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Time-resolved Reflectance Spectroscopy as a Management Tool for Late-maturing Nectarine Supply Chain

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The absorption coefficient of the fruit flesh at 670 nm (μ_a), measured at harvest by time-resolved reflectance spectroscopy (TRS) is a good maturity index for early nectarine cultivars. A kinetic model has been developed linking the μ_a, expressed as the biological shift factor to softening during ripening. This allows shelf life prediction for individual fruit from the value of μ_a at harvest and the fruit categorization into predicted softening and usability classes. In this work, the predictive capacity of a kinetic model developed using μ_a data at harvest and firmness data within 1-2 d after harvest for a late maturing nectarine cultivar ('Morsiani 90') was tested for prediction and classification ability. Compared to early maturing cultivars, μ_a at harvest had low values and low variability, indicating advanced maturity, whereas firmness was similar. Hence, fruit were categorized into six usability classes (from 'transportable-hard' to 'ready-to-eat-very soft') basing on μ_a limits established analyzing firmness data in shelf life after harvest. The model was tested by comparing the predicted firmness and class of usability to the actual ones measured during ripening and its performance compared to that of models based on data during the whole shelf life at 20 °C after harvest and after storage at 0 °C and 4 °C. The model showed a classification ability very close to that of models based on data of the whole shelf life, and was able to correctly segregate the 'ready-to-eat-transportable', 'transportable' and 'transportable-hard' classes for ripening at harvest and after storage at 0 °C, and the 'ready-to-eat-very soft' and 'ready-to-eat-soft' classes for ripening after storage at 4 °C, with lower performance of models for fruit after storage at 4 °C respect to those of the other two ripening.

1. Introduction

It is wellknown that peach and nectarine fruit quality is strictly dependent on its maturity and that there is a large variation in maturity, even within the same harvest date, which could have an impact during subsequent marketing and consumption. In fact, if harvested too early, they lack flavor, and sometimes, ripening capacity whereas when harvested ripe, they have excellent eating quality but may be subjected to mechanical injury and decay during handling (Crisosto and Valero, 2008). Time-resolved reflectance spectroscopy (TRS) is a non-destructive technique based on the injection of a short pulse of monochromatic light in the fruit flesh down to a 1–2 cm in depth from fruit surface and on the analysis of time distribution of re-emitted photons, allowing the differentiation between the absorption coefficient (μ_a), related to chemical composition, and the reduced scattering coefficient (μ'_s), related to physical structure (Cubeddu et al., 2001).
Previous research has shown that maturity of fruit at harvest can be assessed non-destructively by using TRS to measure the absorption coefficient of the fruit flesh at 670 nm (μ_a), near the chlorophyll peak. In nectarines, as fruit maturation and ripening proceed, the μ_a value decreases following a logistic curve (Tijskens et al., 2006) and is synchronized with softening (Tijskens et al., 2007). Hence a kinetic model has been developed linking the μ_a, expressed as the biological shift factor (BSF), to softening during ripening, so including the variations in maturity at harvest in the firmness decay model. In this way from the value of μ_a at harvest, the

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shelf life for individual fruit can be predicted. In order to validate this methodology and to evaluate the predictive capacity of the kinetic model for an early maturing nectarine cultivar, Rizzolo et al. (2009) segregated ‘Spring Bright’ fruit according to their softening capacity (‘will never soften’, ‘dangerously hard’, ‘transportable’, ‘ready to eat-firm’, ‘ready to eat-ripe’ and ‘overripe’) on the basis of the value of μ_a at harvest. With an export trial from Italy to The Netherlands, simulating on a small scale (1000 fruit) the fruit supply chain from the packing-house to the consumer, Eccher Zerbini et al. (2009) showed that ripening classes had been correctly predicted. Applying this methodology at the time of harvest, Rizzolo et al. (2009) found for the early maturing ‘Spring Bright’ nectarines that measuring μ_a on all fruit and firmness on two samples of about 30 fruit, representative of all the μ_a range, the first as soon as possible after harvest and the second after 24 h at 20 °C, it was possible to estimate the parameters of the firmness decay model for the season and cultivar, and hence to compute the time required to reach the midpoint of the firmness decay curve of the μ_a values in each softening class. Then, these time values were used to select fruit with different stages of maturity for different marketing segments, such as distant or close-by markets.
In this work, the predictive capacity of a kinetic model developed for a late maturing nectarine cultivar (‘Morsiani 90’) by Eccher Zerbini et al. (2011) by using μ_a data at harvest and firmness data within 1-2 d after harvest was tested for prediction and classification ability compared to that of models based on data during the whole shelf-life at 20 °C after harvest and after storage at 0 °C and 4 °C.

2. Materials and Methods

2.1 Fruit and Experimental plan

In season 2009, ‘Morsiani 90’ nectarines were picked in Faenza (Italy) at the commercial harvest. The details of the experimental plan have been described by Eccher Zerbini et al. (2011) and Lurie at al. (2011). In this work, fruit assigned for shelf life at 20 °C at harvest as well as those assigned for shelf life at 20 °C after 4 weeks storage at 0 °C and 4 °C were considered. The day after harvest nectarines with defects and bruises were removed, and the resulting fruit were individually measured by TRS at 670 nm using a prototype built at Politecnico di Milano (Torricelli et al., 2008) and then ranked by decreasing μ_a value. The ranked fruit were grouped by 16, with a total of 30 groups, corresponding to 30 levels of μ_a. Each fruit from each group was randomly assigned to a different sample. In this way, 16 samples were obtained each one containing 30 fruit from the whole range of μ_a and dedicated to one time of analysis according to Table 1.

Table 1: Samples and times (h) of shelf life for firmness measurements

Shelf life	Samples	Shelf life times (h)
harvest	0-5	29, 55, 74, 101, 175, 198
after storage at 0 °C	6-10	37, 60, 80, 108, 131
after storage at 4 °C	11-15	37, 60, 80, 108, 131

Firmness (*F*) was measured by a penetrometer (Texture Analyzer TA.XtPlus, Stable Micro Systems, England, 8 mm diameter plunger, crosshead speed 3.33 mm s^{-1}) on opposite sides of each fruit after skin removal approximately on the same spot where also μ_a had been measured.

2.2 Data processing

The μ_a values of individual fruit were converted into the BSF ($\Delta t^*_{\mu a}$) according to the equation developed by Tijskens et al. (2006), and the BSF relative to firmness curve (Δt^*_F) was computed according to Tijskens et al. (2005). In nectarines, the BSF for μ_a and the BSF for firmness are linearly related (Tijskens et al., 2007) according to Eq(1), where α and β are parameters to be estimated.

$$\Delta t^*_F = \alpha(\Delta t^*_{\mu a} + \beta) \tag{1}$$

The firmness decay model has been described by Tijskens et al. (2007) and is reported in Eq(2):

$$F = \frac{F_{max} - F_{min}}{1 + e^{k_f (F_{max} - F_{min})^{t + \Delta t * F}}} + F_{min} \tag{2}$$

where F_{max} is the maximum firmness at minus infinite time, F_{min} is the minimum firmness achieved at infinite time, k_f is the softening rate constant at 20 °C, *t* is time, Δt^*_F is the BFS for firmness.
The parameters of firmness decay model for ripening at 20 °C at harvest, and after storage at 0 °C and 4 °C have been presented and discussed by Eccher Zerbini et al. (2011) and Table 2 summarizes the parameters of the models tested in this work for prediction and classification ability.

Table 2: Parameters of the non-linear regression model for firmness decay estimated in 'Morsiani 90' nectarines kept at 20 °C after harvest or after storage at 0 °C and 4 °C (Eccher Zerbini et al., 2011)

Model	Code	Samples	F_{max}	F_{min}	α	β	$k_{f20°C}$
At harvest + 24 h	H+24h	0-1	77	3.5	1.61	−2.44	0.00031
Ripening after harvest	T harvest	0-5	85	4.7	1.40	−2.27	0.000234
After storage at 0 °C	T 0C	6-10	85	4.7	1.03	−2.72	0.000227
After storage at 4 °C	T 4C	11-15	85	4.7	0.70	−2.31	0.000340

2.3 Prediction ability of firmness decay models

The predicted firmness (F_{pred}) of every fruit during shelf-life, computed from Eqs (1) and (2), was compared to the measured firmness (F_{meas}) by using linear regression analysis. The mean absolute error (MAE), the average deviation (AD), the mean square error (MSE), the root mean standard error of deviation (RMSED) and the ratio of the standard deviation of F_{meas} to RMSED (s/RMSED) were chosen to measure the performance of models and were computed according to the equations reported by Rizzolo et al. (2009).

2.4 Misclassification of models

Fruit were categorized into six μ_a classes of predicted firmness potential for handling and eating (M_i) according to the μ_a limits described and discussed in Results and Discussion, corresponding to different uses and/or softening potentials. Hence, every model was tested for misclassification according to the criteria reported by Rizzolo et al. (2009): in each class M_i based on the μ_a value at harvest, the F_{meas} value after shelf life was compared to the F_{pred} for the limits of the class according to the decay model. The classification was considered: correct when the F_{meas} value fell within the firmness interval predicted by the model for the specific M_i class and acceptable when F_{meas} values fell within the limits of the immediately adjacent M class (firmer, F_{meas} belonging to class M_{i-1}, softer, F_{meas} belonging to class M_{i+1}); prediction related to F_{meas} values which fell within the F_{pred} limits for the M_{i-2} class could be considered acceptable as fruit likely be ripen within a couple of day, whereas the F_{meas} values which fell outside the upper F_{pred} limit of the M_{i-2} class (i.e. fruit which could either ripen in a longer period or never ripen), and F_{meas} values falling outside the lower F_{pred} limit of the M_{i+1} class (fruit which would have a shorter shelf life than predicted and more prone to rot), make the prediction unacceptable. Classification results for each class and model were expressed as percentage to total number of fruit categorized in each class M_i.

3. Results and Discussion

3.1 Distribution of μ_a and classes of usability

The distribution of μ_a measured at harvest for the 'Morsiani 90' nectarines (Figure 1A) highlighted that the range of μ_a is much smaller than that found in the early maturing cultivar 'Spring Bright' (Tijskens et al., 2006). The value of μ_a of 'Morsiani 90' cultivar was low already at harvest, indicating a low chlorophyll content in the pulp. Instead, firmness values decreased from 52±12 N at harvest to values around 10±5 N at the end of shelf life similarly to what found in early maturing cultivars (Eccher Zerbini et al., 2006). Comparing the BSF for firmness computed from parameters of the models for firmness decay prediction reported in Table 2 with that of the early maturing 'Spring Bright' nectarine described by Rizzolo et al. (2009), all plotted in function of BSF for μ_a (Figure 1B), it is evident the different synchronization of μ_a decrease and firmness decay among 'Morsiani 90' and 'Spring Bright' cultivar, already at harvest, with a lower softening rate for the former cultivar respect to that of the latter. For these reasons in order to study the classification performance of 'Morsiani 90' models it was not possible to use the μ_a limits of the usability classes established for 'Spring Bright' cultivar (Rizzolo et al., 2009).

The softening trends of 'Morsiani 90' fruit during ripening after harvest at different μ_a intervals at the time of harvest were considered (Figure 2). For 'Morsiani 90', being fruit softening slower than in 'Spring Bright', the firmness values after 100 h as well as those at 198 h were considered in order to establish the usability classes. Only few fruit exhibited μ_a>0.120 cm^{-1}, and after 100 h firmness was still above 40 N; fruit having μ_a<0.064 cm^{-1} were characterized by F<20 N at t=100 h and lower than 10 N at the last time, with the μ_a<0.049 cm^{-1} ones showing F<30 N already at t=55h. Fruit with μ_a in the range 0.080-0.119 cm^{-1} after 100 h had F values in the 20-50 N range, with the μ_a<0.089 cm^{-1} ones showing some fruit with F≈20 N already after 74 h, whereas fruit with μ_a in the range 0.065-0.079 cm^{-1} at 100 h had F<30 N. Crisosto et al. (2004) reported that a firmness value of about 35 N is proper of a nectarine still firm enough to be transported home and ready to buy, while values below 13.2 N indicate fruit ripe and soft (Crisosto et al., 2006). Basing on these differences in firmness decay, the limits for the six usability classes from “transportable-hard” to “ready-to-eat-soft” were established (Table 3).

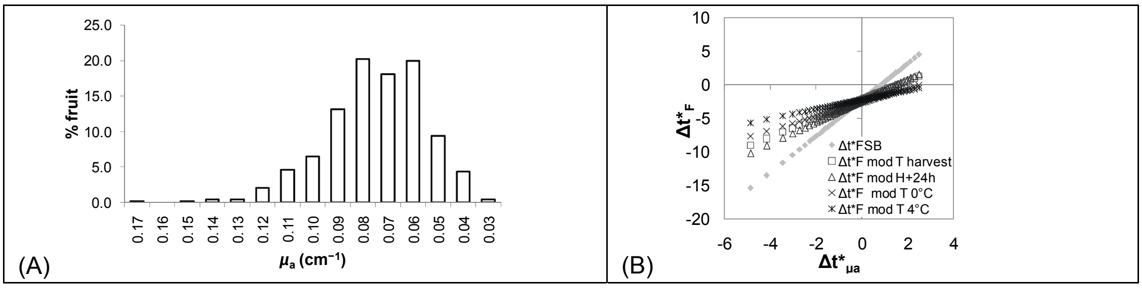

Figure 1: (A) Percentage distribution of absorption coefficient at 670 nm measured at harvest (480 fruits). (B) Plot of BSF for firmness in function of BSF for μ_a for ‘Morsiani 90’ in comparison to ‘Spring Bright’ cultivar (SB, Rizzolo et al., 2009)

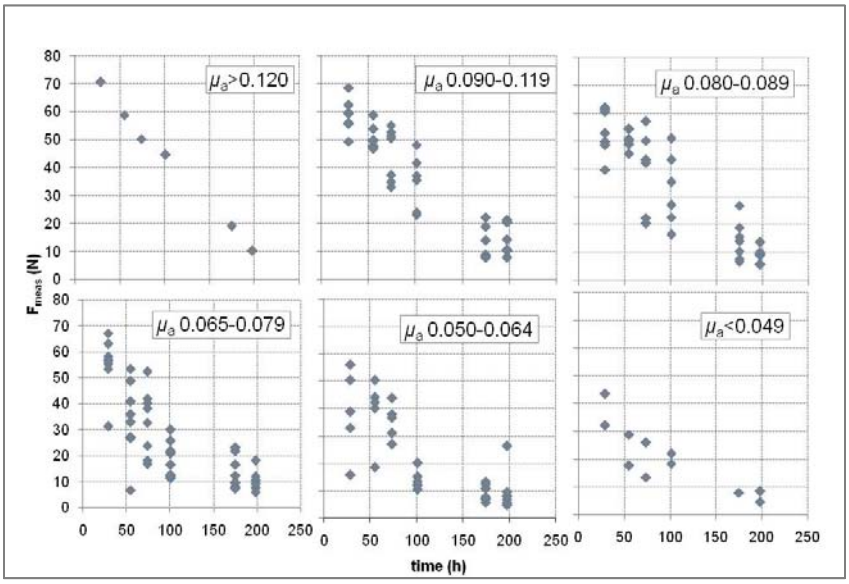

Figure 2: Fruit firmness as a function of time at 20 °C for different levels of μ_a measured at harvest

Table 3: Lower limit of μ_a for each class M_i of predicted firmness potential for handling and eating, total number of fruit and their percent distribution among classes for ‘Morsiani 90’ nectarines during shelf life at harvest, and after storage at 0 °C and 4 °C

n	M_i class	Code	Lower μ_a limit (cm^{-1})	Harvest (% N_{fruit})	0 °C storage (% N_{fruit})	4 °C storage (% N_{fruit})
1	transportable-hard	TH	0.120	6.1	4.0	2.8
2	transportable	T	0.090	18.4	20.1	20.7
3	ready-to-eat-firm-transportable	RFT	0.080	27.4	28.9	28.3
4	ready-to-eat-firm	RF	0.065	21.8	18.8	19.3
5	ready-to-eat-soft	RS	0.050	22.9	24.8	25.5
6	ready-to-eat-very soft’	ORS	<0.049	3.0	3.0	3.4
			N_{fruit}	179	149	145

3.2 Prediction ability of models

Considering the results of regression analyses (Table 4), SEE ranged from about 4 % for the T 4C model to about 7 % for the models T 0C and H+24h applied to fruit after storage at 0 °C. Comparing the results of the three ripening, models after harvest and after storage at 4 °C had R^2_{adj} ranging from about 77 % for model T harvest to about 65 % for model H+24h applied to fruit after storage at 4 °C. Moreover, MAE, AD, RMSED and s/RMSED values indicate that models T harvest and T 4C had higher performance than H+24h and also that H+24h model for ripening at harvest had higher performance than for ripening after storage. In contrast, results of linear regression for models after storage at 0 °C indicate a lower performance of both the T 0C and H+24h models respect to the other ripening. These results are in agreement with the findings on these models discussed by Eccher Zerbini et al. (2011).

Table 4: Results of linear regression models between F_{meas} and F_{pred} from μ_a at harvest for fruit ripened after harvest and after storage at 0 °C and 4 °C

Ripening		After harvest		After storage at 0 °C		After storage at 4 °C	
Model		T harvest	H+24h	T 0C	H+24h	T 4C	H+24h
Intercept	estimate	3.84	0.75	13.07	4.56	4.52	7.56
	SE (sign)	(0.901)***	$(0.956)^{ns}$	(1.391)***	(1.462)**	(0.20)***	(1.089)***
Slope	estimate	0.63	0.66	0.59	0.59	0.72	0.94
	SE (sign)	(0.026)***	(0.027)***	(0.040)***	(0.042)***	(0.038)***	(0.057)***
R^2_{adj}		77.32	77.00	58.89	57.03	71.65	65.24
SEE		6.349	6.732	7.207	7.573	4.428	6.704
MAE		4.862	5.080	5.867	5.987	3.106	4.924
AD		29.11	34.15	34.86	33.42	27.98	61.03
RMSDE		11.7571	13.0612	9.4001	12.6510	5.1689	9.3911
s/RMSDE		1.58	1.42	1.57	1.17	1.89	1.04

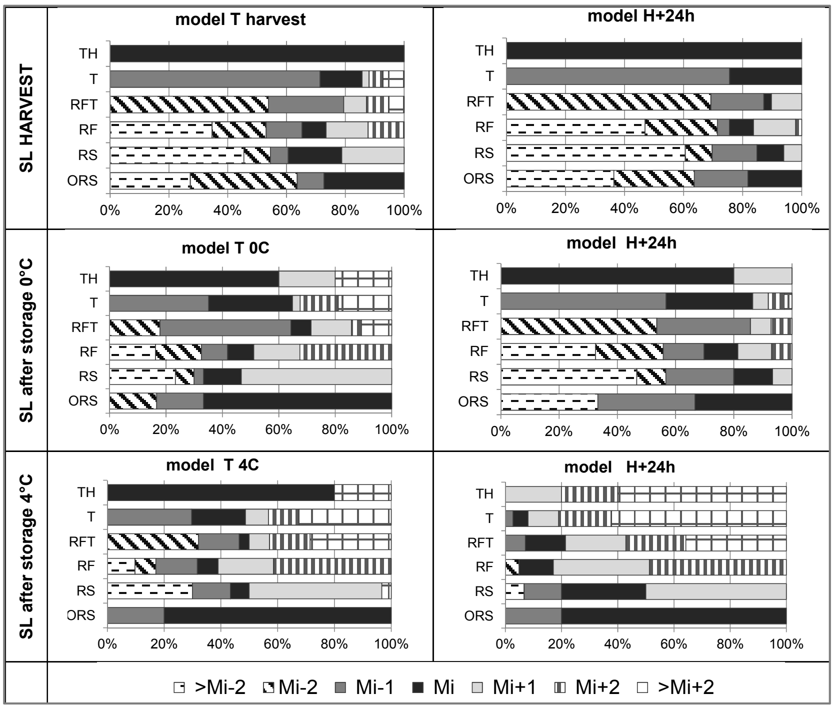

Figure 3: Comparison of classification results for ripening (SL) at harvest and after storage at 0 °C and 4 °C obtained with firmness decay models of Table 2

Figure 3 shows the results of the test for misclassification for the three ripening. Considering the classification results for ripening at harvest, model T harvest classified acceptably (i.e. in the range M_{i-2} – M_{i+1}) more than 70 % of fruit of ORS class, more than 87 % of fruit of RFT and T classes, and all the fruit of TH class, whereas model H+24h at harvest classified acceptably the totality of fruit of RFT, T and TH classes, but only about 64 % of ORS fruit. The F_{meas} values of misclassified fruit of ORS, RS and RF classes corresponded to F_{pred} values for RFT, T and TH classes, respectively. After storage at 0 °C, model T 0C correctly predicted the fruit of ORS class, and acceptably classified more than 85 % of fruit of RS, RFT and TH classes; for the misclassified fruit of RF and T classes the F_{meas} corresponded to F_{pred} for T and ORS classes, respectively. If model H+24h is applied to predict softening of fruit after storage at 0 °C, more than 90 % of fruit of RFT and T classes and the totality of fruit of TH class were acceptably predicted, whereas 33 % of ORS fruit had F_{meas} corresponding to F_{pred} for RF class, 46 % of RS fruit showed F_{meas} corresponding to F_{pred} for T class and 33 % of RF nectarines had F_{meas} corresponding to F_{pred} for TH class. The models T 4C and H+24h applied to predict softening after storage at 4 °C showed the worst performance in classifying nectarines: model T 4C correctly predicted the totality of ORS fruit, 20 % of TH fruit showed F_{meas} values corresponding to F_{pred} for T class and fruit of the other classes were misclassified in proportions ranging from about 33 % of RS class to about 50 % of RF class. If model H+24h is applied to predict softening of fruit after storage at 4 °C, only the totality of ORS fruit and more than 90 % of RS nectarines were acceptably predicted, whereas the majority of fruit of T and TH classes showed F_{meas} values corresponding to F_{pred} for RF and RS classes, respectively. The lower performance of models T 4C and H+24h for fruit after storage at 4 °C respect to those of the other two ripening could be due to the fact that in these fruit chilling injury symptoms appeared (Lurie et al., 2011), and that the same changes in cell wall metabolism which induce the appearance of chilling injury also affect firmness and softening rate (Eccher Zerbini et al., 2011), so having a negative impact on the prediction ability of the kinetic model.

4. Conclusions

Results suggest that the methodology based on the μ_a measured by TRS at harvest and its conversion into BSF might be used as a management tool in the supply chain of late-maturing nectarines. The model H+24h showed a classification ability very close to that of T models based on data of the whole shelf life, and was able to correctly segregate the RFT, T and TH classes for ripening at harvest and after storage at 0 °C, and the ORS and RS classes for ripening after storage at 4 °C.

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