be deduced that the variability of the reference analyses is ascribable to the differences among fruits.

3.2. Spectral data

Regarding the NIR spectra presented in Fig. 2, it is possible to highlight that they are dominated by the water absorption bands due to the O-H bonds [27] at approximately 970, 1450, 1950 and 2250 nm [28]. Absorption bands typically found in fruits and ascribable to starch and sugars are the second (920 nm) and the third (720 nm) overtones of O-H stretching, and the third (910 nm) and the fourth (750 nm) overtones of C-H stretching [29,30]. Monomeric organic acids normally show bands related to the O-H group and, in particular, the first three overtones at about 1445, 1000 and 800 nm, respectively [31]. All these absorption bands are very close to the stronger water absorption
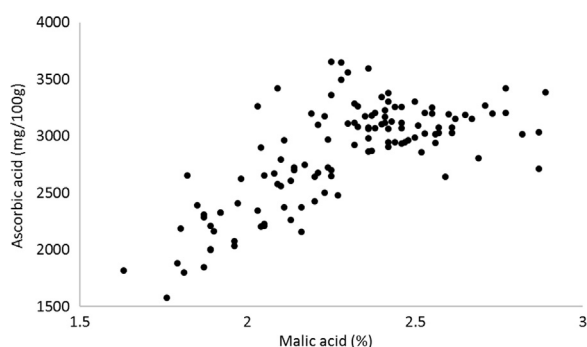

Fig. 1. Determinations of ascorbic acid and titratable acidy contents in 'Junko' acerola fruit at different ripening stages, n=117 samples. Results are presented in a random order on the x-axis; the dotted line indicates the standard deviation of the chemical data.

regions, hindering their visualisation [32]. Only in the spectral range of the benchtop FT-NIR it is possible to highlight the characteristic band of organic acids due to O-H stretching combined with the C-O stretching, around 1890 nm.

The above considerations on the chemical results laid the foundations for the correct interpretation of the regression models implemented with the NIR data. The model parameters, calculated on pre-processed spectra, are presented for both NIR spectrometers in Tables 1, 2, where it is possible to compare the two algorithms applied on both the ascorbic acid and titratable acidity predictions.

Concerning the PLS regression on FT-NIR (Table 1), data gives similar results for both titratable acidity and ascorbic acid content. The coefficient of determination and the root mean square error were similar and satisfactory in calibration for both of the parameters. It is interesting to underline that, in prediction, the accuracy of the model for the titratable acidity ($R^2=0.74$ and RMSEP=0.14%) is higher if compared with that of ascorbic acid ($R^2=0.49$ and RMSEP=342 mg 100 g^{-1}).

SVM, which fits well non-linear models, gives better results in calibration for both of the chemical parameters, with higher R^2 and comparable calibration errors, compared with the more widespread PLS outcomes. This improvement of model ability is not confirmed in prediction, with comparable results between PLS and SVM for titratable acidity and ascorbic acid ($R^2=0.69$, RMSEP=0.16% and $R^2=0.49$, RMSEP=360 mg 100 g^{-1}, respectively).

From the comparison of the two algorithms on FT-NIR data, it is possible to gather that the data are well modelled for both PLS and SVM with better results in calibration than in prediction.

Regarding MicroNIR data (Table 2), PLS modelling gives not fully satisfactory results, with R^2 lower than 0.5. Moreover, the prediction ability for titratable acidity is comparable with the calibration in term of RMSE and seem to be slightly better in term of R^2, allowing to hypothesise an over-fitting of the prediction model. The same models obtained with the SVM algorithm resulted in better calibration and prediction outcomes for both ascorbic and malic acid. For the hand-held device, the improvement due to the non-linear modelling is clear, giving reliable regression models also in prediction. This improvement could be ascribable to technical differences between the two devices, which are reflected in differences in the spectral quality that need a more complex mathematical approach to fit the data.

For all the models presented, the errors in prediction are adequate, considering the standard deviation of the reference methods and the errors of the analytical determination obtained by the repeatability test (s). In fact, the RMSEP values should be lower than the standard deviation of the chemical determination chosen as reference data; moreover, the model errors are expected to be higher than the standard deviations obtained in repeatability condition. The standard deviation is equal to 0.27% while the analytical error is equal to 0.04% for titratable acidity; for the ascorbic acid content, the standard deviation is equal to 448.6 mg 100 g^{-1} while the error associated with the repeatability test is equal to 27 mg 100 g^{-1}.

Regarding the comparison between the benchtop FT-NIR and the portable MicroNIR, the models developed for both titratable acidity and ascorbic acid seem to give comparable results using the traditional FT-NIR. In particular, comparing the best models for both the instruments, the relative RMSEP values (RMSEPx100/mean) for the MicroNIR data modelled with SVM algorithm are 7% and 11% for titratable acidity and ascorbic acidy content, respectively. These results are interesting if compared with the NIR data modelled by PLS regression with a relative RMSEP equal to 6% for titratable acidity and 12% for ascorbic acid.

To verify if the differences among the instruments are statistically significant, Passing-Bablok regression method was performed on the test set data. Thanks to a joint test on slopes and intercepts, the models were compared in pairs analysing the differences between the two instruments and with the reference data, for both linear and non-linear
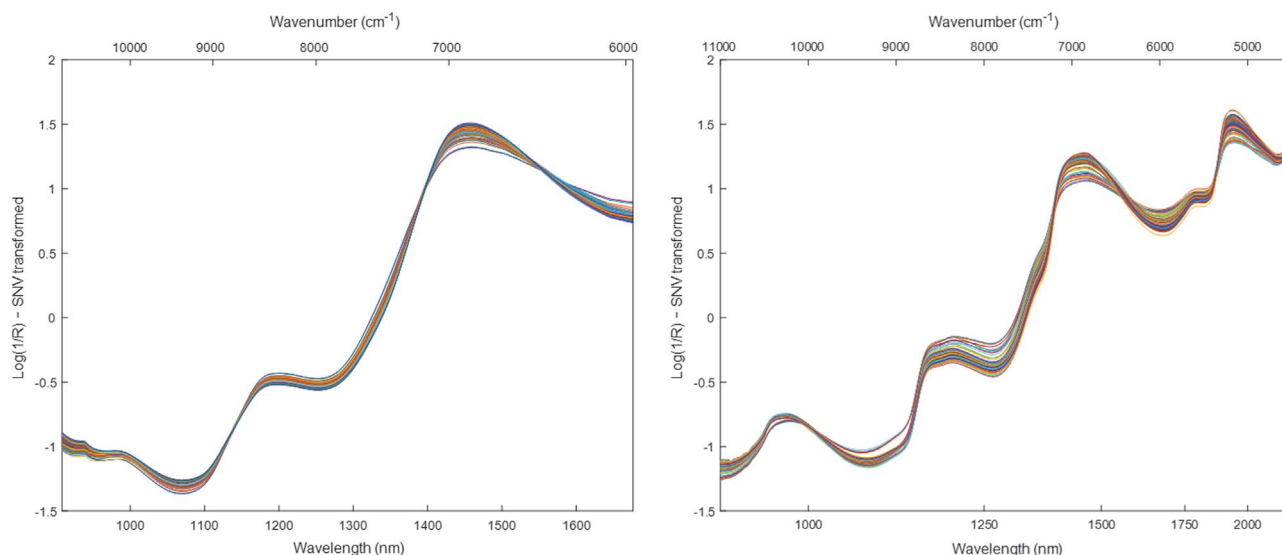
Fig. 2. Spectra of acerola samples after SNV transformation from the two devices (left: MicroNIR, right: FT-NIR).

Table 1
Calibration and prediction models for FT-NIR using two algorithms: SVM and PLS.

PLS	Number of samples		Range		Calibration			Prediction		
	Calibration/Prediction	Mean	(min–max)	S.D.%	R^2	RMSEC	Bias	Q^2	RMSEP	Bias
Titratable acidity (% malic acid)	77/40	2.3	1.6–2.9	11.8	0.63	0.17	0.00	0.74	0.14	−0.02
Ascorbic acid content (mg/100 g)	77/40	2844	1576–3653	15.8	0.65	285	0.00	0.49	342	−29.06
SVM	Number of samples		Range		Calibration			Prediction		
	Calibration/Prediction	Mean	(min–max)	S.D.%	R^2	RMSEC	bias	Q^2	RMSEP	bias
Titratable acidity (% malic acid)	77/40	2.3	1.6–2.9	11.8	0.75	0.14	0.00	0.69	0.16	−0.02
Ascorbic acid content (mg/100 g)	77/40	2844	1576–3653	15.8	0.91	145	4.75	0.49	360	−46.68

Table 2
Calibration and prediction models for MicroNIR using two algorithms: SVM and PLS.

PLS	Number of samples		Range		Calibration			Prediction		
	Calibration/Prediction	Mean	(min–max)	S.D.%	R^2	RMSEC	Bias	Q^2	RMSEP	Bias
Titratable acidity (% malic acid)	77/40	2.3	1.6–2.9	11.8	0.40	0.18	0.00	0.66	0.18	0.00
Ascorbic acid content (mg/100 g)	77/40	2844	1576–3653	15.8	0.42	311	0.00	0.40	404	−24.53
SVM	Number of samples		Range		Calibration			Prediction		
	Calibration/Prediction	Mean	(min–max)	S.D.%	R^2	RMSEC	bias	Q^2	RMSEP	bias
Titratable acidity (% malic acid)	77/40	2.3	1.6–2.9	11.8	0.78	0.11	0.00	0.72	0.16	0.02
Ascorbic acid content (mg/100 g)	77/40	2844	1576–3653	15.8	0.71	221	5.19	0.65	318	−1.64

Table 3
Passing-Bablok regression results for both of the algorithms. A joint test on slope and intercept values of the regression lines, at a 95% confidence level, was performed.

PLS	FT-NIR vs MicroNIR	Ascorbic acid:	H_0 accepted
		Titratable acidity:	H_0 rejected
	Reference vs FT-NIR	Ascorbic acid:	H_0 accepted
		Titratable acidity:	H_0 accepted
	Reference vs MicroNIR	Ascorbic acid:	H_0 rejected
		Titratable acidity:	H_0 rejected
SVM	FT-NIR vs MicroNIR	Ascorbic acid:	H_0 accepted
		Titratable acidity:	H_0 accepted
	Reference vs FT-NIR	Ascorbic acid:	H_0 rejected
		Titratable acidity:	H_0 accepted
	Reference vs MicroNIR	Ascorbic acid:	H_0 rejected
		Titratable acidity:	H_0 accepted

the Passing-Bablok comparison are presented in Table 3.

The linear modelling gives better results in comparing the FT-NIR data and the chemical determinations; instead, less satisfactory results are obtained when the MicroNIR data are fitted with a linear PLS model. SVM non-linear modelling confirms to be suitable for MicroNIR data, in particular for the prediction of titratable acidity. Regarding the comparison between the two devices, the prediction ability of the two instruments is statistically comparable when a non-linear modelling is applied.

Generally, using at least one of the regression algorithms, the models demonstrated to be reliable in predicting ascorbic acid and malic acid contents in acerola fruit with no statistically differences highlighted with the Passing-Bablok test, suggesting comparable and accurate results obtained for both instruments.

modelling. Remembering that the null hypothesis (H_0) is that the slope is not significantly different from 1 and that the intercept is not significantly different from 0, at a 95% confidence level, the results of

4. Conclusions

NIR spectroscopy, combined with regression models, is confirmed to be an interesting tool for non-destructive evaluation of quality

parameters of vegetables and fruit. The SVM regression algorithm gives better results for modelling quality parameters in acerola, laying the basis for the application of the non-linear regression approach in other postharvest applications. MicroNIR demonstrated to be a robust portable device for the application of spectroscopy in field, even though the reduced number of wavelengths. In conclusion, the combination of simple devices with non-linear modelling may offer a very interesting and reliable tool for monitoring fruit quality directly in the field. This approach, if applied through the supply chain, could improve, in a sustainable way, the quality of fruit that reaches consumers tables in everyday life.

Acknowledgements

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