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# Simple and Rapid Quantification of Total Carotenoids in Lyophilized Apricots (*Prunus armeniaca* L.) by Means of Reflectance Colorimetry and Photoacoustic Spectroscopy

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**Summary**

Photoacoustic spectroscopy (PAS) and reflectance colorimetry are suggested as new tools for the analysis of total carotenoids in lyophilized apricot powders. The data obtained by these two techniques from seven apricot cultivars were compared to those acquired by spectrophotometry and high-performance liquid chromatography (HPLC). Best correlations were found between the total carotenoid (TC) content (obtained by VIS spectrophotometry: 1.2–3.4 mg per 100 g of fresh mass) and colorimetric index $a^*$ ($a^*$ represents the redness of the investigated sample), as well as either argon-ion laser- or xenon-lamp-based PAS. In all three cases linear correlations were comparable. However, according to the sensitivity and precision data, expressed *via* limit of detection (LOD) and measurement repeatability, the Xe-lamp-based PAS is a preferred approach, followed by colorimetric index $a^*$ and Ar-ion laser PAS.

Both PAS methods exhibit practically the same Pearson's correlation coefficient (R=0.987 and R=0.991) values. Nevertheless, residual sum of squares (RSS) and residual standard deviation of the linear regression ($s_{y/x}$) differ markedly. For Xe-lamp-based PAS these parameters were much lower than in the case of Ar-ion laser PAS. Likewise, analysis imprecision amounted to relative standard deviation (RSD) of 1–3 % for Xe-lamp PAS and 2–6 % for Ar-ion laser PAS. On the other hand, as expected, the calibration sensitivity achieved for the PAS signal induced by an Ar-ion laser at 481 nm was substantially higher than that of a Xe-lamp at 470 nm. Nevertheless, according to much lower $s_{y/x}$, the corresponding LOD for Xe-lamp PAS was still two times lower than that of Ar-ion-based laser PAS (0.59 *vs*. 1.10 mg per 100 g). Unlike this, Ar-ion laser PAS showed more favourable instrumental precision and standard error of the weighed mean when compared to the Xe-lamp PAS (0.1–0.6 and 0.1–0.3 % *vs*. 0.5–8.0 and 0.4–1.7 %, respectively). As far as colorimetric indices

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are concerned, only $a^*$ proved to be analytically useful; excellent R but rather modest RSS and $s_{y/x}$ resulted in LOD value of 0.70 mg per 100 g and acceptable analysis imprecision of up to 3 %.

The outcome of this research provides sufficient amount of evidence that analytical methods such as reflectance colorimetry and PAS without the use of any chemicals are feasible for reliable quantification of total carotenoids in freeze-dried apricot homogenates.

*Key words:* total carotenoids, β-carotene, apricot (*Prunus armeniaca* L.), photoacoustic spectroscopy, colorimetry

## Introduction

Different levels of vitamins and antioxidants (carotenoids and polyphenols) in apricots contribute to their taste, colour and nutritive value (*1–3*). Carotenoids and anthocyanins, present in all photosynthetic organisms, are responsible for most of red and yellow colours of fruits and flowers (*4*). In apricot, β-carotene is the most abundant carotenoid exceeding 50 % of total carotenoid (TC) content (*5,6*). Other carotenoids such as α-carotene, zeaxanthin and lutein are also found in apricot fruit but in smaller quantities (*7*).

The content of β-carotene in apricot depends mainly on the variety, ripening stage and the geographical origin. In a recent study performed in Germany on six apricot cultivars (Bergeron-I, Bergeron-II, Harogem, Moniqui, Orangered and Redsun), β-carotene content varied between 0.1 and 3.9 mg per 100 g (*8*). Sass-Kiss *et al.* (*6*) investigated the carotenoid content of eleven apricot varieties (Royal, Cegledi orias, Gönci Magyar, Sunglo, H-II 25/37, H-II 20/6, Cegledi arany, Cegledi kedvenc, Stella, Mandula kajszi and Roxana) harvested in Hungary. The quantity of β-carotene per fresh mass found in Royal, Cegledi orias and Gönci Magyar was 3.80, 3.29 and 3.11 mg per 100 g, respectively. Likewise, Ali *et al.* (*9*) studied the TC content per dry mass of six apricot varieties (Alman, Habi, Khakhas, Mirmalik, Neeli and Shai) grown in Pakistan and the values ranged from 10.1 (for var. Shai) to 18.1 (for var. Habi), the mass fractions are expressed in mg per 100 g of β-carotene equivalents per 100 g.

Significant differences in β-carotene content among Turkish apricot varieties (Hacihaliloglu, Soganci, Hasanbey, Kabaasi, Cataloglu and Cologlu) were found in a study of Munzuroglu *et al.* (*10*). The same authors also analyzed wild apricot varieties and concluded that β-carotene content in these samples was substantially lower than in the cultivated products. Based on the colour of their flesh, Ruiz *et al.* (*11*) classified apricots into various groups (white, yellow, light orange and orange). Their measurements indicated that a high carotene content of the fruit correlates with the orange colour of its flesh, with twice or three times more carotenoids in the skin than in the flesh. It is known that the process of ripening in apricots is accompanied by enhanced biosynthesis of carotenoids (*12*). As an example, Németh *et al.* (*13*) compared the content of β-carotene in Gönci Magyar apricot varieties during ripening and observed significant differences between the 60 and 80 % maturity stages.

Colorimetric measurements of Petrisor *et al.* (*14*) established that TC content in apricots increased during the ripening process while chlorophyll a and b decreased drastically. Values of colorimetric indices $a^*$ (redness of the sample) and hue angle ($h°$; 0° means $+a^*$ (red) and 90° refers to $+b^*$ (yellow)), proved reliable indicators in discriminating among different maturity stages of apricots and for predicting their pigment content. In another study, changes in the polyphenolic and carotenoid content of three apricot cultivars (Kečkemetska ruža, Mađarska najbolja and Velika rana) grown in two different geographical regions of Croatia were also investigated (*15*). In all apricot varieties, β-carotene content at immature and mature stages differed by one order of magnitude.

Instrumental methods used to quantify carotenoids in fruits can be classified into two major categories. The first one includes the compulsory, tedious and costly extraction of carotenoids before the sample can be measured by either spectrophotometry or high-performance liquid chromatography (HPLC) (*16,17*). Reflectance spectroscopy, colorimetry, resonance Raman spectroscopy, diversity of photothermal methods, *etc.* are representatives of methods that belong to the second category. All of them have in common that preparation of the sample is not needed, so that the specimens can be studied directly, *i.e.* just as they are (*18–23*). By virtue of their operational principles, such direct methods are potential candidates for a rapid assessment of carotenoids in fruits. The availability of a low-cost instrument for rapid screening/control of carotenoids would certainly be greatly appreciated in practice.

The main objective of the research undertaken in the work described here is to explore the feasibility of two direct methods for quantification of carotenoids in freeze-dried homogenates of seven apricot cultivars. The two approaches comprise the colorimetry and photoacoustic spectroscopy, with either Ar-ion laser or Xe-lamp used as excitation source. The data obtained were compared to those acquired from the same samples by spectrophotometry and HPLC, which served as golden standards.

## Materials and Methods

### *Plant growing conditions*

The apricot fruits were taken from the Experimental and Research Farm of the Faculty of Horticultural Science at Corvinus University of Budapest (47°23'N, 19°08'E), Hungary. The orchard at the altitude of 106 m above the sea level is on a light sandy soil with a humus content of 0.8 to 1 %. The soil of the Research Field is sandy loam with loess (yellow soil) sedimentation. Based on the 50-year monitoring data, the mean temperature, the number of sunshine hours (per annum) and the average rainfall were 10.8 °C, 2014 h and 500 mm, respectively.

### *Plant material*

The fruits of seven apricot (*Prunus armeniaca* L., syn.: *Armeniaca vulgaris* Lam.) cultivars (Budapest, Bergeron, Harogem, Mandulakajszi, Pincot, Sylred and Sylvercot) were examined at 80 % of their commercial maturity. The varieties were grafted on myrabolan (*Prunus cerasifera* L. cv. Myrabolana) seedling; trees were planted at a spacing of 2×3 m in 2005, and the crown form was trained in the form of vase.

### *Chemicals*

The β-carotene standard (CAS number: 7235–40–7) and all analytical grade solvents (methanol (MeOH), acetonitrile (ACN) and tetrahydrofuran (THF)) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The stock solution was prepared from β-carotene standard; 0.00229 g of β-carotene was dissolved in 25 mL of THF and then diluted (ten times; final concentration was 0.00916 mg/mL) in a mixture of ACN:MeOH:THF (50:45:5, by volume, before injecting on the HPLC column.

### *Sample preparation*

About 10 kg of fruits of each cultivar (overall, seven apricot cultivars were analyzed) were picked (manually) from all four tree quarters of ten trees. Fruits were rinsed with tap water and pitted by hand. Pitted fruits (skins and fruit pulp) were homogenized using a mixer. Homogenates were first frozen at –25 °C and then lyophilized at 1 Pa using ScanVac CoolSafe™ freeze dryer (LaboGene ApS, Lynge, Denmark). Thus prepared lyophilized samples were kept at –25 °C in darkness until actual analysis.

### *Sample extraction*

The extraction of carotenoids from 5 mg of lyophilized apricot powder was carried out under subdued light by adding 1 mL of ACN:MeOH:THF (50:45:5, by volume) in Eppendorf tubes and shaking (Edmund Büchler SM 30-control shaker, Hechingen, Germany) at 150 rpm for 2 h. The samples in the Eppendorf tubes were then centrifuged (Hettich Mikro 22R centrifuge, Tuttlingen, Germany) at 8163.1×*g* for 5 min at –5 °C. The supernatant was filtered through 0.45-μm Millex®-HN syringe filter unit (SLHV 013 NL, PVDF Durapore, Millipore Co., Billerica, MA, USA) and finally injected onto the HPLC column. This extract was used for spectrophotometric measurements as well.

### *HPLC analysis*

HPLC instrument from Waters Co. (Milford, MA, USA) includes the 2487 dual λ absorbance detector (analytical wavelength 450 nm), 1525 binary HPLC pump, column thermostat (set to 30 °C), in-line degasser AF and 717 plus autosampler (temperature of the sample compartment set to 5 °C). Empower™ 2 software (Waters) was used to control the analysis. The column type was Symmetry C18, 5 μm, 4.6×150 mm. The pressure on the column was (11.55±0.07) MPa and the volume injected into the column was 20 μL. The conditions regarding mobile phase were modified according to Bushway (*24*). The eluent was a mixture of ACN:MeOH:THF at a volume ratio of 50:45:5, flowing at 1 mL/min. The retention time for β-carotene was about 12 min.

### *Spectrophotometry*

The total carotenoid (TC) content was determined from the absorbance measured at 450 nm on a Hitachi U-2800A spectrophotometer (Tokyo, Japan). The samples extracted with ACN:MeOH:THF (50:45:5, by volume) and the standard diluted in the same solvent mixture were measured and the TC content was expressed on β-carotene basis.

### *Photoacoustic spectroscopy*

Photoacoustic spectroscopy (PAS) implies the illumination of the condensed phase sample with the periodically modulated radiation of selective wavelength (*25*). Some part of incident energy absorbed by the sample is converted into heat by means of radiationless transitions. As a result, the sample warms up and cools down at a frequency of modulation. Generated thermal waves reach sample's surface causing periodic heating and cooling of the gas layer above the sample. Because the volume of the gas in the PA cell is constant, such expansions and contractions give rise to an acoustic wave. The amplitude of this latter is eventually detected (at the modulation frequency) by the microphone as the PA signal. Optical and thermal parameters of the sample and of contacting gas play a decisive role in the process of PA signal generation. To eliminate the effect of the wavelength-dependent variations in the output power of the excitation source, normalization needs to be performed. This is best achieved by dividing the PA signal measured from a sample with a PA signal obtained under identical conditions from a carbon black powder (strongly absorbing reference). Attractive features of the PA method include: (*i*) no need for sample pretreatment and hence shorter analysis time, (*ii*) the approach is essentially non-destructive, and (*iii*) completely opaque specimens that are difficult to analyse by conventional techniques are readily investigated by PAS.

An *in-extenso* description of the PA experimental set-up used in this study can be found elsewhere (*26*). The PA experiments were conducted using two different excitation sources: Xe-lamp (1000 W, Oriel Technologies Pty Ltd, Lane Cove, NSW, Australia) with monochromator (spectral resolution of 16 nm, at 470 nm and 17 Hz, Jobin Yvon H-10, HORIBA Scientific, SAS, Edison, NJ, USA) and a continuous wave (cw) Ar-ion laser, model 85 (481 nm, 30 Hz; Lexel Corporation, Palo Alto, CA, USA). Laser power incident on the surface of the sample was 20 mW (*27*).

Apricot lyophilisate powders were investigated by two variants of PA methods directly (*i.e.* without extraction or other preparation procedure). The PA signal was measured 3 to 4 times. After rejecting the sample, the PA cell (sample volume of 0.25 $cm^3$) was cleaned (using cotton swabs and ethanol) before reloading it again.

### *Colorimetric analysis*

Colour of freeze-dried apricot powder was analysed with a MiniScan XE Plus colorimeter (Hunter Associates Laboratory, Inc, Reston, VA, USA). This instrument allo-

cates to each sample specific indices ($L^*$, $a^*$ and $b^*$) within the CIE (Commission Internationale l'Eclairage) Lab three-dimensional colour space. In the CIE space, index $L^*$ represents the brightness that ranges from 0 (pure black) to 100 (pure white). The positive/negative values of index $a^*$ refer to the intensity of red/green colourations, respectively. Likewise, positive/negative $b^*$ values are related to the intensity of yellow/blue colouration. Characteristics of MiniScan XE Plus are the 45°/0° geometry, D65 standard illumination and 10° standard observer. Chroma is the saturation or the vividness of colour. As chromaticity (chroma index, $C^*$) increases, a colour becomes more intense and *vice versa*. Hue angle ($h$°/rad) is the basic unit of colour and can be interpreted, for example, as 0°=red and 90°=yellow. Both chroma $C^*$ and hue $h$° are derived from indices $a^*$ and $b^*$ by means of equations (*28*):

$$C^*=[(a^*)^2+(b^*)^2]^{½} \quad /1/$$

$$h°=\tan^{-1}(b^*/a^*) \quad /2/$$

for metric chroma and metric hue, respectively. Total colour difference ($dE^*$) computed from:

$$dE^*=[(L^*)^2+(a^*)^2+(b^*)^2]^{½} \quad /3/$$

is represented by a distance between the absolutely white reference and the sample in the colour space. Three independent measurements of the same, re-mixed material were carried out with each sample and the results are expressed as the average of this data.

### *Data analysis*

The goodness-of-fit in linear regression was documented through Pearson's product-moment correlation coefficient (R), residual sum of the squares (RSS), and residual standard deviation of the regression line ($s_{y/x}$).

Precision was expressed as instrumental, intrinsic precision of one single measurement based on 512 readouts of the lock-in amplifier, and repeatability from several independent analyses. Standard error of the weighed mean was also calculated.

The limit of detection (LOD) was calculated from the residual standard deviation of the regression line ($s_{y/x}$) and the slope of the calibration curve (S) according to the formula (*29*):

$$LOD=3.3\cdot s_{y/x}/S \quad /4/$$

## Results

### *Total carotenoid and β-carotene content in apricots*

Table 1 displays the TC content (determined by spectrophotometry and expressed as β-carotene equivalents in mg per 100 g) and β-carotene content (analyzed by HPLC), and the respective standard deviations, found in seven apricot cultivars. Both analytes fit within relatively narrow content ranges in available samples (TC and β-carotene were 1.2–3.4 and 0.6–2.0 mg per 100 g of fresh mass, respectively).

The highest content of TC (3.35 mg per 100 g) was found in Bergeron cultivar, while Sylred and Sylvercot contained the lowest contents of TC (1.22 and 1.23 mg per 100 g, respectively). Bergeron was also the richest in β-carotene (2.04 mg per 100 g) as compared to the minimum (0.63 mg per 100 g) found in Sylred. The last column in Table 1 shows the mass fraction of β-carotene among total carotenoids. With the exception of Mandulakajszi variety (45.7 %), this ratio exceeds 50 % and is the highest for Pincot (77.6 %).

Table 1. Total carotenoid and β-carotene content in apricots

| Apricot variety | $w$(TC) | $w$(BC) | $m$(BC)/$m$(TC) |
|---|---|---|---|
| | mg per 100 g | mg per 100 g | % |
| Sylvercot | 1.23±0.02 | 0.74±0.02 | 60.3 |
| Pincot | 2.00±0.08 | 1.55±0.02 | 77.6 |
| Budapest | 2.27±0.02 | 1.24±0.08 | 54.7 |
| Harogem | 2.04±0.09 | 1.44±0.06 | 70.7 |
| Mandulakajszi | 2.90±0.02 | 1.33±0.11 | 45.7 |
| Sylred | 1.22±0.02 | 0.63±0.001 | 51.8 |
| Bergeron | 3.35±0.14 | 2.04±0.05 | 60.9 |

BC=β-carotene, assayed by HPLC; TC=total carotenoids, assayed by spectrophotometry
TC and BC values are expressed on fresh mass basis
The results for TC are expressed as a mean value±standard deviation (S.D.) of three replicates, while the results for BC are expressed as mean value±S.D. of duplicate measurements

### *Results of colorimetric measurements*

Colorimetric indices $L^*$, $a^*$ and $b^*$ were measured directly, while $dE^*$, $C^*$ and $h$° were calculated from these data according to the equations stated above.

Linear correlation between the red index $a^*$ and TC was higher ($R^2$=0.9633) than that observed for β-carotene ($R^2$=0.7493). The former linear correlation is plotted in Fig. 1. Index $b^*$ showed no significant linear correlation with TC, with $R^2$=0.4845; the same is true for other colorimetric indices with even lower $R^2$ values. Results are summarized in Table 2.

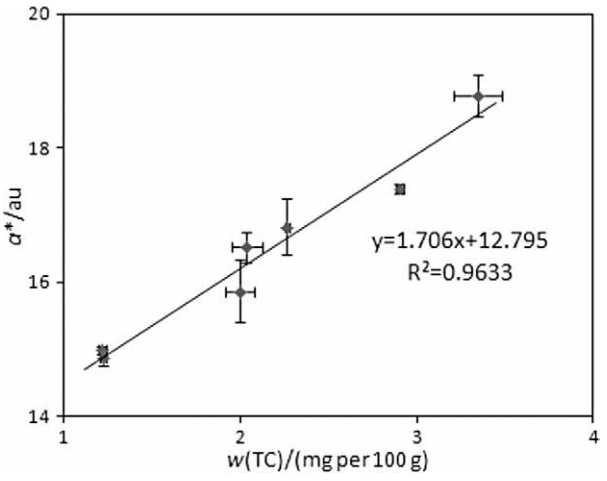


**Fig. 1.** Linear correlation between total carotenoid (TC) content (obtained by spectrophotometry, mean value±S.D. of three independant analyses) and colorimetric index $a^*$ (mean value±S.D. of three repetitions; au=arbitrary unit)

Table 2. Pearson's correlation coefficient (R) for linear fitting of TC and β-carotene content *vs.* the colorimetric indices and photoacoustic signal

| Technique | Colorimetry | | | | | | PAS | |
|---|---|---|---|---|---|---|---|---|
| | $L^*$ | $a^*$ | $b^*$ | $dE^*$ | $C^*$ | $h°$/rad | Xe-lamp | Ar-ion laser |
| TC | –0.165 | 0.981[a] | 0.696 | 0.218 | 0.264 | –0.254[c] | 0.987[a] | 0.991[a] |
| BC | –0.267 | 0.866[b] | 0.419 | 0.022[c] | 0.335 | –0.295[c] | 0.846[b] | 0.859[b] |

BC=β-carotene, assayed by HPLC; PAS=photoacoustic spectroscopy; TC=total carotenoids, assayed by spectrophotometry
TC and BC values are expressed on fresh mass basis
[a]$p<0.01$
[b]$p<0.05$
[c]low calibration sensitivity (slope)
$\lambda$(Xe-lamp)=470 nm; $\lambda$(Ar-ion laser)=481 nm

Data in Table 3 display the analytical figures of merit. Despite somewhat lower calibration sensitivity (slope of the regression line) for $a^*$ *vs.* TC (as compared to $b^*$), the former showed lower imprecision of regression line parameters. Also, higher R but lower residual sum of the squares and residual standard deviation of the linear regression values confirm a markedly stronger linear correlation between $a^*$ and TC than $b^*$ and TC, and additionaly confirm the lack of linear fit between $b^*$ and TC. This was also reflected in the almost four times lower LOD value of TC (0.70 for $a^*$ compared to 2.67 mg per 100 g for $b^*$). However, nearly comparable repeatability was obtained for both indices $a^*$ and $b^*$ (RSD ranging 0.4–2.9 %, with average values of 1.5 and 1.0 %, respectively).

### *Results of studies by PA spectroscopy*

Fig. 2 shows the amplitude of the PA signal (Xe-lamp was used as the excitation source) plotted *vs.* TC content in apricot lyophilized powders. The relationship between the amplitude of the PA signal and the TC content provides the evidence for linear proportionality ($R^2$=0.9735) (Tables 2 and 3 and Fig. 2). The PA signal was in the order of 90 to 120 μV. Each single measurement represents 512 successive readings of the lock-in signal and depends primarily on the power stability of the Xe-lamp. Standard deviation in such 'single load' type of measurements ranged from 0.5 to 8.0 %, with an average of 2.2 %, being reflected in standard error of the weighed mean (SEWM) value of 0.4–1.7 %. In the 'multi-load' type of measurements the achieved relative standard deviation

Table 3. Analytical performance data for the analysis of total carotenoids in apricots

| Technique | | Best linearity fit | | | | | | Precision (RSD/%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $w$(TC range)/mg per 100 g $N/n$ | R/RSS/$s_{y/x}$ | Slope | | Intercept | | $w$(LOD of TC)/mg per 100 g | Intrinsic | Measurement repeatability | SEWM/% |
| | | | | Mean | RSD/% | Mean | RSD/% | | | | |
| PAS | Xe-lamp | 1.22–3.35 7/3 | 0.987[a]/ $1.112\cdot10^{-4}$/ $2.419\cdot10^{-3}$ | 1.36 V | 5.3 | 0.074 mV | 2.2 | 0.59 | 0.5–8.0[c] (av. 2.2) | 1.5–2.7[d] (av. 1.9) | 0.4–1.7 |
| | Ar-ion laser | 1.22–3.35 7/3–4 | 0.991[a]/ 0.485/ 0.156 | 46.85 V | 9.5 | 2.544 mV | 3.9 | 1.10 | 0.1–0.6[c] (av. 0.3) | 1.8–6.2[e] (av. 4.6) | 0.1–0.3 |
| Colorimetry | $a^*$ | 1.22–3.35 7/3 | 0.981[a]/ 2.508/ 0.363 | $1.706\cdot10^5$ au | 6.3 | 12.795 au | 1.9 | 0.70 | – | 0.4–2.9[f] (av. 1.5) | – |
| | $b^*$ | 1.22–3.35 7/3 | 0.696[b]/ 76.267/ 2.004 | $2.480\cdot10^5$ au | 24.0 | 29.529 au | 4.6 | 2.67 | – | 0.4–1.9[f] (av. 1.0) | – |

au=arbitrary unit, LOD (limit of detection)=3.3 $s_{y/x}$/slope, $N$=number of concentration levels, $n$=number of independent measurements at each concentration, PAS=photoacoustic spectroscopy, RSD=relative standard deviation, R=Pearson's correlation coefficient, RSS=residual sum of squares, $s_{y/x}$=residual standard deviation of the regression line, SEWM=standard error of the weighed mean, TC=total carotenoids
TC values are expressed on fresh mass basis
Total carotenoid content was analyzed by spectrophotometry (3 independent analyses)
$\lambda$(Xe-lamp)=470 nm; $\lambda$(Ar-ion laser)=481 nm
number of observed pairs in the statistical analysis was 21–22
[a]significant linear correlation, $p<0.01$
[b]non-significant linear correlation
[c]512 successive readouts of the lock-in
[d]mean value of 3 repetitions
[e]mean value of 3–4 repetitions
[f]three loadings of the same, re-mixed material

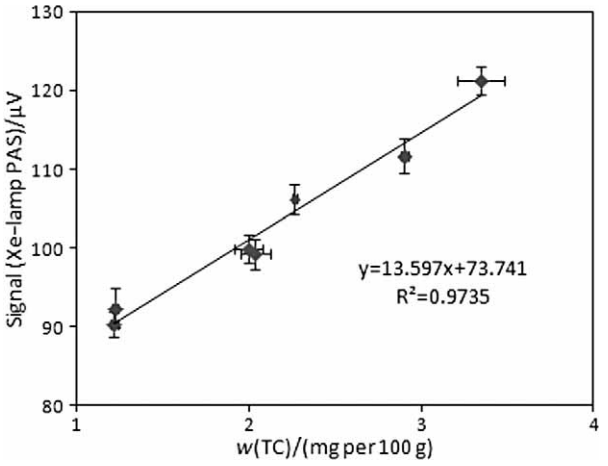


**Fig. 2.** Linear correlation between total carotenoid (TC) content (obtained by spectrophotometry, mean value±S.D. of three independent analyses) and Xe-lamp PAS ($\lambda$=470 nm, $f$=17 Hz, mean value±S.D. of triplicate analyses)

(actually analysis repeatability) that depends on factors such as the stability of the Xe-lamp, the uniformity of samples, *etc.*, did not exceed 3 % with an average of 1.9 %.

PA signals obtained in experiments with the Ar-ion laser tuned to 481 nm are shown in Fig. 3. The experimental conditions were similar to those used in the PA studies conducted with the Xe-lamp. The magnitude of PA signal ranged typically between 3 and 4 mV. The correlation between PA signal and TC content was highly linear ($R^2$=0.983). Instrumental imprecision based on 512 successive readouts of the lock-in was lower than 1 %, on an average of 0.3 % resulting in a low SEWM value (0.1–0.3 %). The RSD of analysis repeatability (with an average value of 4.6 %) did not exceed 6 %.

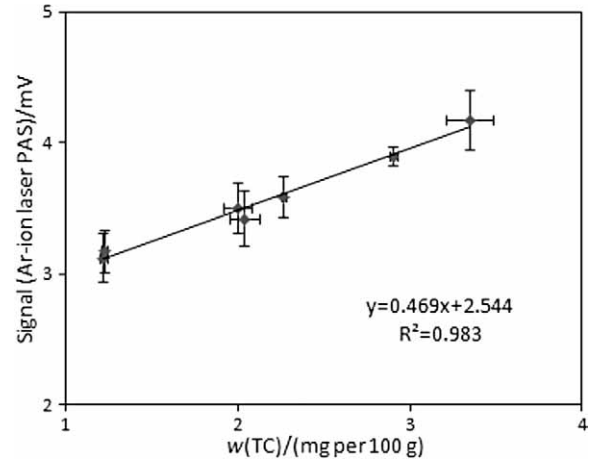


**Fig. 3.** Linear correlation between total carotenoid (TC) content (obtained by spectrophotometry, mean value±S.D. of three independent analyses) and Ar-ion laser PAS ($\lambda$=481 nm, $f$=30 Hz, mean value±S.D. of 3–4 analyses)

Output power of the Ar-ion laser at 481 nm is higher than that of the Xe-lamp at 470 nm. This fact might be responsible for higher calibration sensitivity (almost 35 times), higher instrumental precision (8 times on average) and lower SEWM values (5–7 times) of the laser-based PAS. The R values obtained for both PA methods are comparable. Contrary to this, markedly lower RSS and $s_{y/x}$ values were achieved for the Xe-lamp-based PAS. They undoubtely speak in favour of the higher level of linear correlation *vs.* total carotenoid content and resulted in two times lower LOD value of TC for Xe-lamp PAS than Ar-ion PAS (0.59 against 1.10 mg per 100 g).

## Discussion

Both TC and β-carotene content are apricot genotype dependent. Values for the TC content acquired by means of spectrophotometry and the mass fractions of β-carotene determined by HPLC confirm this. As shown before by Sass-Kiss *et al.* (*6*), the latter is a dominant carotenoid in apricots. Reflectance colorimetry characterizes the colour of the fruit and provides satisfactory estimates of the carotenoid content of apricots. Our data for indices $a^*$ and $b^*$ in freeze-dried apricot homogenates are in accordance with those of Ruiz *et al.* (*30,31*) for peel and flesh of apricot.

It is important to emphasize that statistically significant goodness-of-fit in linear regression was proven for $a^*$ and PAS (both with Xe-lamp and with Ar-ion laser) upon p-values and *t*-statistics. Correlations between the measured colorimetric indices and PA signals against the content of carotenoids are analyte-(β-carotene or TC)-dependent. As expected, when correlating $a^*$ and PA signals with the TC content, the correlations were markedly stronger ($p<0.01$) than those found when correlating the same parameters with the content of β-carotene ($p<0.05$) (Table 2).

## Conclusions

Based on the obtained results, the colorimetry (index $a^*$) as well as both PAS methods (Xe-lamp- and Ar-ion laser-based) could be used as new analytical tools to reliably quantify TC in lyophilized apricot powders. According to sensitivity and average repeatability data, the Xe-lamp-based PAS appears to be the most favourable, followed by the colorimetry (index $a^*$) and Ar-ion laser PAS (LOD of TC in mg per 100 g and RSD (in %): 0.59 and 1.9, 0.70 and 1.5, 1.10 and 4.6 %, respectively) (Table 3). All three methods can assist in selecting new varieties of apricots with higher carotenoid content, assessing the extent of their maturity stage and establishing the optimal harvesting time.

Overall, the outcome of our study suggests realistic prospects for the construction of a compact and affordable instrument applicable for low-cost, reliable and rapid routine analysis of TC in freeze-dried apricot homogenates.

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