

## PECTIC COMPOSITION, OPTICAL PROPERTIES MEASURED BY TIME-RESOLVED REFLECTANCE SPECTROSCOPY AND QUALITY IN 'JONAGORED' APPLES

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### A B S T R A C T

'Jonagored' apples, picked on 30 August and 13 September 2002, were measured by TRS at 630 nm for absorption coefficient ( $\mu_a$ '630) and at 750 nm for transport scattering coefficient ( $\mu_s$ '750) and stored for six months in NA or CA in order to study the relationships among TRS optical properties, quality and pectic composition. Apples were analysed for fruit mass, skin color, firmness, soluble solids (SS), titratable acidity, relative internal space volume (RISV) and pectic substances. All data were processed by Principal Component Analysis. Both at harvest and after storage,  $\mu_a$ '630 was associated with colour characteristics, while  $\mu_s$ '750 was associated with RISV and firmness at harvest and with firmness and SS at the end of storage. Furthermore,  $\mu_s$ '750 was inversely related to oxalate fraction and residual insoluble pectin (RI) at harvest and to protopectin index, RI and firmness after storage. Our results confirmed that, using the absorption coefficient, fruits with different maturity degrees could be separated, and suggested that the transport scattering coefficient is more related to fruit structure and texture, especially to pectin composition.

**Key words:** *Malus domestica* Borkh., non-destructive technique, absorption, scattering, structure

## INTRODUCTION

Time-resolved reflectance spectroscopy (TRS) is a new non-destructive technique which allows the complete optical characterization of highly diffusive media, such as fruits (Cubeddu et al., 2001a). TRS employs a pulsed laser source to estimate at the same time and independently the optical properties, absorption coefficient ( $\mu_a$ ) and transport scattering coefficient ( $\mu_s'$ ), at a depth of 1-2 cm in the fruit flesh. These optical parameters give distinct information about tissue.  $\mu_a$  is related to chemical constituents, including pigments, water and sugars.  $\mu_s'$  mainly reflects discrepancies in refractive index between liquids and membranes and is thus more related to fruit structure. Until now, our studies mainly concerned the absorption coefficient. Little is known about the transport scattering coefficient and its relations with fruit quality and structure. The absorption coefficient at 670 nm ( $\mu_{a670}$ ), related to chlorophyll content, has been used in nectarines to select fruits of different quality in regard to sugar and acid compositions, to sort fruits according to maturity, and to model softening rate during shelf life (Jacob et al., 2006, Eccher Zerbini et al., 2005; 2006). In 'Jonagored' apples, the absorption coefficient at 630 nm ( $\mu_{a630}$ ) made possible the characterization of fruits coming from different harvests, as well as the selection of fruit of different maturity and quality within the same batch (Vanoli et al., 2005). In 'Gala' apples scattering coefficient at 672 nm was related to picking date (Cubeddu et al., 2001b). Scattering variables between 672 and 950 nm were clearly related to firmness variables in peaches and apples, and with acidity in peach fruits (Valero et al., 2004).

The amount and the nature of pectin play an important role in the texture of fruit and vegetables (Van Buren, 1991). This work aimed at studying the absorption coefficient  $\mu_a$  and the scattering coefficient  $\mu_s'$  in relation to apple quality characteristics and to pectic composition.

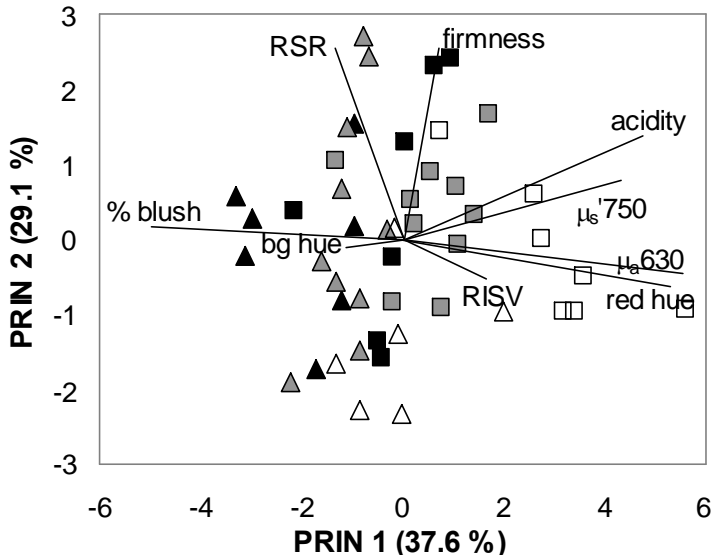
## MATERIAL AND METHODS

'Jonagored' apples were picked on August 30 (H1) and September 13 2002 (H2) in Laimburg (Bolzano, Italy). One hundred and fifty fruits per picking date were weighed, measured on two sides by TRS at 630 nm for absorption ( $\mu_{a630}$ ) and at 750 nm for scattering ( $\mu_{s'750}$ ). The apples were ranked by decreasing  $\mu_{a630}$  from less (high  $\mu_{a630}$ ) to more mature (low  $\mu_{a630}$ ). The 150 ranked fruits from each picking date were divided into three groups of 50 fruits, with high, medium and low  $\mu_{a630}$  values corresponding to three maturity classes: less, medium and more mature. Afterwards, fruits were analysed at harvest and at the end of six months of storage at 1°C in normal

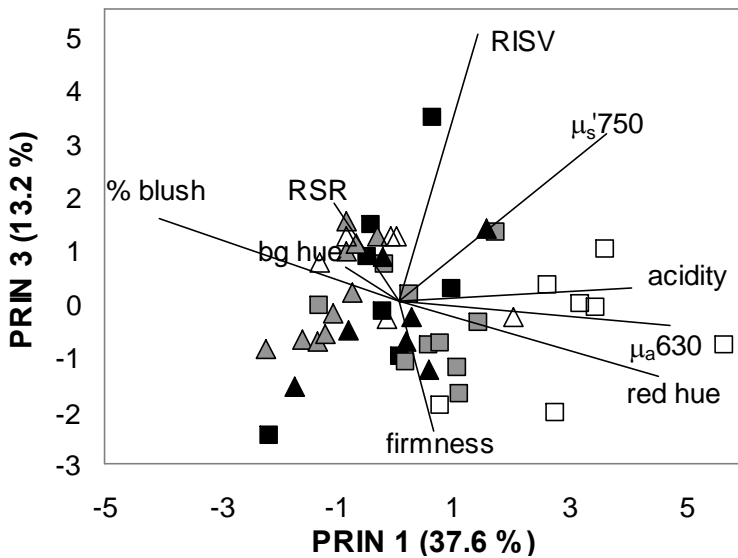
(NA) or controlled atmosphere (CA – 1% O<sub>2</sub>, 2% CO<sub>2</sub>). At harvest, apples were analyzed for skin color (Minolta Chromameter) on the green (background color) and red sides, flesh firmness (11 mm diameter plunger mounted on an Instron UTM, crosshead speed 200 mm/min), soluble solids (SS), titratable acidity and relative intercellular space volume (RISV, Baumann and Henze, 1983). These analyses were repeated at the end of storage, except for RISV. In addition, pectic substances were analyzed at harvest and after storage in the more and less mature fruits, choosing three fruits within the same maturity class, according to firmness: the highest, the lowest and the medium values. Pectins were extracted from alcohol-insoluble substances and fractionated in water soluble pectins (WS), oxalate soluble pectins (OS) and residual insoluble pectins (RI) (Forni et al., 1986). Each fraction was analyzed for galacturonic acid content by HPLC after enzymatic depolymerization of pectic chains (Forni et al., 1994). The protopectin index (PI) was computed according to:  $PI = RI/(WS + OS)$  (Forni et al., 1986). All data were processed by analysis of variance and Principal Component Analysis (PCA) separately for time of analysis and for quality and pectic characteristics (SAS/STAT, SAS Institute Inc., Cary, NC, 1999).

## RESULTS AND DISCUSSION

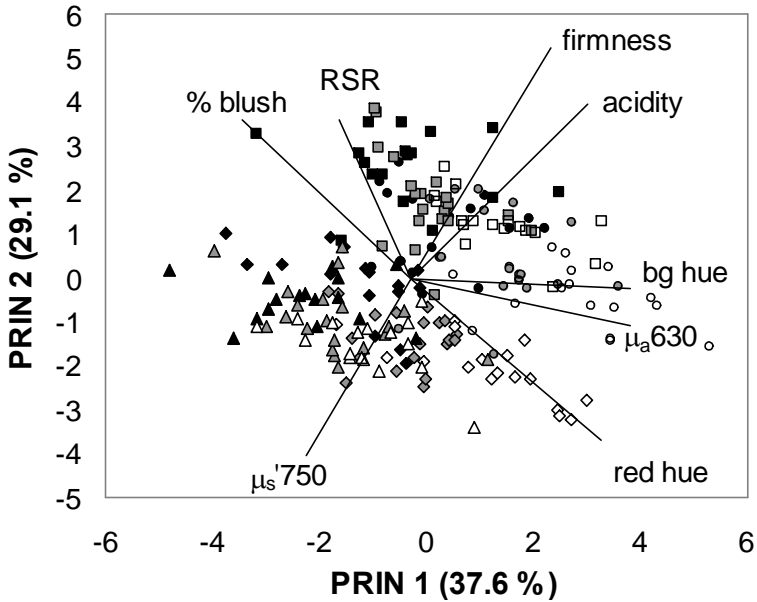
PCA on the optical properties and the quality characteristics of fruit of the three maturity classes allowed selecting four Principal Components at harvest and three Principal Components after storage, which explained 80.5% and 79.8% of the total variability, respectively. At harvest, in the first Principal Component (PRIN 1),  $\mu_a630$  was positively correlated with hue of the red side, acidity and  $\mu_s750$ , and negatively correlated with the percentage of blush (Fig. 1). PRIN 1 scores were higher in H1 apples (Fig. 1). Vanoli et al. (2005) have already found in a previous research that apples which had been picked earlier had higher  $\mu_a630$  values, and that less mature apples had lower percent of blush and greener skin than more mature fruits both at harvest and after storage. At harvest, in PRIN 2 (Fig. 1) SS and firmness were negatively correlated with to RISV, red hue and  $\mu_a630$ , while in PRIN 3 (Fig. 2),  $\mu_s750$  was positively correlated with RISV and negatively correlated with firmness. Therefore, RISV increases with the increase of  $\mu_s750$  values, although the correlation coefficient was low (0.39). PRIN 4, which explained 11.2 % of the total variability, was mainly linked to background hue. At the end of storage, in PRIN 1, the percentage of blush was negatively correlated with  $\mu_a630$ , acidity and skin color (Fig. 3);  $\mu_s750$  was negatively correlated with firmness in PRIN 2 and positively correlated with SS in PRIN 3 (Fig. 3 and 4). The relationship between  $\mu_s750$  and SS could be due to local variations in refractive index which deflect the photons (Cubeddu et al., 2001a).



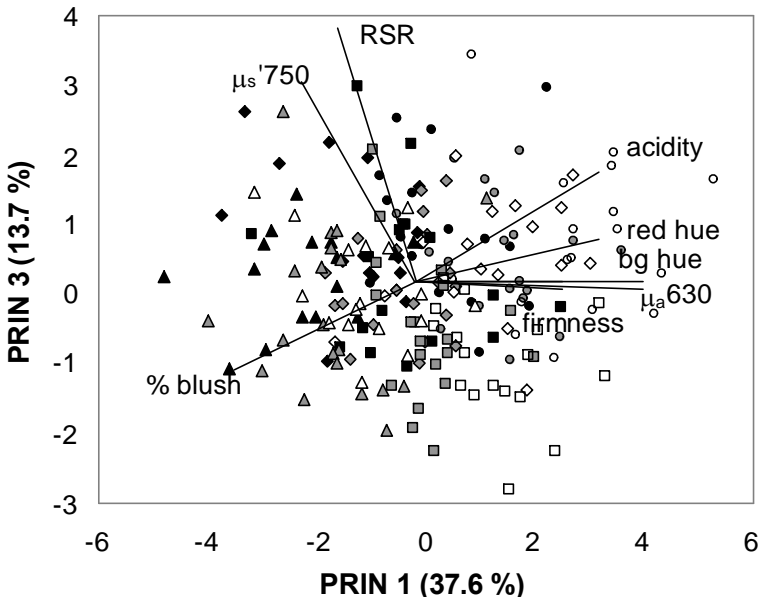
**Figure 1.** Quality characteristics of ‘Jonagored’ apples at harvest: biplot of PRIN 1 vs PRIN 2. Captions: harvests: H1 = square, H2 = triangle; maturity classes: more mature = black, medium mature = gray, less mature = white



**Figure 2.** Quality characteristics of ‘Jonagored’ apples at harvest: biplot of PRIN 1 vs PRIN 3. Captions of symbols, see Figure 1

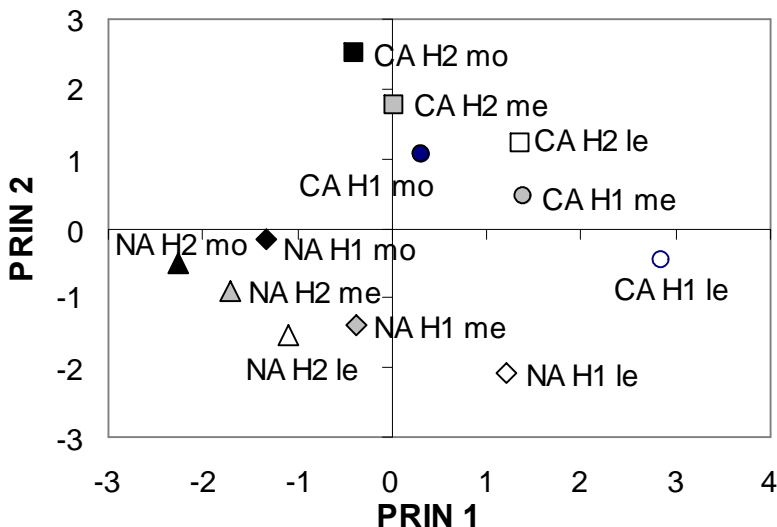


**Figure 3.** Quality characteristics of ‘Jonagored’ apples after storage: biplot of PRIN 1 vs PRIN 2. Captions: harvest and storage atmosphere: H1-CA = circle, H1-NA: diamond, H2-CA = square, H2-NA = triangle; maturity classes: more mature = black, medium mature = gray, less mature = white



**Figure 4.** Quality characteristics of ‘Jonagored’ apples after storage: biplot of PRIN 1 vs PRIN 3. Captions of symbols, see figure 3

The inverse relationship between  $\mu_s750$  and firmness could be due to structural changes in the cell wall during ripening and storage. The average scores reported in the score plot of PRIN 1 vs PRIN 2 (Fig. 5) showed that CA stored apples (firmness = 57 N) were separated from the NA ones (firmness = 34 N) along both PRIN 1 and PRIN 2, except for less mature fruit of H1.



**Figure 5.** Quality characteristics of ‘Jonagored’ apples after storage: score plot of PRIN 1 vs PRIN 2. Only average scores are shown. Maturity classes captions: le = less mature, me = medium mature, mo = more mature

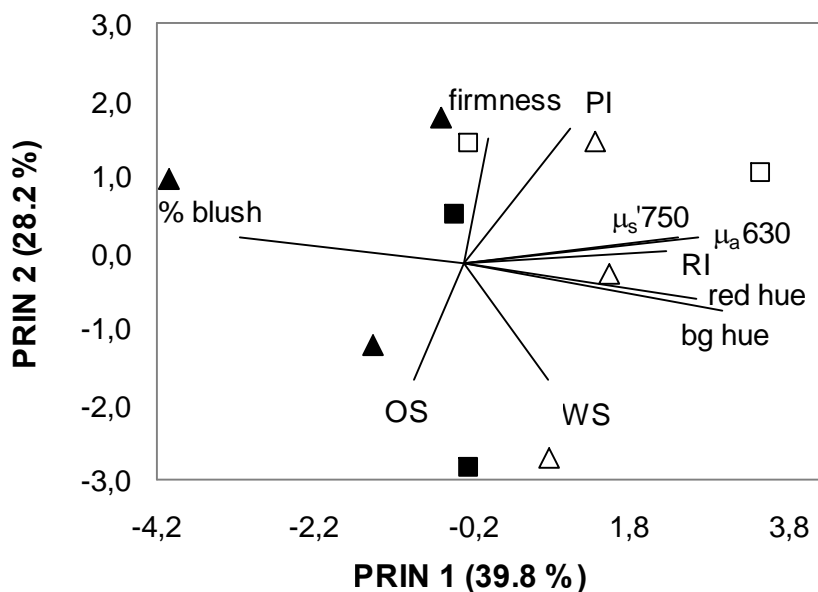
Table 1. Galacturonic acid content (g/100 g f.w.) in pectic fractions and protopectin index (PI) in ‘Jonagored’ apples after storage in relation to harvest date, maturity classes and storage atmosphere (WS = water soluble pectins, OS = oxalate soluble pectins, RI = residual insoluble pectins)

Pectic Fraction	Harvest date			Maturity class by $\mu_a630$			Storage atmosphere		
	H1	H2	P value	less	more	P value	CA	NA	P value
WS	0.077	0.072	ns	0.066	0.083	***	0.051	0.097	***
OS	0.026	0.034	**	0.033	0.027	*	0.024	0.036	***
RI	0.255	0.272	ns	0.264	0.262	ns	0.296	0.226	***
PI	2.756	3.316	***	3.463	2.661	***	4.118	1.771	***

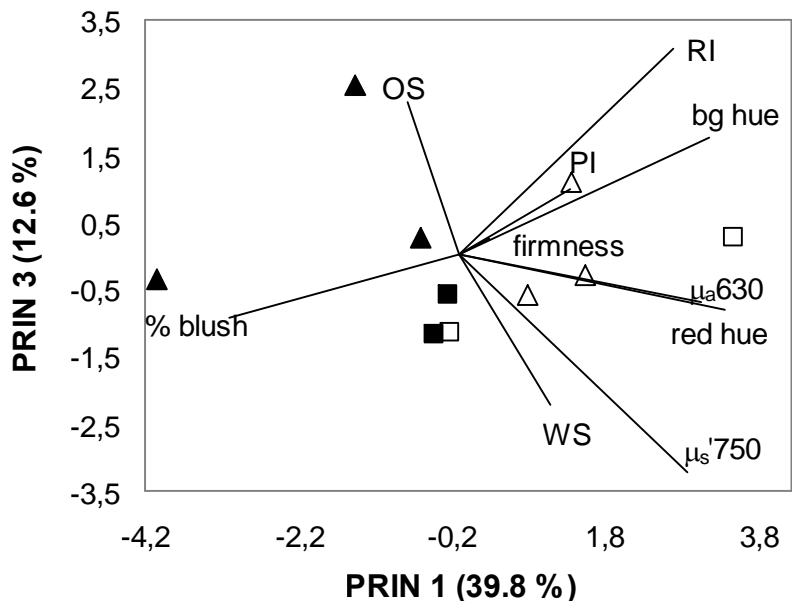
P-value of F ratio: ns = not significantly different, \*P<0.05, \*\*P<0.01, \*\*\*P<0.001

Considering pectic composition, at harvest there was no effect of picking date. Less mature fruits had higher values of PI and RI than more mature ones (less mature: PI = 9.6 and RI = 1.5 g/100 g f.w.; more mature: PI = 7.4 and RI

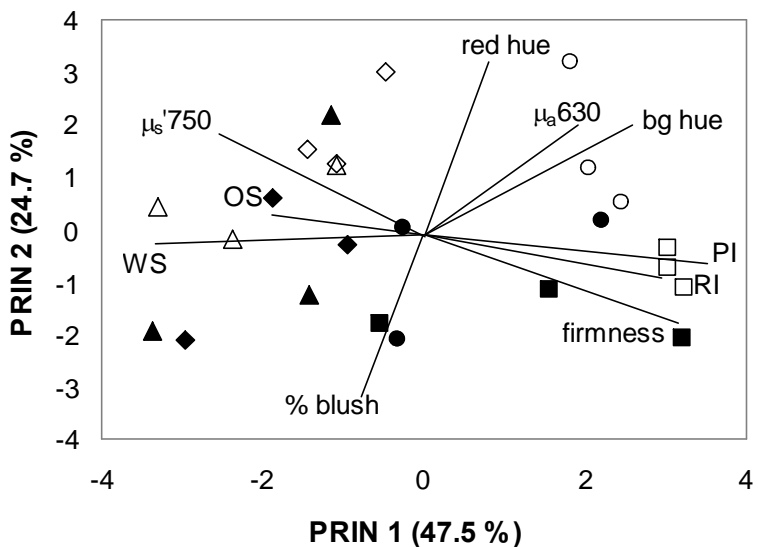
= 1.3 g/100 g f.w.). After storage (Tab. 1), H2 apples had more OS pectins and higher PI than H1 fruit; less mature apples had less WS, more OS and higher PI than more mature ones and CA stored fruit had less WS and OS, more RI and higher PI than NA ones. By using PCA analysis on pectic composition, optical properties, color parameters and firmness of less and more mature fruit, three Principal Components at harvest and two Principal Components after storage were selected, explaining 81.5% and 72.1% of the total variability, respectively. At harvest, in PRIN 1 (Fig. 6),  $\mu_a630$  was positively correlated with background color and red hue and negatively correlated with the percentage of blush. In PRIN 2 (Fig. 6), firmness and PI were negatively correlated with OS and WS pectins. In PRIN 3 (Fig. 7),  $\mu_s750$  and WS pectins were negatively correlated with OS and RI. After storage, in PRIN 1 (Fig. 8), there were inverse relationships between  $\mu_s750$  and RI, PI, and firmness. In PRIN 2, the percentage of blush was negatively correlated with  $\mu_a630$  and skin color (Fig. 8). The scores reported in the bi-plot of PRIN 1 vs PRIN 2 showed that storage atmospheres were separated along PRIN 1, while the maturity classes along PRIN 2 (Fig. 8).



**Figure 6.** Pectins of 'Jonagored' apples at harvest: biplot of PRIN 1 vs PRIN 2. Captions: harvests: H1 = square, H2 = triangle; maturity classes: more mature = black, less mature = white



**Figure 7.** Pectins of ‘Jonagored’ apples at harvest: biplot of PRIN 1 vs PRIN 3. Captions of symbols, see Figure 6



**Figure 8.** Pectins of ‘Jonagored’ apples after storage: biplot of PRIN 1 vs PRIN 2. Captions: harvest and storage atmosphere: H1-CA = circle, H1-NA: diamond, H2-CA = square, H2-NA = triangle; maturity classes: more mature = black, less mature = white



Our data showed that both at harvest and after storage firmness decreased with increasing WS pectins and with decreasing PI, as found by Van Buren et al. (1991). In addition, our results stressed that  $\mu_s^{750}$  was directly related to WS pectins and inversely related to RI pectins, both at harvest and after storage, so we can hypothesize that, in apples, WS pectins increase and RI pectins decrease with increasing of  $\mu_s^{750}$ .

This work confirmed that, using the absorption coefficient, fruits with different maturity degrees could be separated, and suggested that the transport scattering coefficient is more related to the fruit structure and texture, especially to pectin composition.

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## SKŁAD PEKTYN, WŁAŚCIWOŚCI OPTYCZNE MIERZONE ZA POMOCĄ SPEKTROSKOPII FALI ODBITEJ W FUNKCJI CZASU I JAKOŚĆ JABŁEK 'JONAGORED'

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### S T R E S Z C Z E N I E

Dla jabłek 'Jonagored' zebranych 30 sierpnia i 13 września 2002, zostały zmierzone z użyciem spektroskopii fali odbitej mierzonej w funkcji czasu (TRS) absorpcja przy 630 nm ( $\mu_a$ '630) i rozpraszanie przy 750 nm ( $\mu_s$ '750). Następnie owoce przechowywano przez sześć miesięcy w normalnej i kontrolowanej atmosferze w celu sprawdzenia zależności pomiędzy optycznymi właściwościami (mierzonymi z użyciem TRS), jakością i składem pektyn. Jabłka analizowano pod względem masy owoców, koloru skórki, jędrności, związków rozpuszczalnych (SS), kwasowości miareczkowej (TA), względnej objętości przestworów międzykomórkowych (RISV) i związków pektynowych. Wszystkie wyniki zostały przetworzone z wykorzystaniem analizy składowych głównych. Zarówno podczas zbioru, jak i po przechowywaniu  $\mu_a$ '630 było związane z parametrami koloru, podczas gdy  $\mu_s$ '750 było związane z RISV i jędrnością podczas zbioru oraz z jędrnością i SS pod koniec okresu przechowywania. Ponadto,  $\mu_s$ '750 było odwrotnie proporcjonalne do frakcji szczawianów i pozostałych pektyn nierozpuszczalnych (RI) podczas zbioru oraz do indeksu protopektyn, RI i jędrności po przechowywaniu. Nasze rezultaty potwierdzają, że zastosowanie współczynnika absorpcji umożliwia rozdzielenie owoców o różnym stopniu dojrzałości i sugerują, że współczynnik rozpraszania jest związany ze strukturą i teksturą, zwłaszcza ze składem pektyn.

**Słowa kluczowe:** *Malus domestica* Borkh., metody niedestrukcyjne, absorpcja, rozproszenie, struktura