

# Impact of packaging material and storage conditions on polyphenol stability, colour and sensory characteristics of freeze-dried sour cherry (*Prunus cerasus* var. Marasca)

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**Abstract** The aim of this study was to evaluate the influence of packaging materials and storage conditions on polyphenols stability, colour and sensory characteristics of freeze-dried sour cherry (*Prunus cerasus* var. Marasca). Freeze-dried sour cherries were packed in high barrier metalized polypropylene and aluminium packaging (PET/PPmet/PE and PET/Al/PE) for up to 12 months at 4, 20 and 37 °C. Characterisation of polyphenol compounds was done by HPLC UV/Vis PDA and in all samples individual anthocyanins (ANTs), flavonolglycosides (FGs) and hydroxycinnamic acids (HCAs) were determined. Polyphenol content was not markedly affected by freeze-drying and decreases were amounted 1.5–5 %. Furthermore, obtained results indicated that minimal loss of polyphenol content in freeze dried sour cherries were achieved at 4 °C and 3 months of storage. Regardless of the type of packaging materials, samples stored at lower temperature during 12 months, retained the higher content of FGs (quercetin-3-glucoside, kaempferol-3-glucoside, kaempferol-3-rutinoside) and HCAs (neochlorogenic, chlorogenic, *p*-coumaric, caffeic and ferulic acid) than ANTs (cyanidin-3-glucosylrutinoside, cyanidin-3-rutinoside, cyanidin-3-glucoside, cyanidin-3-sophoroside). The same trend was confirmed with kinetic parameters, also. Sour cherry products packed in both type of laminate and stored at lower temperature retained characteristic dark red colour and sensory properties. This study showed that freeze-dried cherry products

have pleasant sensory and very good nutritional properties, and storage in both type of laminates at 4 and 20 °C up to 6 months ensured good product quality.

**Keywords** Freeze dried sour cherries · Storage · Packaging · Polyphenols · Sensory characteristics

## Introduction

Sour cherry Marasca (*Prunus cerasus* var. Marasca) is very important seasonal crop in Croatia, and from 2013 this autochthonous cultivar received the designation of origin (Ministry of Agriculture, Republic of Croatia, 2013) and annual yield is approximately 2000 t. The fruit has dark red colour and high dry matter, approximately 27.3 % (Pedisić et al. 2007), specific sweet and sour aroma derived from volatile compounds such as alcohols, carbonyls, esters and terpenes (Levaj et al. 2010) and therefore is valuable raw material in food industry.

Regarding their phytochemical composition, sour cherries are rich source of polyphenol compounds which strongly influence the quality and nutritional value of the fruits and contributing to their sensorial attributes (Ferretti et al. 2010). Anthocyanins (ANTs) [cyanidin-3-glucosylrutinoside (Cy-3-GR), cyanidin-3-rutinoside (Cy-3-R), cyanidin-3-glucoside (Cy-3-G), cyanidin-3-sophoroside (Cy-3-S)], flavonol glycosides (FGs) [quercetin-3-glucoside (Q-3-G), kaempferol-3-glucoside (K-3-G), kaempferol-3-rutinoside (K-3-R)], hydroxycinnamic acids (HCAs) [neochlorogenic (NChA), chlorogenic (ChA), *p*-coumaric (*p*-CA), caffeic (CA) and ferulic acid (FA)] are the most abundant phenols in sour cherries (Ferretti et al. 2010), including Marasca cultivar (Pedisić et al. 2010; Elez Garofulić et al. 2013; Zorić et al. 2014). These bioactive compounds have attracted the interest of many researchers and the general public due to the potential

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beneficial actions on human health and well-being (Ferretti et al. 2010). To avoid problems related to seasonality and short postharvest life of sour cherries, various preservation methods are used to prolong their shelf life and retain the amount of biologically active compounds (BACs). Fruit drying is one of the most important methods to extend shelf life and to minimize distribution of raw materials with high moisture content. However, the drying process may cause physical, structural, chemical and biological changes that can affect quality attributes like colour, texture, flavour and nutritional value, due to the loss of nutrients and phytochemicals, which are relatively unstable to heat (Kwok et al. 2004). Therefore, it is important to select and to optimize drying method, as well as storage conditions, in order to minimize all factors adversely affecting the quality of the product.

Freeze-drying (FD), is one of the most effective methods of drying which ensures maximum preservation of nutritional, bioactive and sensory properties of the product and therefore is widely used for fruits with thermo-labile antioxidants such as polyphenols. According to Sablani et al. (2011) FD improved retention of polyphenols in berries during processing and in some cases showed enhancement of polyphenols concentration compared to air drying. Despite these advantages, freeze-dried samples exhibit strong hygroscopic properties, and they may be adversely affected by moisture during storage period what may be reflected on the quality of dried fruit. Food quality is also affected by storage temperature and may affect polyphenol stability during storage. Major types of deteriorations of dried fruits are browning, flavour and nutrient losses. Colour change of the dehydrated fruit results from both enzymatic and non-enzymatic oxidation of polyphenol compounds as well as from Maillard reaction (McEvily et al. 1992). Aside from appropriate temperature and storage period, adequate packaging material also showed great impact on quality and sensory properties of dried fruit (Gvozdenović et al. 2007; Piasecka et al. 2013; Henríquez et al. 2013). Complex films such as laminated materials and metalized films made from polyethylene and aluminium foils offer good protection to dried foods because of improved barrier properties and therefore are mainly used to package snacks and high value foods. According to Henríquez et al. (2013) total phenols (TP) of apple peel powder samples were the best preserved in metalized films of high barrier during storage. Several studies researched the impact of drying processes and storage conditions on fruit antioxidants for periods till six months (Del Caro et al. 2004; Henríquez et al. 2013). According to Randelović et al. (2014) PET/Al/PE laminate provided the best protection of TP content in comparison with other packaging laminates in dried apricot stored at room temperature during 12 months. To date, there is a lack of studies which concurrently determine the nutritional and sensorial changes of freeze dried sour cherry Marasca (FDSCM) fruits packaged in various packaging materials during storage. Due

to high BAC's content and pleasant sensory profile, FDSCM have a great potential to be a valuable ingredient for functional fruit products (Pedisić et al. 2010). Economic considerations usually limit the widespread use of FD commercially, but above-mentioned Marasca cherry properties could justify FD process.

Considering all the aforementioned, the **objective** of this study was to evaluate the stability of polyphenol compounds, antioxidant capacity, colour and sensory attributes of FDSCM fruit, packed in two different packaging materials (laminate PET 12 µm/PP 18 µm met/PE 100 µm and PET 12 µm/Al 9 µm/PE 85 µm), stored at the different temperatures (4 °C, 20 °C and 37 °C) during 12 months (samples are excluded at 0, 3, 6, 9, 12 months).

Additionally, kinetic parameters (reaction rate constant, half-life and activation energy) for predicting the quality of stored FDSCM were applied.

## Materials and methods

### Chemicals and standards

Methanol, formic acid and acetonitrile were HPLC grade, purchased from BDH Prolabo, VWR (Lutterworth, England). Water was Milli-Q quality (Millipore Corp., Bedford, USA). Standards Cyanidin-3-O-glucoside chloride, Q-3-G, *p*-CA, FA, CA and ChA were purchased from Sigma (Steinheim, Germany), Cyanidin-3-O-sophoroside chloride, Cyanidin-3-O-rutinoside chloride and K-3-R were obtained from Extrasynthese (Lyon, France), 2,2-diphenyl-1-picrylhydrazyl (DPPH) was purchased from Sigma and (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) from Fluka (Neu-Ulm, Germany).

### Plant material

The sour cherry fruits (*Prunus cerasus* var. Marasca) were harvested at the plantation of Maraska factory (Zadar, Croatia) at technological stage of maturity. After harvesting, the samples were immediately transported to a laboratory in a portable refrigerator at 4 °C, subsequently deppited and frozen using liquid nitrogen, and kept at -60 °C (ScanCool SCL210P, LaboGene™, Lyngø, Denmark) until FD.

### Freeze-drying of sour cherries

For FD of deppited sour cherries (previously frozen at -60 °C), 500 g of the sample were placed on each tray. Five trays were placed in a laboratory freeze-dryer (CoolSafe PRO, Labogene, Denmark) and the FD process was performed for 24 h under high vacuum (0.13–0.55 hPa), with isothermal

(heating) plate temperatures of 20 °C. The final water content of dried fruits was 9.7 %.

### Packaging and storage conditions of freeze-dried sour cherries

Approximately 10 g of FDSCM were packed in bags (12 × 12 cm) of the two different commercially available laminates: Pet 12 µm/PP 18 µm met/PE 100 µm (Pet/PPmet/PE) and Pet 12 µm/Al 9 µm/PE 85 µm (Pet/Al/PE) (Folijaplast Ltd., Zadar, Croatia) and stored at three temperatures: 4 °C, 20 °C and 37 °C. Relative humidity and temperatures were controlled (data logger EBI 20TH1, Ebro, Germany) every 6 h for the samples stored at room temperatures. At the end of the storage period average temperature and relative humidity was 19.73 °C and 62.35 %, respectively. Temperature value is round up to 20 °C.

### Extraction of phenols

The polyphenol compounds from all samples were extracted using procedure previously described by Elez Garofulić et al. (2013). All extracts were prepared in triplicate and analysed by HPLC.

### HPLC analysis

Polyphenol compounds were determined by HPLC Agilent 1260 quaternary LC Infinity system (Agilent Technologies, Santa Clara, CA, USA) equipped with diode array detector (DAD), an automatic injector and ChemStation software on a Nucleosil 100-5C18, 5 µm (250 × 4.6 mm i.d.) column (Macherey-Nagel). The solvent composition and the used gradient conditions were described previously by Zorić et al. (2014). Identification of phenols was carried out by comparing retention times and spectral data with those of the authentic standards (anthocyanins were identified at 520 nm, flavonol glycoside at 360 nm and phenolic acids at 280 nm).

Identification was confirmed using characteristic UV/Vis spectra, polarity, previous literature reports (Elez Garofulić et al. 2013), and also by another study on sour cherry Marasca products done with LC-MS/MS (data not yet published).

Quantitative determination was carried out using the calibration curves of the standards. Cy-3-GR was determined according to Cy-3-G, kaempferol-3-glucoside (K-3-G) according to K-3-R and neochlorogenic acid (NChA) according to ChA.

The concentration of all polyphenol compounds were expressed as mg per 100 g of dry matter, as mean value ± standard deviation ( $N = 3$  replicates).

### Antioxidant capacity

The scavenging capacity was determined according to DPPH method as previously reported in literature (Brand-Williams et al. 1995) with some modifications as follows: an aliquot (2 mL) of phenolic extracts or methanol solution of Trolox (25–300 mM) was mixed with 2 mL of methanol and 1 mL of 0.5 mM DPPH methanolic solution. The mixture was kept in the dark for 20 min, after which the absorbance was measured at 517 nm against a blank of methanol without DPPH. Measurements were performed by the Uviline 9400 spectrophotometer (Secomam, France). The results were calculated according to calibration curve for Trolox (25–300 mM). DPPH values were expressed as mmol Trolox equivalents (TE) per 100 g of dry matter, as mean value ± standard deviation ( $N = 3$  replicates).

### Colour analysis

Colour analysis was performed using a colorimeter (CM-3500 d, Konica Minolta, Japan) at CIE Standard Illuminant D65 by 30 mm thick plate. The colour values were expressed as  $L^*$  (whiteness or brightness/darkness),  $a^*$  (redness/greenness) and  $b^*$  (yellowness/blueness), respectively. Three measurements were made at different points of the samples, and this procedure was repeated three times to get the average values.

Hue angle ( $H$ ), chroma ( $C$ ) and total colour difference ( $\Delta E$ ) were calculated from:

$$H^* = \tan^{-1} \left( \frac{b^*}{a^*} \right) \quad (1)$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

$$\Delta E_{ab}^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (3)$$

Where all  $\Delta L^{*2}$ ,  $\Delta a^{*2}$  and  $\Delta b^{*2}$  were calculated in reference to the zero time of storage.

### Sensory evaluation

For sensory evaluation of FDSCM samples quantitative descriptive analysis (QDA) was chosen, since this method provides a detailed description of the tested samples (Meilgaard et al. 1999). The procedure was performed according to methods described in ISO 6564, ISO 8587 and ISO 11036 in a sensory laboratory equipped according to ISO 8589. After the storage, sensory analysis was carried out by a trained panel consisting of 21 members per session (11 female and 10 male). Panellists were staff members of the Faculty of Food Technology and Biotechnology (Zagreb, Croatia). After a series of discussion sessions, the panellists were required to list the terms seemed appropriate for the description of colour,

odour, flavour, taste and texture. Finally, total of 17 descriptive terms as major sensory attributes were evaluated: colour intensity, odour intensity, sour cherry odour, off-odour, sour cherry flavour, flowery flavour, fruity flavour, sour taste, sweet taste, harmony taste, sour cherry taste, astringent taste, aftertaste, off-taste, firmness, stickiness, and chewiness. The panellists scored the samples for every sensory characteristic, using a line intensity scale, with scores awarded on a scale of 1–7 to show the relative intensity of each attribute, in which 1 indicated total absence ('none') of the sensory attribute and 7 a very definite attribute ('intense').

### Statistical analysis

Statistical analysis was carried out using the software Statistica ver. 10.0 (Statsoft Inc., Tulsa, OK, USA). In order to explore the influence of storage time, storage temperature and packaging material on FDSCM polyphenols, antioxidant capacity and colour parameters multivariate analysis of variance (MANOVA) was performed and marginal means were compared with Tukey HSD test. Differences at  $p \leq 0.05$  were considered statistically significant. For the sensory data principal component analysis (PCA) was performed.

### Calculation of kinetic parameters

Previous studies have shown that thermal degradation of anthocyanins followed first-order reaction kinetics (Verbeyst et al. 2010; Zorić et al. 2014). This kinetic type can generally be expressed as Eq. 4 with  $c(t)$  as the concentration at time  $t$ ,  $c_0$  as the initial concentration (mg/100 g dry matter of sample),  $t$  as the storage time (months) and  $k$  as the first order degradation rate constant (month<sup>-1</sup>):

$$c(t) = c_0 \cdot \exp.(-k \cdot t) \quad (4)$$

The half-life ( $t_{1/2}$ ) of the reaction is obtained assuming the first-order kinetics as:

$$t_{1/2} = -\ln 0.5 / k \quad (5)$$

The linear relationship between  $\ln k$  and  $1/T$  can be expressed by the Arrhenius Eq. (3).

$$k(T) = k_0 \cdot \exp \left[ -\frac{E_a}{R \cdot T} \right] \quad (6)$$

where  $E_a$  is the activation energy (kJ/mol),  $T$ —absolute temperature (K) and  $R$  is the universal gas constant (8.314 · 10<sup>-3</sup> kJ/K·mol). The Arrhenius activation energy ( $E_a$ ) was calculated by plotting  $\ln(k)$  against  $1/T$ .

## Results and discussion

The polyphenol content in fresh and freeze-dried Marasca sour cherries, and the effect of packaging materials, temperature and storage time on polyphenol content in FDSCM is summarized in Tables 1 and 2.

### The influence of freeze-drying on polyphenols stability in Marasca sour cherries

Marasca cherry phenols were characterised using HPLC with UV/Vis PDA detection and include ANTs, FGs and HCAs. Fresh Marasca sour cherries had the substantial levels of ANTs (69.08 % of total polyphenol content), while content of HCAs (23.20 %) and FGs (7.72 %) were determined in lower levels. All researched samples contained four ANTs: Cy-3-S, Cy-3-GR, Cy-3-G and Cy-3-R. The major ANT in fresh sour cherry Marasca was Cy-3-GR which represented 62.12 % of total ANTs, followed by Cy-3-R (26.59 %). The results obtained were similar with previous data for Marasca sour cherries (Pedisić et al. 2010; Elez-Garofulić et al. 2013; Zorić et al., 2014). Anthocyanin content is affected by numerous factors (agrotechnical procedures, geographical origin, cultivation, stage of maturity, harvesting, climatic and storage conditions etc. (Ferretti et al. 2010). Wojdyło et al. (2014b) researched 33 Polish cherry cultivars and results indicated cultivar influence on individual ANTs content. The FGs in Marasca cherries included K-3-G, K-3-R and the most abundant Q-3-G which represented 40.27 % of total FGs. Five phenolic acids, NChA, ChA, CA, *p*-CA and FA were determined in range from 7.81 to 39.70 mg/100 g d.m. The most abundant HCAs were *p*-CA, NChA and CA which individually represented approximately 30 % of the total HCAs what is in accordance with previously reported results for 33 Polish sour cherry cultivars, (NChA ~47 %, ChA ~ 30 %) (Wojdyło et al. 2014a, b).

FD did not considerable affect the polyphenol content in cherry samples, therefore decrease in total HCAs, ANTs and FG was only 5.02 %, 4.28 % and 1.49 %, respectively. In FDSCM among HCAs, the highest decrease was for FA almost 40 %, while the most stable was ChA which decrease of 2.82 %.

ANTs in FDSCM were retained in high proportion between 94.56 % (Cy-3-GR) to 99.86 % (Cy-3-R). The results of this study are consistent with those reported in the literature which showed that FD provided greater retention of polyphenol compounds with respect to other drying techniques (Michalczyk et al. 2009; Wojdyło et al. 2014b). Previous study on FDSCM paste showed that the heating temperature and duration affect the anthocyanins considerably more than the other phenols in terms of degradation what is linked with their cation structure (Zorić et al. 2014).

**Table 1** Anthocyanins and flavonol glycosides in freeze-dried Marasca sour cherry packed in two laminate and storage in three different temperature after 0, 3, 6, 9 and 12 months

Packaging material	Storage conditions	Months	Anthocyanins (mg/100 g dry matter)			Flavonol glycosides (mg/100 g dry matter)					
			Cy-3-S <sup>a</sup>	Cy-3-GR	Cy-3-G	Cy-3-R	TA	Q-3-G	K-3-G	K-3-R	TFG
PET/PPmet/PE	4 °C	Fresh fruit	27.71 ± 0.17	231.60 ± 0.77	14.38 ± 0.35	99.15 ± 0.37	372.84 ± 1.67	16.79 ± 0.03	13.92 ± 0.01	10.98 ± 0.03	41.69 ± 0.07
		Freeze-dried (0/control)	25.37 ± 0.33	219.00 ± 2.95	13.52 ± 0.10	99.01 ± 0.35	356.90 ± 3.72	16.62 ± 0.03	13.68 ± 0.03	10.78 ± 0.05	41.07 ± 0.11
		3	22.40 ± 0.11 <sup>a</sup>	215.35 ± 0.41 <sup>a</sup>	15.32 ± 0.08 <sup>a</sup>	103.98 ± 0.12 <sup>a</sup>	357.05 ± 0.73 <sup>a</sup>	14.08 ± 0.04 <sup>a</sup>	12.99 ± 0.03 <sup>a</sup>	11.92 ± 0.03 <sup>a</sup>	38.99 ± 0.09 <sup>a</sup>
		6	20.79 ± 0.38 <sup>b</sup>	198.28 ± 0.05 <sup>b</sup>	14.01 ± 0.09 <sup>b</sup>	92.47 ± 0.18 <sup>b</sup>	325.55 ± 0.71 <sup>b</sup>	13.68 ± 0.03 <sup>b</sup>	12.41 ± 0.03 <sup>b</sup>	10.54 ± 0.01 <sup>b</sup>	36.62 ± 0.07 <sup>b</sup>
	20 °C	9	20.16 ± 0.25 <sup>b</sup>	166.04 ± 0.25 <sup>c</sup>	12.30 ± 0.27 <sup>c</sup>	70.77 ± 0.17 <sup>c</sup>	269.26 ± 0.95 <sup>c</sup>	12.79 ± 0.05 <sup>c</sup>	11.67 ± 0.04 <sup>c</sup>	10.16 ± 0.04 <sup>c</sup>	34.62 ± 0.13 <sup>c</sup>
		12	17.73 ± 0.12 <sup>c</sup>	162.10 ± 0.12 <sup>d</sup>	10.36 ± 0.14 <sup>d</sup>	68.42 ± 0.10 <sup>d</sup>	258.61 ± 0.47 <sup>d</sup>	6.61 ± 0.02 <sup>d</sup>	6.04 ± 0.03 <sup>d</sup>	9.46 ± 0.03 <sup>d</sup>	22.10 ± 0.08 <sup>d</sup>
		3	10.14 ± 0.06 <sup>a</sup>	107.56 ± 0.11 <sup>a</sup>	5.91 ± 0.05 <sup>a</sup>	50.91 ± 0.10 <sup>a</sup>	174.52 ± 0.32 <sup>a</sup>	9.60 ± 0.01 <sup>a</sup>	9.61 ± 0.02 <sup>a</sup>	7.66 ± 0.04 <sup>a</sup>	26.87 ± 0.07 <sup>a</sup>
		6	5.72 ± 0.17 <sup>b</sup>	77.68 ± 0.08 <sup>b</sup>	4.62 ± 0.13 <sup>b</sup>	48.53 ± 0.08 <sup>b</sup>	136.54 ± 0.46 <sup>b</sup>	8.33 ± 0.05 <sup>b</sup>	7.92 ± 0.03 <sup>b</sup>	5.98 ± 0.04 <sup>b</sup>	22.23 ± 0.11 <sup>b</sup>
	37 °C	9	4.44 ± 0.17 <sup>c</sup>	58.06 ± 0.11 <sup>c</sup>	2.65 ± 0.10 <sup>c</sup>	32.62 ± 0.08 <sup>c</sup>	97.77 ± 0.46 <sup>c</sup>	7.50 ± 0.01 <sup>c</sup>	6.81 ± 0.03 <sup>c</sup>	5.43 ± 0.03 <sup>c</sup>	19.73 ± 0.06 <sup>c</sup>
		12	3.10 ± 0.13 <sup>d</sup>	39.53 ± 0.15 <sup>d</sup>	2.21 ± 0.04 <sup>d</sup>	25.27 ± 0.01 <sup>d</sup>	70.10 ± 0.33 <sup>d</sup>	6.17 ± 0.04 <sup>d</sup>	5.96 ± 0.04 <sup>d</sup>	4.38 ± 0.01 <sup>d</sup>	16.51 ± 0.09 <sup>d</sup>
		3	0.25 ± 0.04 <sup>a</sup>	4.02 ± 0.10 <sup>a</sup>	0.65 ± 0.05 <sup>a</sup>	5.71 ± 0.03 <sup>a</sup>	10.63 ± 0.21 <sup>a</sup>	11.49 ± 0.03 <sup>a</sup>	13.34 ± 0.03 <sup>a</sup>	11.33 ± 0.03 <sup>a</sup>	36.16 ± 0.08 <sup>a</sup>
		6	0.10 ± 0.01 <sup>b</sup>	2.00 ± 0.02 <sup>b</sup>	0.21 ± 0.01 <sup>b</sup>	0.73 ± 0.03 <sup>b</sup>	3.03 ± 0.07 <sup>b</sup>	6.82 ± 0.01 <sup>b</sup>	7.48 ± 0.02 <sup>b</sup>	6.25 ± 0.02 <sup>b</sup>	20.55 ± 0.05 <sup>b</sup>
PET/Al/PE	4 °C	9	–	0.02 ± 0.02 <sup>c</sup>	0.03 ± 0.02 <sup>c</sup>	0.03 ± 0.01 <sup>c</sup>	0.08 ± 0.06 <sup>c</sup>	3.71 ± 0.02 <sup>c</sup>	6.65 ± 0.02 <sup>c</sup>	5.78 ± 0.01 <sup>c</sup>	16.13 ± 0.05 <sup>c</sup>
		12	–	–	–	–	–	0.15 ± 0.02 <sup>d</sup>	0.42 ± 0.03 <sup>d</sup>	0.40 ± 0.02 <sup>d</sup>	0.97 ± 0.08 <sup>d</sup>
		3	25.03 ± 0.09 <sup>a</sup>	214.53 ± 0.11 <sup>a</sup>	16.70 ± 0.07 <sup>a</sup>	95.33 ± 0.07 <sup>a</sup>	351.59 ± 0.34 <sup>a</sup>	16.36 ± 0.03 <sup>a</sup>	12.79 ± 0.02 <sup>a</sup>	9.74 ± 0.03 <sup>a</sup>	38.89 ± 0.08 <sup>a</sup>
		6	23.60 ± 0.10 <sup>b</sup>	203.60 ± 0.11 <sup>b</sup>	13.61 ± 0.05 <sup>b</sup>	92.90 ± 0.05 <sup>b</sup>	333.70 ± 0.31 <sup>b</sup>	15.28 ± 0.02 <sup>b</sup>	10.36 ± 0.02 <sup>b</sup>	9.55 ± 0.01 <sup>b</sup>	35.19 ± 0.05 <sup>b</sup>
	20 °C	9	21.20 ± 0.03 <sup>c</sup>	188.52 ± 0.05 <sup>c</sup>	13.16 ± 0.10 <sup>b</sup>	77.70 ± 0.07 <sup>c</sup>	300.58 ± 0.25 <sup>c</sup>	13.35 ± 0.01 <sup>c</sup>	11.49 ± 0.22 <sup>b</sup>	8.96 ± 0.03 <sup>c</sup>	33.80 ± 0.25 <sup>c</sup>
		12	16.27 ± 0.12 <sup>d</sup>	162.96 ± 0.11 <sup>d</sup>	9.80 ± 0.13 <sup>c,d</sup>	73.15 ± 0.06 <sup>d</sup>	262.18 ± 0.42 <sup>d</sup>	11.10 ± 0.04 <sup>d</sup>	6.01 ± 0.08 <sup>c</sup>	7.01 ± 0.01 <sup>d</sup>	24.11 ± 0.13 <sup>d</sup>
		3	7.45 ± 0.06 <sup>a</sup>	75.41 ± 0.77 <sup>a</sup>	4.41 ± 0.03 <sup>a</sup>	37.85 ± 0.05 <sup>a</sup>	125.12 ± 0.92 <sup>a</sup>	11.93 ± 0.03 <sup>a</sup>	10.67 ± 0.04 <sup>a</sup>	8.02 ± 0.02 <sup>a</sup>	30.63 ± 0.08 <sup>a</sup>
		6	4.84 ± 0.01 <sup>b</sup>	59.65 ± 0.20 <sup>b</sup>	3.53 ± 0.04 <sup>b</sup>	35.28 ± 0.02 <sup>b</sup>	103.29 ± 0.27 <sup>b</sup>	8.09 ± 0.03 <sup>b</sup>	6.63 ± 0.02 <sup>b</sup>	5.08 ± 0.02 <sup>b</sup>	19.79 ± 0.07 <sup>b</sup>
	37 °C	9	3.32 ± 0.05 <sup>c</sup>	50.40 ± 0.09 <sup>c</sup>	2.61 ± 0.02 <sup>c</sup>	30.51 ± 0.04 <sup>c</sup>	86.84 ± 0.19 <sup>c</sup>	5.58 ± 0.02 <sup>c</sup>	4.75 ± 0.04 <sup>c</sup>	3.86 ± 0.02 <sup>c</sup>	14.19 ± 0.08 <sup>c</sup>
		12	2.22 ± 0.04 <sup>d</sup>	40.01 ± 0.10 <sup>d</sup>	2.57 ± 0.03 <sup>c,d</sup>	28.02 ± 0.05 <sup>d</sup>	72.82 ± 0.22 <sup>d</sup>	5.30 ± 0.03 <sup>d</sup>	4.22 ± 0.04 <sup>d</sup>	3.36 ± 0.05 <sup>d</sup>	12.88 ± 0.12 <sup>d</sup>
		3	–	7.25 ± 0.04 <sup>a</sup>	1.00 ± 0.06 <sup>a</sup>	8.30 ± 0.02 <sup>a</sup>	16.55 ± 0.12 <sup>a</sup>	10.57 ± 0.02 <sup>a</sup>	11.82 ± 0.03 <sup>a</sup>	9.25 ± 0.02 <sup>a</sup>	31.63 ± 0.07 <sup>a</sup>
		6	–	0.10 ± 0.02 <sup>b</sup>	0.07 ± 0.01 <sup>b</sup>	0.11 ± 0.02 <sup>b</sup>	0.28 ± 0.06 <sup>b</sup>	8.99 ± 0.03 <sup>b</sup>	6.90 ± 0.04 <sup>b</sup>	7.19 ± 0.03 <sup>b</sup>	23.08 ± 0.10 <sup>b</sup>
12	9	–	0.01 ± 0.01 <sup>c</sup>	0.03 ± 0.00 <sup>b,c</sup>	0.03 ± 0.02 <sup>b,c</sup>	0.07 ± 0.03 <sup>c</sup>	5.04 ± 0.03 <sup>c</sup>	4.86 ± 0.04 <sup>c</sup>	6.85 ± 0.04 <sup>c</sup>	16.75 ± 0.11 <sup>c</sup>	
	12	–	–	–	–	–	0.86 ± 0.03 <sup>d</sup>	0.37 ± 0.03 <sup>d</sup>	1.37 ± 0.03 <sup>d</sup>	2.60 ± 0.10 <sup>d</sup>	

The results in the individual lines marked by the same letters do not differ statistically at  $p \leq 0.05$

<sup>a</sup> cyanidin-3-sophoroside (Cy-3-S), cyanidin-3-glucosylrutinoside (Cy-3-GR), cyanidin-3-glucoside (Cy-3-G), cyanidin-3-rutinoside (Cy-3-R); Total anthocyanins (TA), quercetin-3-glucoside (Q-3-G); kaempferol-3-glucoside (K-3-G), kaempferol-3-rutinoside (K-3-R), Total flavonol glycosides (TFG)

**Table 2** Phenolic acids in freeze-dried Marasca sour cherry packed in two laminate and storage in three different temperature after 0, 3, 6, 9 and 12 months

Packaging material	Storage conditions	Months	Phenolic acids (mg/100 g dry matter)					
			NChA <sup>A</sup>	<i>p</i> -CA	ChA	CA	FA	TPA
		Fresh fruit	37.24 ± 0.06	39.70 ± 0.67	3.90 ± 0.02	36.58 ± 0.02	7.81 ± 0.04	125.23 ± 0.81
		Freeze-dried (0/control)	36.51 ± 0.05	39.43 ± 0.03	3.79 ± 0.03	35.94 ± 0.03	3.04 ± 0.01	118.94 ± 0.15
PET/PPmet/PE	4 °C	3	36.43 ± 0.03 <sup>a</sup>	39.11 ± 0.04 <sup>a</sup>	2.12 ± 0.02 <sup>a</sup>	35.59 ± 0.03 <sup>a</sup>	2.49 ± 0.02 <sup>a</sup>	112.15 ± 0.19 <sup>a</sup>
		6	35.67 ± 0.03 <sup>b</sup>	38.74 ± 0.05 <sup>b</sup>	1.30 ± 0.05 <sup>b</sup>	34.26 ± 0.04 <sup>b</sup>	2.19 ± 0.03 <sup>b</sup>	92.26 ± 0.30 <sup>b</sup>
		9	29.93 ± 0.06 <sup>c</sup>	31.69 ± 0.04 <sup>c</sup>	0.86 ± 0.06 <sup>c</sup>	28.41 ± 0.12 <sup>c</sup>	1.37 ± 0.01 <sup>c</sup>	87.01 ± 0.38 <sup>c</sup>
		12	29.52 ± 0.05 <sup>d</sup>	29.21 ± 0.04 <sup>d</sup>	0.81 ± 0.04 <sup>c,d</sup>	26.43 ± 0.03 <sup>d</sup>	1.03 ± 0.02 <sup>d</sup>	70.25 ± 0.26 <sup>d</sup>
	20 °C	3	22.08 ± 0.02 <sup>a</sup>	22.82 ± 0.02 <sup>a</sup>	0.78 ± 0.03 <sup>a</sup>	23.13 ± 0.03 <sup>a</sup>	1.44 ± 0.02 <sup>a</sup>	93.85 ± 0.16 <sup>a</sup>
		6	20.34 ± 0.03 <sup>b</sup>	21.94 ± 0.05 <sup>b</sup>	0.64 ± 0.01 <sup>b</sup>	21.16 ± 0.02 <sup>b</sup>	1.10 ± 0.03 <sup>b</sup>	65.18 ± 0.21 <sup>b</sup>
		9	16.47 ± 0.04 <sup>c</sup>	16.32 ± 0.04 <sup>c</sup>	0.58 ± 0.01 <sup>b,c</sup>	18.19 ± 0.03 <sup>c</sup>	0.77 ± 0.02 <sup>c</sup>	52.32 ± 0.17 <sup>c</sup>
		12	13.42 ± 0.04 <sup>d</sup>	13.16 ± 0.04 <sup>d</sup>	0.54 ± 0.02 <sup>c,d</sup>	13.64 ± 0.04 <sup>d</sup>	0.55 ± 0.02 <sup>d</sup>	41.31 ± 0.22 <sup>d</sup>
	37 °C	3	10.71 ± 0.02 <sup>a</sup>	11.99 ± 0.04 <sup>a</sup>	3.56 ± 0.02 <sup>a</sup>	17.96 ± 0.05 <sup>a</sup>	1.23 ± 0.03 <sup>a</sup>	45.45 ± 0.21 <sup>a</sup>
		6	10.36 ± 0.01 <sup>b</sup>	11.67 ± 0.04 <sup>b</sup>	3.08 ± 0.03 <sup>b</sup>	14.25 ± 0.00 <sup>b</sup>	1.08 ± 0.03 <sup>b</sup>	40.44 ± 0.17 <sup>b</sup>
		9	5.56 ± 0.03 <sup>c</sup>	7.67 ± 0.02 <sup>c</sup>	2.64 ± 0.02 <sup>c</sup>	9.78 ± 0.02 <sup>c</sup>	0.01 ± 0.01 <sup>c</sup>	25.66 ± 0.16 <sup>c</sup>
		12	0.24 ± 0.04 <sup>d</sup>	0.30 ± 0.04 <sup>d</sup>	0.15 ± 0.01 <sup>d</sup>	0.41 ± 0.03 <sup>d</sup>	-	1.56 ± 0.12 <sup>d</sup>
PET/Al/PE	4 °C	3	36.69 ± 0.04 <sup>a</sup>	30.05 ± 0.05 <sup>a</sup>	1.79 ± 0.03 <sup>a</sup>	34.80 ± 0.03 <sup>a</sup>	2.28 ± 0.03 <sup>a</sup>	105.61 ± 0.18 <sup>a</sup>
		6	36.15 ± 0.05 <sup>b</sup>	28.30 ± 0.03 <sup>b</sup>	1.21 ± 0.03 <sup>b</sup>	34.74 ± 0.02 <sup>a</sup>	2.18 ± 0.01 <sup>a</sup>	102.58 ± 0.14 <sup>b</sup>
		9	27.00 ± 0.07 <sup>c</sup>	27.49 ± 0.01 <sup>c</sup>	0.86 ± 0.01 <sup>c</sup>	23.67 ± 0.01 <sup>b</sup>	1.23 ± 0.03 <sup>b</sup>	80.25 ± 0.12 <sup>c</sup>
		12	25.06 ± 0.04 <sup>d</sup>	27.31 ± 0.03 <sup>d</sup>	0.74 ± 0.06 <sup>c,d</sup>	21.75 ± 0.05 <sup>c,d</sup>	0.85 ± 0.02 <sup>c,d</sup>	75.72 ± 0.20 <sup>d</sup>
	20 °C	3	22.29 ± 0.03 <sup>a</sup>	24.11 ± 0.04 <sup>a</sup>	0.80 ± 0.02 <sup>a</sup>	23.38 ± 0.02 <sup>a</sup>	1.73 ± 0.01 <sup>a</sup>	72.31 ± 0.12 <sup>a</sup>
		6	16.80 ± 0.01 <sup>b</sup>	16.24 ± 0.03 <sup>b</sup>	0.71 ± 0.02 <sup>b</sup>	17.28 ± 0.03 <sup>b</sup>	1.02 ± 0.03 <sup>b</sup>	52.05 ± 0.12 <sup>b</sup>
		9	13.64 ± 0.03 <sup>c</sup>	14.49 ± 0.04 <sup>c</sup>	0.43 ± 0.02 <sup>c</sup>	12.68 ± 0.03 <sup>c</sup>	0.96 ± 0.01 <sup>b</sup>	42.19 ± 0.13 <sup>c</sup>
		12	11.58 ± 0.05 <sup>d</sup>	11.92 ± 0.02 <sup>d</sup>	0.31 ± 0.02 <sup>c,d</sup>	11.72 ± 0.03 <sup>d</sup>	0.77 ± 0.03 <sup>c,d</sup>	36.30 ± 0.15 <sup>d</sup>
	37 °C	3	12.49 ± 0.02 <sup>a</sup>	13.33 ± 0.05 <sup>a</sup>	4.47 ± 0.04 <sup>a</sup>	16.03 ± 0.03 <sup>a</sup>	1.53 ± 0.05 <sup>a</sup>	48.11 ± 0.18 <sup>a</sup>
		6	10.75 ± 0.04 <sup>b</sup>	12.22 ± 0.03 <sup>b</sup>	3.14 ± 0.04 <sup>b</sup>	14.89 ± 0.04 <sup>b</sup>	1.01 ± 0.03 <sup>b</sup>	42.00 ± 0.17 <sup>b</sup>
		9	9.01 ± 0.05 <sup>c</sup>	12.07 ± 0.03 <sup>c</sup>	2.11 ± 0.03 <sup>c</sup>	14.42 ± 0.05 <sup>c</sup>	0.17 ± 0.02 <sup>c</sup>	37.77 ± 0.17 <sup>c</sup>
		12	2.70 ± 0.04 <sup>d</sup>	3.91 ± 0.03 <sup>d</sup>	1.86 ± 0.01 <sup>d</sup>	5.08 ± 0.05 <sup>d</sup>	-	13.35 ± 0.13 <sup>d</sup>

The results in the individual lines marked by the same letters do not differ statistically at  $p \leq 0.05$

<sup>A</sup> Neochlorogenic acid (NChA), *p*-coumaric acid (*p*-CA), chlorogenic acid (ChA), caffeic acid (CA), ferulic acid (FA), Total phenolic acids (TPA)

### The influence of packaging material and storage conditions on polyphenols stability and AOC in freeze-dried Marasca sour cherries

The optimal combination choice of the packaging material and storage conditions is very important for retaining the quality of FDSCM during storage. Multi-layer polymer materials such as PET/Al/PE and PET/PPmet/PE laminates used in this study have good barrier properties against light, gas and vapour (Gvozdenović et al. 2007).

After 6 months of storage total ANT content decreased in the cherry products packed in PET/PPmet/PE laminate less than 10 % at 4 °C, while at 20 °C and at 37 °C decrease was for 61.75 % and 99.15 %, respectively. At same storage conditions, samples packed in PET/Al/PE laminate showed similar trend, also. Compared to control samples (after FD) the

content of total ANTs was slightly higher in cherry samples stored in PET/Al/PE laminate at 4 °C after 12 month of storage (262.18 mg/100 g d.m.) than in samples stored in PET/PPmet/PE laminate (258.61 mg/100 g d.m.). Same trend was observed for samples stored at room temperature (20 °C). Individual ANTs were stable in both types of packaging at 4 °C, while greater stability was observed in PET/Al/PE laminate at 20 °C. In order to determine the level of degradation in extreme storage conditions, the samples were also stored at 37 °C and regardless of the packaging type more than 90 % of total ANTs were lost after 3 months of storage. ANT degradation can be result of different oxidation processes especially at elevated temperature and cleavage of a covalent bond. At elevated storage temperature, ANT glycosides loss sugar moieties and in next step aglycons degrade to aldehydes and benzoic acid derivatives (Zhang et al. 2012). According to

Fracassetti et al. (2013) storage at different temperatures reduced individual and total ACN content of freeze-dried blueberry powder; it was slower at 25 °C (−3 % after 2 weeks), whereas it was faster at 60 °C (−60 %) and at 80 °C (−85 %) after 3 days. Total ANTs of freeze dried blackcurrant packed in PE/PA bags at 18 °C for 5 months decreased about 21 % (Kampuse et al. 2009). Piasecka et al. (2013) reported losses of ANTs about 6 % in convectively dried sour cherry samples packed hermetically in seal laminated foil bags at 18 °C after 12 months of storage. FGs of FDSCM were more stable than ANTs during storage and after 12 months of storage, the lowest degradation was observed at 4 °C, while maximal degradation was at 37 °C, as expected. Comparing packaging materials at the same storage conditions, samples had similar total FG content. Degradation of FGs was more than 60 % in samples packed in both laminates and stored at 20 °C during 12 months of storage. The most stable individual FG at all storage temperatures after 12 months was K-3-R. According to Pérez-Gregorio et al. (2011) all flavonols were stable in freeze-dried onion powder stored at room temperature in air- and water-tight glass bottles for up to 6 months.

Stability of FGs was similarly as the stability of HCAs at same storage conditions (Table 2). In samples stored at 20 °C decreases in total HCAs were more intensively in first 3 months of storage especially in samples packed in PET/Al/PE (57 %) and after 12 months of storage was about 65 % in both packaging material. Piasecka et al. (2013) reported significant decrease of total HCAs of dried sour cherry samples packed in seal laminated foil bags at 18 °C during the first 3 months of storage.

It could be explain that degradation is more rapid in samples with higher dry matter due to reacting molecules become closer to polyphenol compounds and accelerate the rate of chemical reactions (Wang and Xu 2007).

The most stable HCAs at 4 °C and 20 °C after 12 months of storage were NChA, *p*-CA and CA which decreased in PET/PPmet/PE in range from 19.15 % - 62.05 % and in PET/Al/PE in range from 30.74 % - 69.77 %. At the same storage period ChA had the lowest decrease in samples stored at 37 °C in PET/Al/PE (50.92 %), while in samples stored in PET/PPmet/PP laminate decreased for 96.04 %.

At least 50 % of initial polyphenol content (expressed as sum of ANTs, FGs and HCAs) in cherry samples stored at 20 °C packed in PET/PPmet/PE was retained during 6 months of storage, whereas samples packed in PET/Al/PE retained the same percentage during 3 months. Randelović et al. (2014) researched quality changes of dried apricot packed in different packaging materials during 12-months storage period at room temperature and results showed the highest polyphenol stability in PET/Al/PE laminate. According to Henriquez et al. (2013) in the apple peel powder stored at 38 °C for 120 days the loss of polyphenols was higher when packed in high density polyethylene than in metalized films of high

barrier. In dried *Moringa oleifera* leaves packed in PET/Al/PE total phenols decreased for 19 % at 15 °C during up to 6 months of storage (Potisate et al. 2015). Del Caro et al. (2004) showed that different polyphenol groups may differ significantly in stability during storage.

In this study, ANOVA showed that storage time and temperature significantly affected polyphenol stability during storage ( $p \leq 0.05$ ).

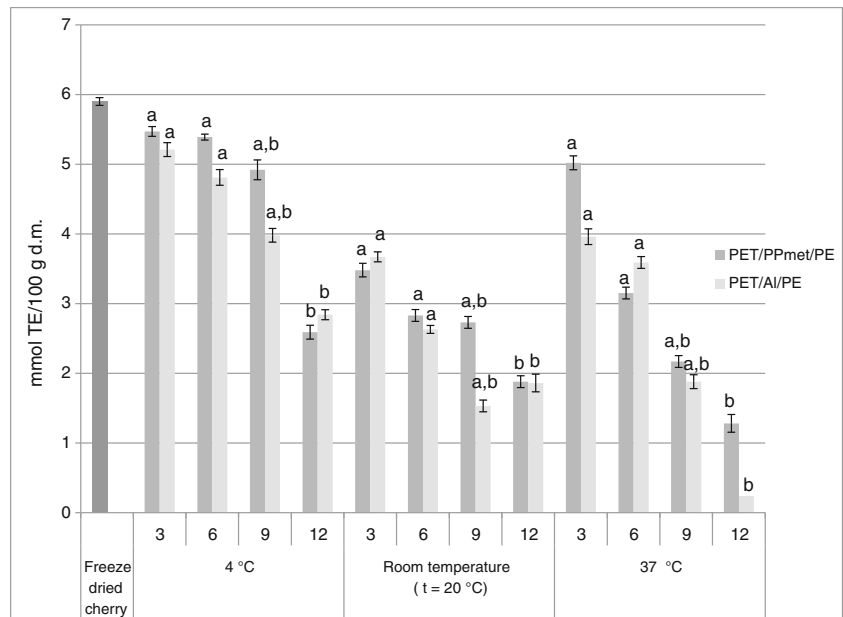
The antioxidant capacity (AOC) of the FDSCM decreased significantly during storage (Fig. 1). The lowest AOC in FDSCM packed in both type of packaging materials was determined in products stored at 37 °C after 12 months, while the highest AOC values was determined in products stored at 4 °C after 3 months. Significant reduction of the AOC in FDSCM packed in PET/PPmet/PE, stored at 4 °C after 9 months was observed, whereas in the samples packaged in PET/Al/PE significant reduction of AOC is determined after 6 months of storage. It seems that the decrease in AOC do not follows the same pattern as polyphenol (ANTs) reduction in the stored samples what is in accordance with other reports (Zafrilla et al. 2003). FDSCM are very complex matrix, and correlation between individual groups of polyphenols and AOC revealed that FGs ( $r = 0.93$ – $0.95$ ) make greater contribution to the AOC of FDSCM than ANTs ( $r = 0.79$ – $0.96$ ) and HCAs ( $r = 0.77$ – $0.83$ ).

According to MANOVA, storage conditions (temperature and time), affected AOC in FDSCM, *regardless of the type of packaging material*, ( $p \leq 0.05$ ). This variation in the AOC is related with structural differences of the antioxidant compounds involved (Rice-Evans et al. 1996). Some authors reported that delphinidin and Cy-3-R are less active in the DPPH scavenging activity than the corresponding monoglucosides (Kähkönen and Heinonen 2003). According to Razzaghi-Asl et al. (2013) the presence of an unsaturated bond on the side chain of HCAs is vital to their activity. During storage *polyphenol compounds* are *susceptible* to oxidation what probably have major impact on AOC in FDSCM products.

### The influence of packaging material and storage conditions on colour characteristics in freeze-dried Marasca sour cherries

Colour is one of the important quality parameters that affect the acceptability of the final product and depend on processing and storage conditions. The colour of FDSCM during storage was reported as CIE  $L^*$ ,  $a^*$ ,  $b^*$  and  $H$  values and the results are shown in Table 3. Marasca sour cherry products have intense dark red almost black colour. The results showed similar changes in the colour of FDSCM packed in both packaging materials and they had high values of colour parameter  $a$  (redness of samples), which is attributed to ANTs content. The highest decrease in  $a$  was in samples stored at 37 °C in both

**Fig. 1** Antioxidant capacity of freeze-dried cherry Marasca before and after packaging in two types of laminates (PET/PPmet/PE and PET/Al/PE) during 12 months of storage at three different temperature



<sup>a,b</sup>The results in the individual lines marked by the same letters do not differ statistically at  $p \leq 0.05$ .

packaging materials after 9 and 12 months of storage. Parameter  $L^*$ , which represents lightness of sample, increased among cherry samples during storage regardless of storage conditions. Decrease in  $a^*$  and increase in  $L^*$  values is an indication of discoloration, which could be influenced by the degradation of ANT<sub>s</sub> (Estupiñan et al. 2011).

The chroma value ( $C$ ) represents colour intensity, while hue angle ( $H^\circ$ ) depicts how an average person will perceive that colour (Siddiq et al. 2011). The highest decrease of  $C$  values was in samples stored at 37 °C regardless of the packaging material what suggests instability of red colour in stored samples. The greatest increase of  $H^\circ$  was in samples stored at 37 °C after 9 and 12 months of storage, but stored samples maintained  $H^\circ < 40^\circ$  what indicates that samples conserved dark red colour (McGuire R.G. 1992). Presented results of the  $\Delta E$  values indicate that all stored samples are darker than the initial samples of FDSCM what is consistent with previous reports (Wojdyło et al. 2014a). Formation of dark brown pigment during storage is possible as a result of non-enzymatic browning reactions or to a lesser extent as result of Maillard reaction and caramelisation (Sloan et al. 1969).

The TA in packed FDSCM products decreased linearly during storage with losses of >60 % after 6 month of storage and change of Lab colour values indicate the formation of dark coloured pigments as result of condensation (polymerization) reactions of anthocyanins with other phenolic compounds. Consistent with the showed results storage of FDSCM products at 4 °C is a suitable way to stabilize the colour (redness).

### The influence of packaging material and storage conditions on sensory characteristics in freeze-dried Marasca sour cherries

Currently, consumer demand has increased for processed products that keep more of their original characteristics with preserved nutritional value. Results of sensory evaluation were summarised and displayed by Principal Component Analysis (PCA) to explore the inter-relationship between storage conditions and sensory parameters; in other words, which sensory attributes were characteristic in describing the sensory profile of the samples investigated. The variables were 17 sensory attributes and the cases were freeze dried samples. The first two factors (PC1 and PC2) represent 76.38 % of the initial data variability (Fig. 2). Figure 2 gives a visual representation of the differences between FDSCM packed in two different laminates, storage at 4 °C, 20 °C and 37 °C during 3, 6, 9 and 12 months. First principal component (PC1, 60.99 %) separated samples considering storage time, and second principal component (PC2, 74.91 %) separated samples considering storage temperature. Consequently, samples stored 9 and 12 months were mostly positioned on the left, and samples stored at 3 and 6 months as well as control sample, on the right side of the PC1. Samples stored at 4 °C were the most characterized by colour intensity. That is reasonable considering that FD has been shown to positively affect the stability of the colour, thus freeze-dried materials are usually more colourful, than the conventional air-dried samples (Ratti 2001). Sensory attributes of odour intensity, sour cherry odour, sour cherry flavour, fruity flavour, sour

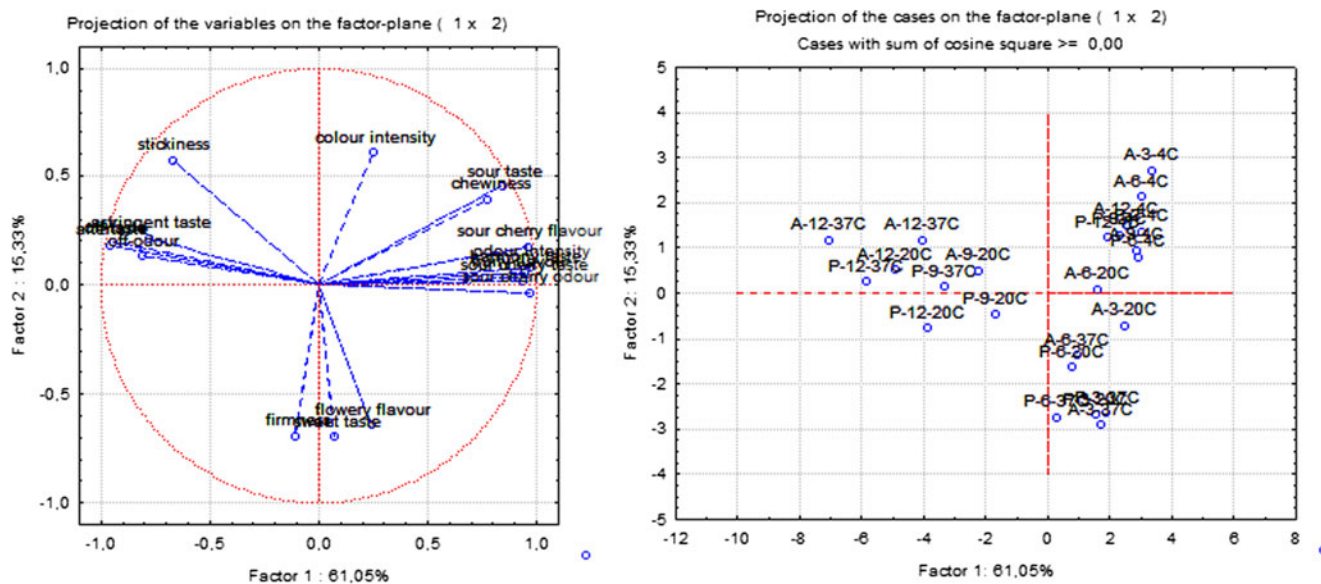


**Table 3** Colour parameters of freeze-dried Marasca sour cherry packed in two laminate and storage in three different temperature after 0, 3, 6, 9 and 12 months

Storage conditions (months)	Packaging material	PET/Al/PE											
		PET/PPmet/PE					PET/Al/PE						
		L*(D65)	a*(D65)	b*(D65)	H(D65)	C*(D65)	ΔE	L*(D65)	a*(D65)	b*(D65)	H(D65)	C*(D65)	ΔE
4 °C	Freeze-dried sour cherries	15.13 ± 0.03	10.37 ± 0.03	0.65 ± 0.03	3.54 ± 0.03	10.43 ± 0.03		15.13 ± 0.03	10.37 ± 0.03	0.65 ± 0.03	3.54 ± 0.03	10.43 ± 0.03	
		15.2 ± 0.02 <sup>d</sup>	14.6 ± 0.02 <sup>b</sup>	3.64 ± 0.01 <sup>b</sup>	13.98 ± 0.02 <sup>d</sup>	15.03 ± 0.01 <sup>b</sup>	5.19 ± 0.03 <sup>d</sup>	11.41 ± 0.01 <sup>d</sup>	16.92 ± 0.02 <sup>a</sup>	4.63 ± 0.01 <sup>a</sup>	15.23 ± 0.03 <sup>b</sup>	17.57 ± 0.02 <sup>a</sup>	8.52 ± 0.02 <sup>d</sup>
		21.7 ± 0.01 <sup>c</sup>	9.89 ± 0.02 <sup>c</sup>	2.74 ± 0.02 <sup>d</sup>	15.58 ± 0.01 <sup>c</sup>	10.24 ± 0.01 <sup>c</sup>	7.00 ± 0.03 <sup>c</sup>	23.39 ± 0.02 <sup>b</sup>	16.60 ± 0.01 <sup>b</sup>	4.49 ± 0.02 <sup>a</sup>	15.05 ± 0.03 <sup>c</sup>	17.17 ± 0.01 <sup>b</sup>	11.03 ± 0.02 <sup>b</sup>
		26.63 ± 0.02 <sup>a</sup>	16.03 ± 0.02 <sup>a</sup>	4.77 ± 0.01 <sup>a</sup>	16.52 ± 0.01 <sup>b</sup>	16.76 ± 0.03 <sup>a</sup>	13.46 ± 0.00 <sup>a</sup>	22.06 ± 0.01 <sup>c</sup>	3.99 ± 0.04 <sup>d</sup>	0.97 ± 0.03 <sup>c,d</sup>	13.47 ± 0.01 <sup>d</sup>	14.06 ± 0.02 <sup>d</sup>	9.43 ± 0.02 <sup>c</sup>
20 °C		25.25 ± 0.03 <sup>b</sup>	9.61 ± 0.01 <sup>d</sup>	3.15 ± 0.01 <sup>c</sup>	18.08 ± 0.02 <sup>a</sup>	10.09 ± 0.02 <sup>d</sup>	10.45 ± 0.05 <sup>b</sup>	25.92 ± 0.02 <sup>a</sup>	15.23 ± 0.01 <sup>c</sup>	4.23 ± 0.03 <sup>a</sup>	15.61 ± 0.02 <sup>a</sup>	15.82 ± 0.01 <sup>c</sup>	12.36 ± 0.03 <sup>a</sup>
		22.07 ± 0.02 <sup>d</sup>	14.47 ± 0.01 <sup>a</sup>	3.72 ± 0.02 <sup>a</sup>	14.45 ± 0.01 <sup>c,d</sup>	14.94 ± 0.02 <sup>a</sup>	8.62 ± 0.03 <sup>d</sup>	12.80 ± 0.01 <sup>d</sup>	13.13 ± 0.02 <sup>a</sup>	4.15 ± 0.03 <sup>a</sup>	17.59 ± 0.01 <sup>a</sup>	13.79 ± 0.01 <sup>a</sup>	5.03 ± 0.05 <sup>d</sup>
		22.99 ± 0.01 <sup>c</sup>	5.76 ± 0.05 <sup>d</sup>	1.52 ± 0.01 <sup>d</sup>	15.02 ± 0.02 <sup>b</sup>	5.91 ± 0.02 <sup>d</sup>	9.16 ± 0.00 <sup>c</sup>	17.31 ± 0.02 <sup>c</sup>	4.09 ± 0.01 <sup>d</sup>	0.97 ± 0.01 <sup>d</sup>	13.37 ± 0.01 <sup>d</sup>	4.22 ± 0.02 <sup>d</sup>	6.66 ± 0.01 <sup>c</sup>
		24.66 ± 0.01 <sup>a</sup>	9.79 ± 0.02 <sup>c</sup>	2.65 ± 0.02 <sup>c</sup>	15.00 ± 0.02 <sup>b</sup>	10.16 ± 0.02 <sup>c</sup>	9.75 ± 0.02 <sup>a</sup>	24.10 ± 0.02 <sup>a</sup>	9.65 ± 0.02 <sup>c</sup>	2.85 ± 0.01 <sup>c</sup>	16.46 ± 0.01 <sup>b</sup>	10.05 ± 0.01 <sup>c</sup>	9.26 ± 0.00 <sup>a</sup>
37 °C		24.13 ± 0.02 <sup>b</sup>	11.85 ± 0.01 <sup>b</sup>	3.27 ± 0.01 <sup>b</sup>	15.34 ± 0.01 <sup>a</sup>	12.31 ± 0.01 <sup>b</sup>	9.48 ± 0.05 <sup>b</sup>	22.39 ± 0.01 <sup>b</sup>	11.35 ± 0.01 <sup>b</sup>	3.12 ± 0.02 <sup>b</sup>	15.30 ± 0.01 <sup>c</sup>	11.77 ± 0.01 <sup>b</sup>	7.73 ± 0.02 <sup>b</sup>
		18.01 ± 0.01 <sup>d</sup>	2.35 ± 0.01 <sup>b</sup>	0.69 ± 0.02 <sup>c</sup>	15.90 ± 0.01 <sup>c</sup>	2.43 ± 0.03 <sup>b</sup>	8.52 ± 0.00 <sup>d</sup>	21.90 ± 0.01 <sup>c</sup>	9.05 ± 0.01 <sup>b</sup>	2.35 ± 0.02 <sup>b</sup>	14.62 ± 0.03 <sup>d</sup>	9.34 ± 0.01 <sup>b</sup>	7.10 ± 0.00 <sup>d</sup>
		21.22 ± 0.02 <sup>b</sup>	3.06 ± 0.03 <sup>a</sup>	1.05 ± 0.01 <sup>a</sup>	19.23 ± 0.01 <sup>b</sup>	3.21 ± 0.01 <sup>a</sup>	9.52 ± 0.00 <sup>c</sup>	23.44 ± 0.00 <sup>a</sup>	12.47 ± 0.01 <sup>a</sup>	5.66 ± 0.01 <sup>a</sup>	24.42 ± 0.01 <sup>a</sup>	13.70 ± 0.01 <sup>a</sup>	9.93 ± 0.01 <sup>b</sup>
		22.01 ± 0.01 <sup>a</sup>	1.45 ± 0.02 <sup>d</sup>	0.29 ± 0.01 <sup>d</sup>	11.89 ± 0.01 <sup>d</sup>	1.48 ± 0.01 <sup>d</sup>	11.27 ± 0.02 <sup>a</sup>	22.61 ± 0.03 <sup>b</sup>	2.35 ± 0.01 <sup>c</sup>	1.72 ± 0.02 <sup>c</sup>	36.35 ± 0.02 <sup>a</sup>	2.95 ± 0.03 <sup>c</sup>	11.02 ± 0.03 <sup>a</sup>
	20.09 ± 0.02 <sup>c</sup>	1.77 ± 0.03 <sup>c</sup>	0.95 ± 0.02 <sup>b</sup>	27.41 ± 0.01 <sup>a</sup>	2.04 ± 0.02 <sup>c</sup>	9.93 ± 0.02 <sup>b</sup>	17.41 ± 0.02 <sup>d</sup>	1.03 ± 0.03 <sup>d</sup>	0.77 ± 0.01 <sup>d</sup>	35.77 ± 0.01 <sup>b</sup>	1.28 ± 0.02 <sup>d</sup>	9.61 ± 0.03 <sup>c</sup>	

*L\** whiteness or brightness/darkness, *a\** redness/greenness, *b\** yellowness/blueness, *H* hue angle, *C* chroma, *ΔE* total colour difference

<sup>a-d</sup> The results in the individual lines marked by the same letters do not differ statistically at *p* ≤ 0.05



**Fig. 2** PC1 vs. PC2 for sensory properties of freeze-dried sour cherry Marasca (a) and for storage conditions (b). A – samples packed in PET/Al/PE; P – samples packed in PET/PPmet/PE

**Table 4** Influence of storage temperature and packaging materials on the  $k$ ,  $t_{1/2}$  and  $E_a$  values of phenolic compounds degradation in freeze-dried sour cherry Marasca paste at 4 and 37 °C

Packaging material		PET/PPmet/PE				PET/Al/PE			
Compound	Temperature (°C)	$k^b \cdot 10^{-2} \text{ (week)}^{-1}$	$R^2$	$t_{1/2}^c \text{ (week)}$	$E_a^d \text{ (kJ/mol)}$	$k \cdot 10^{-2} \text{ (week)}^{-1}$	$R^2$	$t_{1/2} \text{ (week)}$	$E_a \text{ (kJ/mol)}$
Cy-3-S <sup>a</sup>	4	0.7114	0.93	97.43	86.254	0.6217	0.79	111.49	140.784
	37	38.3387	1.00	1.81		416.6467	1.00	0.17	
Cy-3-GR	4	0.5563	0.85	124.60	88.378	0.4363	0.85	158.87	90.276
	37	33.0721	0.99	2.10		28.3165	1.00	2.45	
Cy-3-G	4	0.2798	0.38	247.73	97.295	0.2613	0.23	265.27	95.607
	37	25.1198	0.99	2.76		21.6978	1.00	3.19	
Cy-3-R	4	0.6503	0.72	106.59	77.802	0.548	0.87	126.49	78.625
	37	23.7117	1.00	2.92		20.7568	1.00	3.34	
Q-3-G	4	1.1951	0.77	57.99	26.289	0.6278	0.86	110.41	36.784
	37	4.0287	0.96	17.21		3.4376	0.93	20.16	
K-3-G	4	0.9049	0.65	76.99	22.210	1.8507	0.96	66.49	23.090
	37	2.5262	0.78	27.49		2.176	0.81	22.87	
K-3-R	4	0.1666	0.37	416.05	56.679	0.6796	0.88	101.99	23.528
	37	2.2882	0.73	30.29		2.0164	0.78	34.38	
NChA	4	0.3876	0.75	178.83	63.263	0.6079	0.70	114.02	49.039
	37	7.2172	0.90	9.60		5.8652	0.86	11.82	
p-CA	4	0.4866	0.75	142.45	56.793	0.9805	0.23	70.69	36.744
	37	6.7187	0.88	10.32		5.3589	0.77	12.93	
ChA	4	4.1237	0.97	16.81	37.46	4.6179	0.95	15.01	32.74
	37	1.791	0.66	38.70		1.083	0.58	64.00	
CA	4	0.5259	0.82	131.80	46.474	0.8354	0.74	82.97	32.647
	37	4.5067	0.94	15.38		3.7781	0.77	18.35	
FA	4	1.9054	0.95	36.38	26.305	2.1766	0.92	31.85	20.929
	37	6.4277	0.92	10.78		5.7271	0.97	12.10	

<sup>a</sup> cyanidin-3-sophoroside (Cy-3-S), cyanidin-3-glucosylrutinoside (Cy-3-GR), cyanidin-3-glucoside (Cy-3-G), cyanidin-3-rutinoside (Cy-3-R); quercetin-3-glucoside (Q-3-G); kaempferol-3-glucoside (K-3-G), kaempferol-3-rutinoside (K-3-R), neochlorogenic acid (NChA), *p*-coumaric acid (*p*-CA), chlorogenic acid (ChA), caffeic acid (CA), ferulic acid (FA)

<sup>b</sup> Rate constant  
<sup>c</sup> Half life  
<sup>d</sup> Activation energy

and harmony taste showed strong correlation with the PC1 thus are attributes that best characterize samples stored at 4 °C. Sensory attributes such as flowery flavour and astringent taste were more observed in samples stored at 37 °C.

### The influence of packaging material and storage conditions on kinetic parameters in freeze-dried Marasca sour cherries

The results of determined kinetic parameters, the rate constant ( $k$ ), half-life values ( $t_{1/2}$ ) and activation energy ( $E_a$ ) confirmed also significant influence of storage temperature on the stability of BAC's in FDSCM samples (Table 4).

Comparing  $k$ -values in samples stored at 37 °C and at 4 °C, for Cy-3-GR as predominant ANT, the  $k$ -values increased about 60 folds and amounted 33.0721 weeks<sup>-1</sup> for samples packed in PET/PPmet/PE packaging and 28.316 weeks<sup>-1</sup> in samples packed in PET/Al/PE, respectively. The  $t_{1/2}$  of the individual ANTs in samples stored at 37 °C was from 0.17 (Cy-3-S in samples packed in PET/Al/PE packaging) to 3.34 weeks (Cy-3-R in samples packed in PET/Al/PE packaging). The  $t_{1/2}$  were higher in samples stored at 4 °C and amounted 97.43 weeks (Cy-3-S in samples in PET/PPmet/PE) to 126.49 weeks (Cy-3-R in samples in PET/Al/PE), respectively (Table 4).

FGs have similar values for kinetic parameters as ANT in samples stored at 4 °C. However, in samples stored at 37 °C all FGs showed more stability compared to the ANTs in both types of packaging. Half-life ( $t_{1/2}$ ) was from 17.21 weeks (Q-3-G in samples packed in PET/PPmet/PE) to 34.38 weeks (K-3-R) in samples packaged in PET/Al/PE, respectively. Van der Sluis et al. (2005) reported that the FGs and their derivatives are submissive to degradation during storage.

According to kinetic parameters, HCAs showed the highest stability compared to other groups of polyphenol compounds. In samples stored at 37 °C, the most stable HCA was ChA (in samples packed in PET/Al/PE), while NChA was the most unstable in samples packed in PET/PPmet/PE, respectively (Table 4).

The  $E_a$  in stored cherry samples was from 20.929 (FA) to 140.784 kJ/mol (Cy-3-S) what is approximately 1–3 folds higher than in FDSCM paste samples where degradation of polyphenol compounds during heat treatments was monitored (Zorić et al. 2014). These differences indicate positive effect of used packaging material on polyphenol stability in stored FDSCM.

Kinetic parameters indicate that phenolic stability depending on structure properties and composition of compounds present in FDSCM products as well as storage conditions.

## Conclusion

The results of this study showed that PET/PPmet/PE and PET/Al/PE can be effectively used for packaging of FDSCM during storage at 4 and 20 °C, with preservation BACs, colour and sensory properties. However, PET/PPmet/PE foil offer better retention of almost all group of polyphenols in FDSCM during 12 months of storage. Storage at lower temperatures prolongs shelf-life of cherry products and sensory and colour properties are better maintained, what is important for consumer's perception.

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