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Direct photothermal techniques for rapid quantification of total anthocyanin content in sour cherry cultivars

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ABSTRACT

The analytical performance of the newly proposed laser-based photoacoustic spectroscopy (PAS) and of optothermal window (OW) method for quantification of total anthocyanin concentration (TAC) in five sour cherry varieties is compared to that of the spectrophotometry (SP). High performance liquid chromatography (HPLC) was used to identify and quantify specific anthocyanins. Both, PAS and OW are direct methods that unlike SP and HPLC obviate the need for the extraction of analyte. The outcome of the study leads to the conclusion that PAS and OW are both suitable for quick screening of TAC in sour cherries. The correlation between the two methods and SP is linear with $R^2 = 0.9887$ for PAS and $R^2 = 0.9918$ for OW, respectively. Both methods are capable of the rapid determination of TAC in sour cherries without a need for a laborious sample pretreatment.

1. Introduction

Flavonoids that constitute an important subgroup of phenolic compounds are among the most important components present in many fruits and vegetables and contribute to their color and sensory properties [1]. Among others, flavonoids are located in chloroplasts scavenging the singlet oxygen and reducing the oxidative damage induced by UV-B light [2]. Due to their multiple functions in photoprotection and health effectiveness in humans, flavonoids are referred as nutraceuticals [1,2]. Anthocyanin pigments that belong to the subgroup of flavonoids are responsible for orange, red, purple, violet, fuchsia and blue colors in fruits and vegetables [3]. In addition, owing to their attractive colors, anthocyanins are often used as food additives. Anthocyanins are glycosides of 18 anthocyanidins that differ in the degree of hydroxylation and methoxylation. The most common naturally occurring anthocyanins such as cyanidin, delphinidin, malvinidin, pelargonidin, peonidin and petunidin [4,5] are important in human nutrition [6]. Increased public interest in anthocyanins is associated with their health benefits and potential nutritional effects demonstrated in numerous clinical studies. For example, the presence of anthocyanins in foods has been linked with the health-promoting benefits such as antioxidant and anti-cancer activities [7]. They were also proven to influence the fixation of the reactive oxygen [8], inhibit the oxidation of lipoproteins [9,10] and prevent the development of cardiovascular diseases [11]. According to Seymour and his team the consumption of sour cherries reduced the concentration of lipids in the liver of experimental animals [12]. Anthocyanins in cherries are also known to possess the anti-inflammatory, anticancer, antidiabetic, antiobese [13] and antibacterial [14] properties and capacity to relieve the stress and strengthen the immune system. Likewise, these compounds can be used to supplement chemotherapy and other treatments prescribed for patients suffering of cancer and HIV infection [15].

Anthocyanins constitute the most important group of the water-soluble pigments in fruits and plants. They are found in high concentrations in berry fruits [16], sour cherry [17], bunch-berries

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[18] and plum [19]. However, considerable differences in the chemical composition among different cultivars have been reported [20].

Sour cherry is rich in anthocyanins with cyanidine-3-glucoside, cyanidine-3-rutinoside, cyanidine-3-sophoroside and cyanidine-3-glucosylrutinoside, dominating the composition. Other anthocyanins found in sour cherry include peonidin-3-glucoside, malvinidin-3-glucoside, delphinidin-3-glucoside and pelargonidin-3-glucoside. The total anthocyanin concentration (TAC) in sour cherries was found to vary from a few milligrams to tens of milligrams per 100 g fresh product mass. Because the level of consumer's knowledge about the nutritional value of sour cherry is generally low, it is desirable to gather more information about the identity and the amount of various anthocyanins in different sour cherry varieties. The identification of anthocyanins and their quantification by means of the high performance liquid chromatography (HPLC) and spectrophotometry (SP) have been attempted by many authors [21,22]. Both approaches are time consuming and costly as they require a tedious and laborious extraction of the sample prior to the analysis. Besides these two destructive methods there exists a variety of non-invasive techniques (examples are colorimetry, reflectance spectroscopy and chlorophyll fluorescence spectroscopy) that permit fruit to be analyzed with a minimum of pretreatment or of no preparation at all [23].

This paper is dealing with the application of the laser-based photoacoustics (PA) and optothermal window (OW) methods in order to quantify TAC in several sour cherry varieties. Both methods offer the possibility for a direct quantification of TAC which eliminates the need for the extraction step and therefore significantly reduces the overall analysis time. A calibration against the methods such as HPLC or SP is a necessity since neither PA nor OW are yet the absolute techniques for measurements of concentration.

Essential to the OW and PAS is the spectral coincidence between the wavelength of the incident radiation and the absorption wavelength of anthocyanins. Provided the above requirement is being met, the absorption of the laser radiation by anthocyanins will lead to the generation of heat (and thermal waves) in sour cherry causing its temperature to rise. In this study the SP served as the reference method for TAC quantification, while HPLC was used for the identification and quantification purposes.

As stated already, unlike HPLC and SP, the photothermal methods require no extraction leaving the production of a thawed homogenate the only pretreatment needed.

2. Materials and methods

2.1. Plant material

Samples of five sour cherry (*Prunus cerasus* L. syn.: *Cerasus vulgaris* Mill.) cultivars [Gerema (GE), Maliga emléke (ME), Érdi bőtermő (EB), Érdi jubileum (EJ), Kántorjánosi (KJ)] were harvested in the year 2009. Fruit-trees were grown on a lowland chernozem [fertile, black-coloured soil containing a high percentage (7–15%) humus, phosphoric acids, phosphorus and ammonia, with lime deposits and mildly alkaline in the topsoil] at Érd-Elvira [Experimental Station of the Research Institute for Fruit Growing and Ornamentals Budapest-Érd, Hungary central region]. The number of sunshine hours was 2000, the mean temperature during the vegetation period was 16.8 °C and the mean annual rainfall deposition was between 550 and 570 mm.

Fruits (about 5000 g) of each cultivar were picked (manually) from all four tree quarters of 15 trees at the optimal ripening stage. Fruits were rinsed with a tap water and the pits manually removed. The pitted fruits (skins and fruit-pulp) were homogenized with a mixer and homogenates stored at −25 °C until analysis.

2.2. Chemicals

The anthocyanin standards, pelargonidin 3,5-di-O-glucoside (pelargonin chloride) (CAS number: [17334-58-6]), cyanidin-3,5-di-O-glucoside (cyanin chloride) (CAS number: [2611-67-8]), peonidin chloride (CAS number: [134-01-0]), malvidin-3-galactoside chloride (primulin) (CAS number: [30113-37-2]), delphinidin chloride (CAS number: [528-53-0]) and petunidin chloride (CAS number: [1429-30-7]), as well as all HPLC analytical grade solvents were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO, USA). The standards (0.5 mg/mL) were 500× diluted with methanol containing 0.1% (V/V) hydrochloric acid before applying to HPLC.

2.3. Sample preparation

For HPLC analysis 1.5 mL of thawed fruit homogenate was centrifuged (Hettich Mikro 22R at 15,000 rpm) during 5 min in Eppendorf-tube. The supernatant was filtered through a 0.45-μm MILLEX®-HV Syringe Driven Filter Unit (SLHV 013 NL, PVDF Durapore), purchased from Millipore Co. (Bedford, MA, USA).

For SP analysis thawed homogenate was centrifuged (Hettich EBA 21 at 15,000 rpm) for 5 min. Aliquots of the supernatant (0.1 mL) were then mixed with 0.2 mL hydrochloric acid (10 mol L^{-1}) in 10.0-mL volumetric flasks, and the volume was adjusted to the mark using 96% EtOH. The samples were kept in darkness for 30 min.

2.4. HPLC

WATERS High Performance Liquid Chromatograph (Waters Co., 34 Maple Street, Milford, MA, USA) equipped with 2487 Dual λ Absorbance Detector, 1525 Binary HPLC Pump, In-Line Degasser, Column Thermostat (set at 40 °C) and 717 plus Autosampler (set at 5 °C) controlled with EMPOWER™2 software was used for HPLC analysis. The samples were injected on a SYMMETRY C18 5-μm 4.6 mm × 150 mm column. The mobile phase was a mixture of water (containing 5% acetic acid):MeOH:ACN (70:10:20, V/V/V). Selected isocratic flow rate was 1 mL min^{-1}. The pressure on the column at 40 °C was about 16.1 ± 0.1 MPa and the time needed to complete the single HPLC run was 14 min. The volume injected on a column was 20 μL. The detection was performed at analytical wavelength of 530 nm. The retention times (in min) of the standards were: 1.566 (cyanidin), 3.340 (pelargonidin), 4.431 (delphinidin), 5.761 (malvidin), 8.670 (peonidin) and 13.71 (petunidin). Repeated HPLC analyses (n = 3–4) were performed and concentrations calculated from the areas of the corresponding peaks. The concentrations of the different anthocyanin compounds were expressed in mg/100 g homogenate.

2.5. Spectrophotometry

The absorbance at 530 nm was measured on a Hitachi U-2800A spectrophotometer; three to four independent analyses were performed. The TAC (in mg/100 g homogenate) was calculated according to the approach described by Füleki and Francis [24] and Lee, Durst and Wrolstad [25] and was expressed as cyanidin-3-glucoside equivalents (M_r = 449.2, ε = 26,900 L mol^{-1} cm^{-1}).

2.6. Photoacoustic spectroscopy

The PAS implies the illumination of a condensed phase sample by the modulated beam of (laser) radiation the emission wavelength of which coincides with that at which the absorption of the sample is preferably high. The fraction of energy absorbed by the sample is converted to heat; as a result of this the temperature of

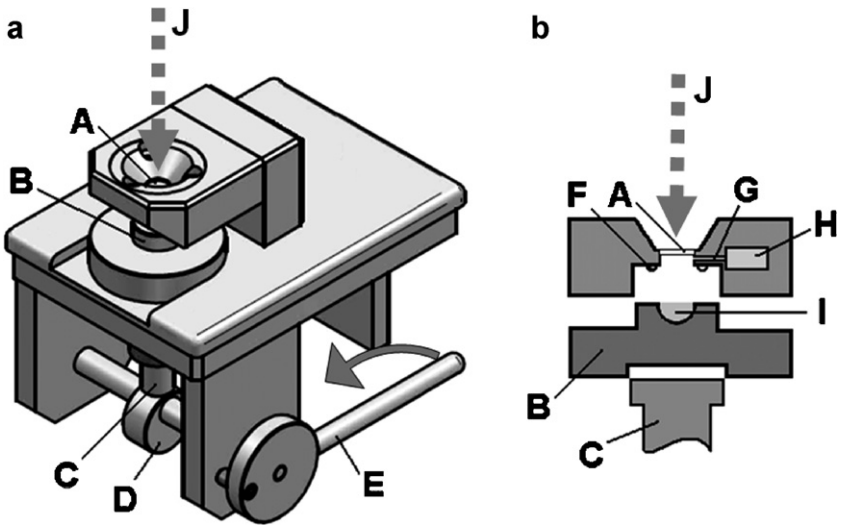

Fig. 1. (a) The sample holder and the PA detector. The modulated laser beam enters the PA cell through the transparent window. Absorption of the incident radiation by the sample leads to the generation of thermal waves. In a gas layer above the sample in the closed PA cell these thermal waves generate the sound waves which are eventually detected by a microphone. (b) The cross-sectional view of the PA cell. A: transparent quartz window; B: sample holder; C: metal rod; D: eccentric wheel; E: lever of sample holder; F: O-ring; G: capillary tube; H: microphone; I: sample; J: modulated laser beam.

the sample oscillates periodically at a frequency identical to that of the modulation. Generated thermal waves reach the sample's surface causing the periodic heating and cooling of the contacting layer of the surrounding gas. Finally, the expansions and contractions of this gas layer give rise to the acoustic wave, the amplitude of which is detected as a voltage (termed PA signal) by means of a microphone. It is obvious that optical and thermal parameters of the sample and the contacting gas both play a decisive role in the generation of PA signal.

The PA spectrometer used in this study comprised the GLP-III-30, green laser pointer (532 nm, power 16 mW) as a light source, a home made modulator and the PA cell. The mechanically chopped (17 Hz) laser beam (J) was focused into the PA cell (Fig. 1). Radiation enters the PA cell through a half-inch diameter quartz window (A). The sampling volume (I) and a miniature (4.2 mm × 4.75 mm) microphone (Sennheiser KE 4-211-2) (H) are acoustically coupled by means of a 3-mm long capillary (G). The PA cell is a sealed (closed) when the lever of the sample holder (E) is rotated through 180°. In such a position the metal rod (C) presses the sample holder (B) against the O-ring (F) which seals the PA detector due to the eccentricity of the wheel (D). Sour cherry homogenate (100 μL) (I) was loaded into a semispherical cavity manufactured in the sample holder (B). The PA signal was processed by a dual phase lock-in amplifier (Stanford SR530) connected to the computer. With each loading 512 successive readings of lock-in amplifier have been taken and the average value and a standard deviation computed. The sour cherry homogenate was then removed from the PA cell and PA cell cleaned simply using a kitchen towel paper. A fresh quantity of the same sour cherry homogenate was then loaded into the PA cell and the whole procedure repeated. This was done for three to four loadings; the average of measured values was considered representative for the analysis.

2.7. Optothermal window

The experimental arrangement for OW analysis used in this study is shown in Fig. 2. The 532 nm radiation (16 mW) emitted by a green laser pointer (GLP-III-30) was periodically modulated at 8 Hz by a mechanical chopper. The latter was provided with a LED and a photodiode (to generate reference signal for the lock-in amplifier). Before impinging on a sample the laser beam was allowed to pass through a highly transparent, 0.3-mm thick sapphire disk (characterized by a large thermal expansion coefficient) that carries the annular ring of lead zirconate titanate (PZT) piezoelectric material glued to a disk's rear side. The sapphire disk and the PZT together constitute the optothermal window (OW). An iris diaphragm mounted coaxially with the OW, prevented the incoming radiation from directly heating the piezoelectric transducer thereby causing unwanted OW signal.

Sour cherry homogenate is deposited directly atop the sapphire disk. Due to the good thermal contact between the sample and the sapphire disk, the temperature of the disk changes causing it to expand and contract periodically. The piezoelectric transducer (glued to a sapphire disk) detects the induced stress and produces a periodic voltage signal which is detected (at the modulation frequency) by means of the-lock-in amplifier.

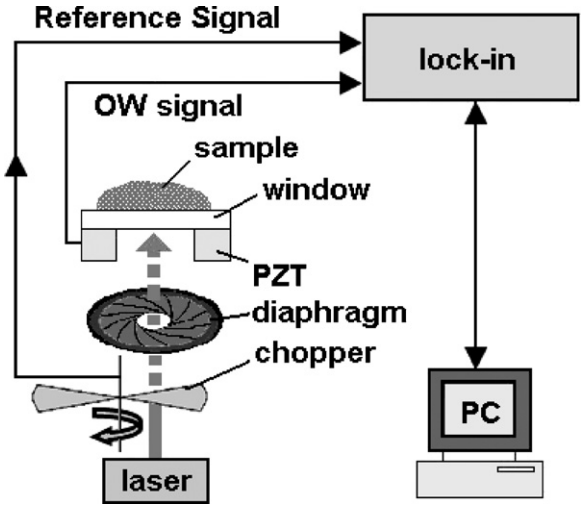

Fig. 2. The schematic diagram of the OW setup. The modulated laser beam passes through the iris diaphragm and a transparent sapphire disk window before being absorbed by the sample. The generation of heat in the sample causes the window to expand; such mechanical deformation is measured by the PZT piezoelectric sensor.

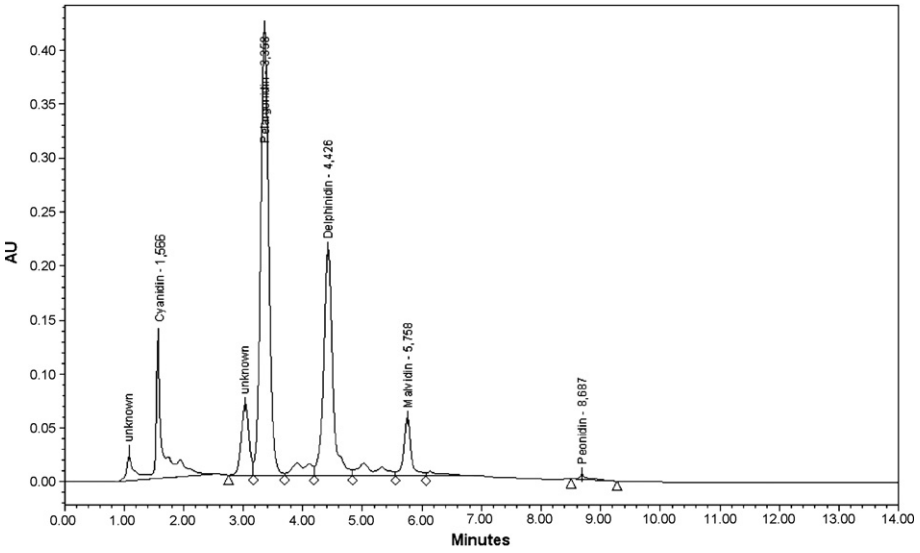

Fig. 3. Typical chromatogram of sour cherry (variety Maliga emléke) recorded at 530 nm.

Table 1
Total anthocyanin concentration (TAC) of sour cherry homogenates as measured by spectrophotometry.

Sour cherry variety	TAC (mg/100 g)[a]
EJ	43.1 ± 5.8
EB	15.5 ± 1.0
ME	26.4 ± 4.3
KJ	23.3 ± 0.4
GE	79.0 ± 4.9

[a] Mean ± *SD*, *n* = 3–4.

A small quantity of sour cherry homogenate (about 200 μL) is sufficient for the OW analysis because the test sample must cover only the irradiated portion (circular region 4 mm in diameter) of the disk. The output of OW detector is fed to the input of the Stanford SR-530 two phase lock-in amplifier, detected (at 8 Hz and the time constant of 3 s) and processed by the computer. Overall 512 consecutive readings of the lock-in amplifier were taken and the average value and standard deviation computed. Removing the sample and cleaning of the OW detector was easily achieved by cotton swabs dipped in ethanol. All OW experiments were performed in triplicate.

3. Results and discussion

3.1. Total anthocyanin concentration in sour cherries by SP

The TAC (determined by SP) and the corresponding standard deviation (expressed as cyanidin-3-glucoside equivalents in mg/100 g) of anthocyanins in five sour cherry varieties are displayed in Table 1. The TAC is highest in GE cultivar (78.98 mg/100 g) while the lowest TAC is that of EB (15.52 mg/100 g).

3.2. Identification and quantification of anthocyanins in sour cherries by HPLC

Glycosides of cyanidin, delphinidin, malvidin, pelargonidin, peonidin and petunidin are the most common anthocyanins in sour cherries and some cultivars of blueberries [21,22]. In a current research HPLC was used to identify and estimate concentrations of these anthocyanins in several Hungarian sour cherry cultivars. Petunidin-3-glucoside was detectable in neither of the samples investigated in this study. Fig. 3 represents a typical HPLC chromatogram of cv. Maliga emléke sour cherry, with pelargonidin accounting for approximately 81% of total identified antocyanins.

As it is seen in Table 2, TAC values measured by HPLC are comparable to TAC data obtained by SP (Table 1); the only exception is the cultivar EJ. Summing the concentrations of five anthocyanins found in this cultivar gives a value that is only about 33% of TAC determined by SP. The presence of unknown anthocyanins is most likely the cause for this discrepancy.

Cyanidin was the major anthocyanin identified in EB (ca. 51%) while the fraction of pelargonidin in ME, KJ and GE is 81, 75 and 87%, respectively. Malvidin dominates (ca. 58%) in EJ followed by cyanidin (28%), pelargonidin (9%) and some unknown anthocyanins. Pelargonidin, the highest concentration of which was found in ME, KJ and GE, is responsible for most of sour cherry's color.

3.3. PA spectroscopy

Fig. 4 shows the amplitude of the PA signal at 532 nm plotted versus the TAC (determined by SP) in sour cherry samples. In all PA experiments the power of the laser, the experimental geometry and the modulation frequency (17 Hz) were the same. The correlation between the PA response and TAC is linear (R^2 = 0.9887)

Table 2
Major anthocyanin compounds identified and quantified in sour cherry varieties by HPLC.[a]

Sour cherry variety	Cyanidin (mg/100 g)	Pelargonidin (mg/100 g)	Malvidin (mg/100 g)	Delphinidin (mg/100 g)	Peonidin (mg/100 g)	TAC (mg/100 g)
EJ	4.03 ± 0.05	1.35 ± 0.19	8.31 ± 0.04	0.40 ± 0.00$_3$	0.12 ± 0.00$_3$	14.20 ± 0.20
EB	6.64 ± 0.21	5.98 ± 0.06	0.27 ± 0.01	0.01 ± 0.00$_1$	0.01 ± 0.00$_1$	12.90 ± 0.28
ME	3.41 ± 0.70	21.14 ± 0.37	1.41 ± 0.05	0.16 ± 0.01	0.02 ± 0.00$_4$	26.14 ± 0.80
KJ	4.57 ± 0.61	15.42 ± 0.56	0.53 ± 0.03	0.09 ± 0.00$_3$	0.01 ± 0.00$_1$	20.61 ± 1.16
GE	6.10 ± 0.06	64.36 ± 0.63	2.66 ± 0.09	0.52 ± 0.05	0.19 ± 0.01	73.83 ± 0.82

TAC – total anthocyanin concentration.
[a] Mean ± *SD*; *n* = 3–4.

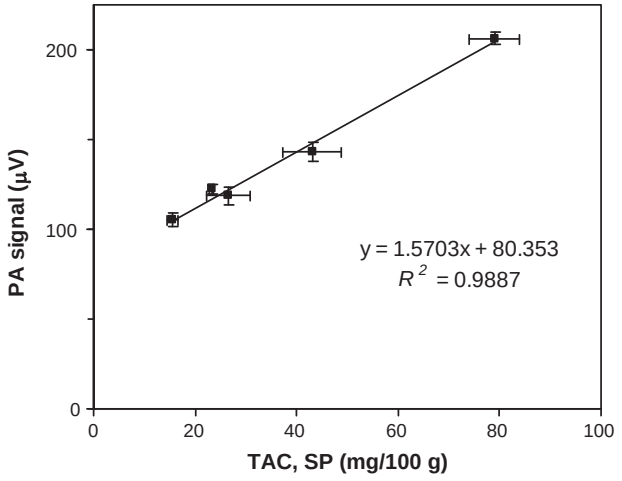

Fig. 4. The PA signal (at 532 nm and 17 Hz) plotted versus the total anthocyanin concentration (TAC) in sour cherry homogenates. Mean ± *SD*, *n* = 3–4. The TAC values were determined spectrophotometrically (SP) at 530 nm.

as shown in Fig. 4. Data points in Fig. 4 are the averages of three to four consecutive independent measurements. Each single measurement represents 512 successive readings of the lock-in signal. Standard deviation in such "single load" type of measurements varied between 1 and 6% of the measured value, with an average of 2%. In the "multi-load" type measurements the achieved standard deviation (actually repeatability) that depends on factors such as the stability of laser power, the uniformity of sample, etc., did not exceed 4%.

3.4. Optothermal window

The OW response to a varying TAC in sour cherry samples is displayed in Fig. 5. Values shown are the averages of triplicate measurements and the error bars indicate one standard deviation. The experimental conditions were similar to those used in the PA study, the only exception being the modulation (8 Hz). Under given operating conditions the magnitude of the background OW signal (i.e., signal obtained without the sample atop the sapphire disc) was typically of the order of a few microvolts.

In general, the magnitude of the lock-in signal depends, in a complex manner, on a variety of parameters including the power density of the incident radiation, the modulation frequency, the

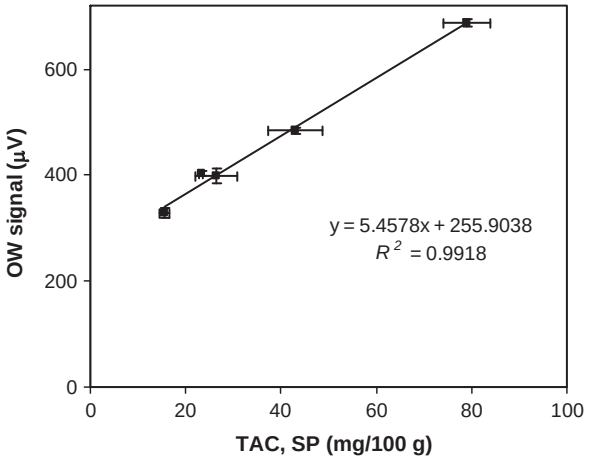

Fig. 5. The OW signal (at 532 nm and 8 Hz) plotted versus the total anthocyanin concentration (TAC) in sour cherry homogenates. Mean ± *SD*, *n* = 3–4. The TAC values were determined spectrophotometrically (SP) at 530 nm.

Table 3
Regression data for total anthocyanins in sour cherries.[#]

Technique	Best-goodness of linearity fit		Slope		Intercept		*DL* estimate (mg/100 g)	Precision		*SEWM* (%)
	Conc. range (mg/100 g), *N*/*n*	R^2/*RSS*	Mean ($\times 10^5$ μV)	*RSD* (%)	Mean (μV)	*RSD* (%)		Instrument precision (%)	Measurement repeatability (%)	
OW (532 nm)[x]	15.5–79.0, 5/3	0.9918/6.31 × 10^2	5.458	5.3	255.90	4.9	7.58	0.5–8.0 (512 readings)	1.0–3.4 (*n* = 3)	0.01–0.1
PAS (532 nm)[x]	15.5–79.0, 5/3–4	0.9887/72.06	1.570	6.2	80.35	5.3	8.91	1.4–5.7 (512 readings)	0.4–3.8 (*n* = 3–4)	0.1–0.9

DL (detection limit) = 3.3SD_{int}/slope. *N* – number of concentration levels. *n* – number of independent measurements (loadings) at each concentration. OW – optothermal window. PAS – photoacoustic spectroscopy. *RSD* – relative standard deviation. R^2 – coefficient of determination. *RSS* – residual sum of the squares. SD_{int} – standard deviation of the regression line intercept. *SEWM* – standard error of the weighted mean.

[#] Concentrations are reported for the homogenates measured by SP at 530 nm (3–4 independent analyses).

[x] Results based on gross signals.

sensitivity of the piezoelectric detector, thermal and optical properties of both, anthocyanins and sapphire disk, etc. If the experimental conditions (in the first place, the modulation frequency) are properly chosen, the OW signal becomes solely dependent on the absorption coefficients of anthocyanins themselves and hence on their concentrations. The relationship between the OW signal and TAC resembled that found the same samples in the PA studies. Under practically identical experimental circumstances the amplitude of the OW signal obtained from each sour cherry sample was higher (factor 3.5) than that of the PA signal. Again, the observed correlation between the OW signal and TAC is linear and the coefficient of determination high (R^2 = 0.9918). The instrument precision ranged between 1 and 8% (2% on average), and the measurement repeatability was 1–3%.

Analytical performances of the newly established PAS and OW assays are summarized in Table 3.

4. Conclusions

The sum of the concentrations of the three anthocyanins (pelargonidin, cyanidin and malvidin) found in the investigated samples constitutes between 2 and 87% of the TAC. For example, in GE pelargonidin is the most abundant anthocyanin making as much as 87% of the TAC. On the other hand in cultivar EB the concentration of malvidin is only 2% of the TAC. When comparing the TAC data obtained for investigated samples by HPLC and SP, one concludes that HPLC values are at least 96% of TAC data collected in SP analysis. This finding provides the evidence that the three anthocyanins quoted above indeed are the dominant compounds. The relatively simple fingerprint of anthocyanins identified (HPLC) in this study is in agreement with data obtained previously from sour cherries [26]. It consists of four to five major compounds, the major constituent of which accounts for at least 50% of the total concentration. The concentration of the specific component varies significantly in different cultivars.

As to cultivar EJ, the TAC found in this study was higher than that reported by Šimunić et al. [22]. The TAC depends on a fruit variety and is also influenced by local climatological conditions (rain, number of sunshine hours, temperature, soil type, etc.). This explains why the TAC of one and the same sour cherry variety can differ depending on the geographical origin.

The PAS and OW, two photothermal methods, were evaluated in terms of their potential to quantify TAC in sour cherry homogenates. The SP measurements confirmed that TAC in sour cherries varies from several milligrams to tens of milligrams per 100 g fresh fruit. The response of PAS and OW was calibrated against SP; the range of TAC in sour cherries extends from 16 to 79 mg/100 g. The correlation between the PA signal and the TAC (SP results) is highly linear; the same conclusion applies to OW data. Furthermore, precision data for regression line parameters is favourable for both photothermal methods. Calculated DL values are between 7 and 9 mg/100 g TAC. The standard errors of the weighted mean and the repeatability data suggest a high and comparable precision for both photothermal methods. The sensitivity of the OW method is slightly better than that of PAS. As far as calibration sensitivity is concerned increasing the TAC by 1 mg/100 g corresponds to a 5.5 μV increase of the OW signal as compared to 1.6 μV increment observed for the PA signal.

In conclusion, PAS and OW were both demonstrated useful for assaying TAC in sour cherry homogenates. As such they will be welcome in the product quality control. The two methods appear interchangeable; the preference for using a specific approach will in the first instance rely on a desired sensitivity and the availability of instrumentation.

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