Quantification of Physico-chemical Changes during Apricot Ripening through Non-destructive Methods

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In this paper spectrometry in reflectance was utilized to determine parameter of apricot fruits color during different stages of ripening. Texture analysis with an acoustic impulse response technique and ethylene quantification by chromatography were carrying out. Also we discussed relationship between parameter of color, texture, ethylene concentration and other quality parameters to establish feasibility of methods developed to characterize the final quality of fruits. Fruits of two Romanian apricot varieties (Dacia and Nicusor) harvested at different ripening stages were used in this study. Among chromatic parmeters CIELAB, a and h° values are indicators to distinguish of different maturity stage of apricot fruit and for prediction of their pigments content. Acoustic impulse response gave a realiable indication of the change in texture properties of apricot fruit during ripening. The physiological criteria could be used as markers for monitoring of fruit ripening but the technique is difficult and can not be used outside the laboratory.*

Key words: acoustic firmness index, ethylene concentration, color, carotenoids

Apricot fruit quality is a multicomponent concept, defined by physical, biochemical and physiological attributes such as colour, texture, sugars, organic acids, pigments, phenolic compounds, volatiles, ethylene concentration and respiration rate [1-6]. Most instrumental techniques currently used for measuring these parameters are distructive, expensive, and involve a considerable amount of manual work and time consuming. For these reasons, there is a demand for new and rapid analytical methods for assessing fruit quality attributes.

Recently, spectrometry in reflectance [7-12] and acoustic impulse response [13, 14] had become accepted methods for determination of fruit components since they achieve high analysis speed and do not require sample preparation.

A characteristic of apricot fruit ripening is very short maturation phase together with a fast post harvest evolution. The physiological maturity of apricot fruit at harvest greatly influences the final fruit quality [6]. Over mature fruits are likely to become soft and mealy and have insipid flavor soon after harvest [7]. Ethylene is responsabile for fruit maturation and quality and and its well known role in controlling fruit respiration, flesh softening and color changes[18, 20].To quantitative determination of ethylene were used cromatographic [26] or optic methods [27].

The carotenoids of ripe apricots have been poorly studied [10, 12]; changes in the individual and total carotenoids pigments content during apricot ripening and storage[12, 28] have also received little attention. Determination of the total and individual carotenoids was made by different analytic methods spectrometric and chromatographic [16]. The aim of this study was to quantification apricot quality traits such as color, texture by reflectance spectrometry and acoustic impulse response as a nondestructive methods, and establish relationship of these parameters with pigments, soluble solids, titratable acidity, dry matter and ethylene.

Experimental part

The biologic material was consisted of two Romanian apricot varieties: Dacia with early maturation and Nicusor with medium maturation. The fruits of both varieties were harvested at four maturation stage (green mature, half-ripe, ripe, over-ripe) from experimental orchard of Research Station for Pomiculture, Baneasa. Representative samples at least 25 apricots fruits were harvested from at least five different trees in the same orchard for each cultivar and then they were pooled. Four replicates of each variety were selected and analyzed.

In order to determine the color parameters, each fruit was analyzed on two sides (the more colorful and the lesser color side) in the equatorial zone of fruit. Reflectance spectrometry determination was carried with a HunterLab MiniScan Xe Plus spectrophotometer calibrated with a white standard reflective plate using Illuminant D65.

Reflectance spectra were recorded between 400 and 700nm. From these spectra CIELAB, coordinates L*, a*, b*, C* and h° were calculated. Coordinate a* is related with the red-green visual opposition and b* is related with the yellow-blue opposition. Chroma $C^* = \sqrt{a^{*2} + b^{*2}}$ measures color saturation and the hue angle $h^o = tg^{-1}\frac{b^*}{a^*}$ determines the red, yellow, blue, green or intermediate color between adjacent pairs of these basic colors [15].

Acoustic firmness were measured at the equator of the unpeeled fruit using an AWETA Acoustic Firmness Sensor. An acoustic signal is generated by means of gentle impact on the equator of the fruit. This signal is processed and transformed to obtain a peak of natural frequency, which is used to calculate the stiffness factor as $f^2 \times m^{2/3}$, where f represents frequency and m is fruit mass.

Carotene content was determined from pulp and peel by measuring the absorbance at λ=450 nm of acetone extract with UV-VIS spectrophotometer [16]. Results were expressed as mg carotenoids / 100 g fresh weight.

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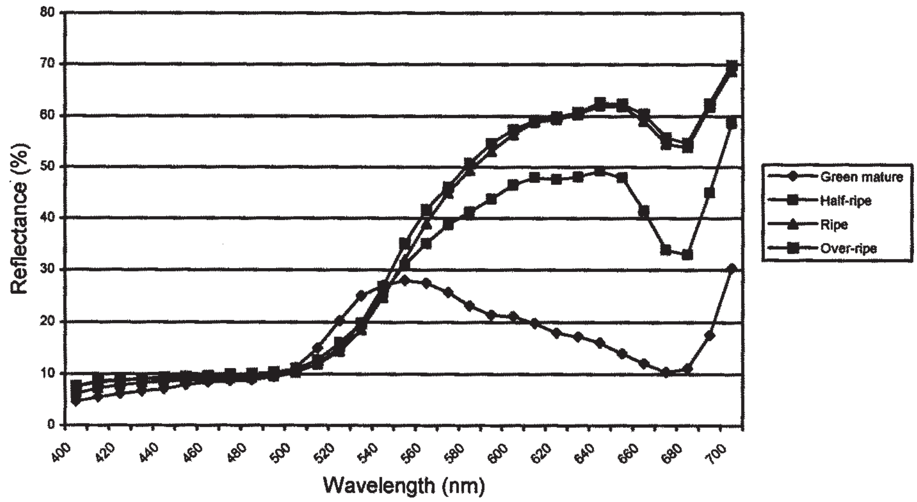

Fig. 1 Reflectance spectras of Dacia cultivar in different stages of maturation

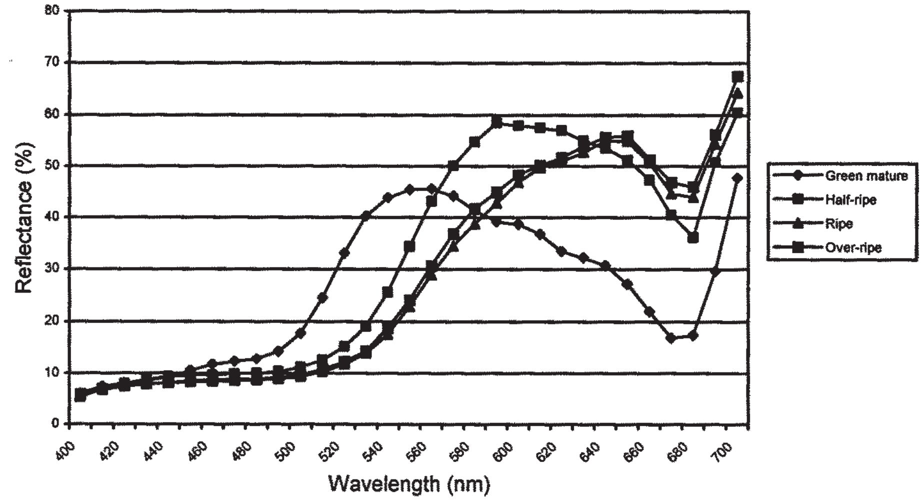

Fig.2 Reflectance spectras of Nicusor cultivar in different stages of maturation

For determination of chlorophyll pigments, the fruits were ground and extracted in acetone 80% (v/v) with calcium carbonate added to prevent pheophytinization. Homogentes were centrifugate 5 min at 5000rpm. Extracts were immediately assayed spectrophotometric at λ=663 nm and λ=645 nm [17], and chlorophyll concentration was calculated according to the equation below:

Chlorophyll a=$12.7A_{663}$-$2.69\ A_{645}$

Chlorophyll b =$22.6\ A_{645}$-$4.68\ A_{663}$

Results were expressed as mg chlorophyll a / g fresh weight.

Dry matter concentration was measured by drying some slices from each side of equatorial part of fruits to a constant weight in an oven at 105° C. The results were expressed in percentage (w/w).

The weight of fruit expressed in grams was determined through measurement of 30 fruits chosen randomly for each cultivar.

Soluble solids content (SSC) was determined by a refractometer at 20°C from juice extracted from the fruits and values were expressed in °Brix. Titratable acidity (TA) was quantified in juice by titration with 0.1N NaOH up to *p*H 8.1. The ripening index was obtained as the ratio of soluble solids to titratable acidity (SSC/TA).

Determination of physiological parameters (respiratory activity and C_2H_4 concentration) was carried out following the closed-system method at 20°C [18]. Apricots were placed in hermetic glass containers (1500mL) equipped with rubber sampling ports. Four replicates were prepared from each maturity stage.

Concentration of CO_2 produced in respiration time of apricots were determined using a IR-RIKEN analyzer in accordance with the method from [27]. Respiratory intensity of fruit were expressed in mg CO_2 $kg^{-1}h^{-1}$.

Concentration of C_2H_4 was determined in accordance with the method from [26] using a Fisons GC 9000 series gas chromatograph with a flame ionization detector EL980 and a Chrompack CP-Carboplot P7 column (inside diameter 0.53mm, length 10 m). The temperature of the oven was 60° C and the detector temperature was 100° C. The carrier gas used was H_2. The values were expressed in $\mu L\ C_2H_4\ kg^{-1}h^{-1}$.

All data obtained are means of four replicates composed of 10 fruits with standard deviation. Correlation coefficients were determined by Pearson's coefficients. Results analyses were performed using SPSS 13.0 version.

Results and discussions

Spectral reflectance curves obtained for the different stages of maturity of both cultivars are plotted in figure 1 and 2. We observed from spectra shape that in green stage there is a peak at 550nm and a minim at 670 nm for both cultivars studied. In half-ripe there are two maximum at 610 nm and 640 nm and a minimum at 680 nm. The ripe and over ripe fruits spectra present a maximum at 650 nm and a minimum at 680 nm.

The lower values of reflectance (30-50%) are related to higher chlorophyll content. Corresponding to decrease in chlorophyll content, the reflectance between 580-700 nm increases (60-70%) as a result of the ripening process. With advancing maturity grade, the spectral reflectance curves flatten. Using these optical spectral criteria a very accurate monitoring of fruit development and establishing of an optimal harvest time could be possible [23-25].

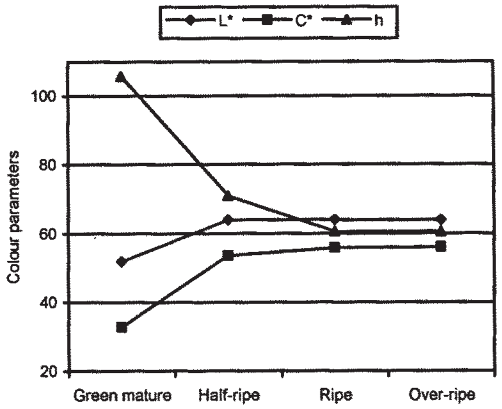

Fig. 3. Evolution of L*,C*,h° parameters during Dacia cultivar ripening

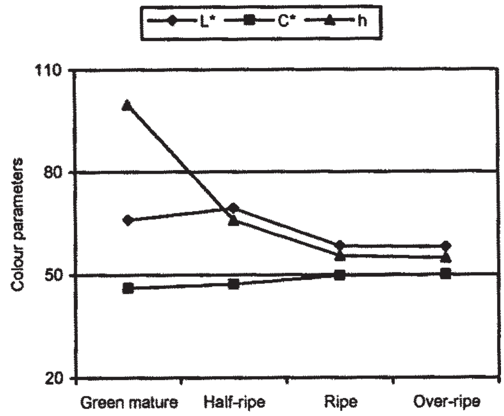

Fig. 4. Evolution of L*,C*,h° parameters during Nicusor cultivar ripening

The experimental results for color parameters at different ripening stage are shown in figure 3 and 4. It can be seen that a increase in the a*, b* and a decrease in the h° and L* parameters which corresponded with advancing of ripening apricot color changed from green to orange. Decrease of lightness (L*) value is highlight through darkening of color and this was observed at cultivar with mid season Nicusor. But, in case of Dacia cultivar with early maturation, we observed an increase of L* value that means a brightness of fruit color. However, the values of lightness differ little during apricot ripening to h° thus this color parameter is less useful in determination of maturity stage of fruit (fig. 3 and 4).

Values of a* increase during the ripening period from negative values to positive ones, denoting loss of green colour related to the disappearance of chlorophyll.Values of b* tend to increase through the ripening period, leveling off after the optimum time of harvest. Our results shown that the value of h° is a useful indicator of maturity stage, as it decreases linearly throughout ripeness, showing that apricots change from green to yellow-orange (fig. 3 and 4) from value between 100-110 (corresponding green color) to value between 55-60 (corresponding orange color). This results are in agreement with study of other authors [7, 12, 23]. Chroma values (C*) reflects the difference in intensity of fruit color. We observed a trend of increasing (fig. 3 and 4) of this color parameter among maturity stage that indicate a marked intensity and uniformity of color. However narrow range of variation of C* values and a little difference between maturity stage and even among cultivars suggested that, this color parameter is less useful than hue angle (h°) for determining of color modification during fruit ripening.

There is an irreversible transformation of the basic colour from green to orange as a result of chlorophyll degradation, especially during the days preceding ethylene burst and is in agreement with studies of authors [5, 20]. In apricot varieties studied, total carotene content increases during the maturity process to about 0.9 mg/100 fresh weight (f.w.) to 4 mg/100 fresh weight (f.w.) the end of study (table 1). These values are in accordance with those found in other study for apricot [12, 20-23].

Medium weight increased during the ripening of the apricot. Weight gain was more significant during the first stage and the less significant beyond four stages. It can be remarked a considerable weight still from green mature stage which is around 20 g for both varieties studied (table 1). Fruits of both varieties reached in ripening stage a weight between 75 to 80 g evidenceing thus fruits with medium size.

Dry matter content increased during ripening reaching appreciably value ~20% (w/w) at ripe stage (table 1). This denoting that fruits of both varieties have a high consistency and compacticity.

The ripening index (SSC/TA) increased progressively during maturation of both cultivars studied (table 1). It has been described previously that for an optimal taste, apricot should show a ripening index (SSC/TA) higher than 8 and lower than 15 [19]. Values above 8 are achieved in ripe stage for both varieties.

Table 1

VARIATION OF PHYSICO-CHEMICAL PARAMETERS OF APRICOT FRUIT DURING RIPENING

Variety	Maturity stage	Weight g	Dry matter % (w/w)	SSC/TA	Acoustic Firmness Index	Total carotenoids mg/100f.w	Chlorophyll a mg/g f.w.	Chlorophyll b mg/g f.w.
Dacia	Green mature	19.7	9.8	2.39	13.5	0.95	18.62	7.76
	Half-ripe	58.2	15.24	6.82	7.8	1.8	1.40	0.46
	Ripe	74.3	18.17	12.64	2.9	4.1	0.96	0.42
	Over-ripe	75.6	18.9	13.5	2.8	4.3	0.80	0.37
Nicusor	Green mature	25.39	14.29	1.97	13.6	0.81	13.45	5.65
	Half-ripe	40.2	14.62	5.95	7.8	1.46	3.87	2.65
	Ripe	78.5	19.36	9.72	3.4	3.5	0.9	0.85
	Over-ripe	79.4	19.7	10.5	3.2	3.78	0.85	0.70

Table 2
ETHYLENE CONCENTRATION AT DACIA AND NICUSOR CULTIVARS DURING RIPENING EXPRESSED IN µL C_2H_4 $kg^{-1}h^{-1}$

Replicate	Dacia			Nicuşor		
	Half ripe	Ripe	Over-ripe	Half ripe	Ripe	Over-ripe
P1	0.11	0.32	0.28	0.08	0.17	0.13
P2	0.11	0.28	0.24	0.07	0.18	0.12
P3	0.13	0.31	0.23	0.10	0.17	0.14
P4	0.15	0.33	0.22	0.09	0.14	0.11
Average	0.13	0.31	0.24	0.09	0.17	0.13

Table 3
RESPIRATORY INTENSITY AT DACIA AND NICUSOR CULTIVARS DURING RIPENING EXPRESSED IN mg CO_2 $kg^{-1}h^{-1}$

Replicate	Nicusor			Dacia		
	Half ripe	Ripe	Over-ripe	Half ripe	Ripe	Over-ripe
P1	14.72	32.87	24.53	24.74	52.74	50.46
P2	14.29	35.72	23.73	23.47	47.65	40.24
P3	18.29	32.01	26.29	27.88	49.84	36.60
P4	17.02	29.34	23.53	31.09	52.26	39.67
Average	16.08	32.49	24.52	26.79	50.62	41.74

Table 1 present the experimental results of acoustic firmness index during ripening of apricot varieties studied. This parameter with almost the the same change trends as fruit ripening, decreased linearly for both cultivars. However, the decreasing rates were different during the ripening stages: faster rate in the initial stages and low in the final stage. Firmness values at maturity grades beyond ~3 are in the limit of those accepted by literature. Beyond this point the fruit do not increase either weight or size appreciably. Acoustic impulse response technique can contribute through acoustic firmness index as well as quality attribute for determination of apricot maturity stage in a nondestructive way.

Variation of exogenous ethylene concentration at Dacia variety (table 2) is reduced between the last two stages. Characteristic evolution of ethylene concentration remarked during analysis time had impact on respiratory intensity influencing directly appearance of climacteric maximum. Analyzing respiratory intensity we observed a increase from value of 23.74 mg CO_2 kg^{-1} h^{-1} at half-ripe stage to value of 52.74 mg CO_2 kg^{-1} h^{-1} at ripe stage. This respiratory maxim support that Dacia variety has a rapid

Table 4
CORRELATION COEFFICIENTS BETWEEN CHROMATIC COORDINATES, CHEMICAL AND PHYSIOLOGICAL ATTRIBUTES OF DACIA APRICOT FRUIT AT RIPENING STAGE

	L*	a*	b*	C*	h°
Total carotenoids	0.66*	0.92**	0.45	0.23	0.97**
Total chlorophylls	0.83**	0.79**	0.74**	0.56	0.91**
Acoustic firmness index	0.003	0.21	0.15	0.12	0.32
Ethylene	0.31	0.68*	0.70*	0.45	0.93**
Titratable acidity	0.25	0.18	0.08	0.02	0.04
Soluble solids	0.25	0.62*	0.31	0.28	0.40

Pearson;s correlation coeficients *, **, significant at $P \leq 0.05$ or 0.01, respectively

Table 5
CORRELATION COEFFICIENTS BETWEEN CHROMATIC COORDINATES, CHEMICAL AND PHYSIOLOGICAL ATTRIBUTES OF NICUSOR APRICOT FRUIT AT RIPENING STAGE

	L*	a*	b*	C*	h°
Total carotenoids	0.57*	0.80**	0.29	0.58*	0.82**
Total chlorophylls	0.43	0.70**	0.37	0.46	0.84**
Acoustic firmness index	0.52	0.21	0.16	0.40	0.48
Ethylene	0.25	0.43	0.49	0.50	0.87*
Titratable acidity	0.27	0.27	0.06	0.22	0.15
Soluble solids	0.62*	0.50	0.04	0.30	0.25

Pearson's correlation coefficients *, **, significant at $P \leq 0.05$ or 0.01, respectively

evolution (table 3). The maturation of Dacia fruit variety achieved without abrupt variation of respiratory intensity compared with initial moment of experiment.

In case of mid season variety Nicusor we observed in general lowest value of ethylene concentration (table 2) than early variety Dacia. The value of ethylene concentration at Nicusor variety increase 1.5 fold at ripe stage as further this values decrease very little. Analyzing respiratory activity of this variety it was observed a lower intensity of this with value of 1.5-2.5 less than early variety Dacia. Respiratory activity of Nicusor fruit (table 3) has an upward dynamics similar emission of ethylene during first two stage of maturation.It can be concluded that Nicusor variety have a slower evolution that confirmed of respiratory intensity.

Correlation analysis was carried out to determine the strength of the relationship between color parameters and quality parameters. High levels of correlation coefficient of 0.97 ($P \leq 0.01$) for Dacia variety and of 0.82 ($P \leq 0.01$) for Nicusor cultivar, were found between the parameter h and the total content of carotenoids showing that the relationship between total carotenoids and color was strong (table 4 and 5). Also, the color parameter a* showed good correlation with total carotenoids and total chlorophyll. Also it was observed a strong correlation between ethylene concentration and h° parameter (R=0.87 for Nicusor cultivar and R=0.93 for Dacia cultivar (table 4 and 5)).

It was observed no correlation between color parameters and soluble solids, titratable acidity, ratioSSC/TA and acoustic firmness index; whereas a poor correlation coefficients was shown between ethylene concentration and L*, a*, b*, C*. The results suggested the influence of ethylene emission on color and firmness and a clear influence of the variety on ethylene concentration. Our results on apricot fruits are in agreement with previous studies from literature [10; 20].

Conclusions

From CIELAB chromatic characteristics, a* and h° are feasible and objective indices to distinguish the different maturity stage. These parameters showed good correlation with total carotenoids and total chlorophylls and they could be used for prediction pigments content of apricot. Because L* and C* values varied little between maturity stage during fruit ripening, they are less useful than quality indices in ascertaining the changes during fruit maturation and for establishing the appropriate harvest time. The spectral data have a promising potential to be added as objective quality indices of the fruit together with color parameters (a*, h°).

Our experiments confirmed that acoustic impulse response technique for non-destructive determination of texture can be successfully used to distinguish different stages of ripeness. This was confirmed by correlation with other indices of quality such as dry matter content and ethylene concentration.

The physiological criteria studied (ethylene concentration and respiratory intensity) are markers for monitoring of fruit evolution during maturation and for establishing their ability for storage. However, the difficulty determination of ethylene concentration and respiratory intensity by chromatography makes these parameters not easy to use than non-destructive parameters.

We propose for varieties studied a combination of parameters for the quantification of the physicochemical changes during apricot ripening (color parameters a*and h°, acoustic firmness index, weight and ripening index (SSC/TA)).

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