OPEN ACCESS Potravinarstvo Slovak Journal of Food Sciences

potravinárstvo® Slovak Journal of Food Sciences

Potravinarstvo Slovak Journal of Food Sciences
vol. 12, 2018, no. 1, p. 254-261
doi: https://doi.org/10.5219/902
Received: 11 February 2018. Accepted: 13 March 2018.
Available online: 21 March 2018 at www.potravinarstvo.com

ISSN 1337-0960 (online)

CHARACTERISTICS OF PAPRIKA SAMPLES OF DIFFERENT GEOGRAPHICAL ORIGIN

Václav Štursa, Pavel Diviš, Jaromír Pořízka

ABSTRACT

This study investigated 11 different kinds of ground paprika of different geographical origin and tried to find some correlations between their measured chemical composition and country of origin. The parameters examined in ground paprika were as follows: sample moisture, total content of ash, total content of lipids, total content of nitrogen, content of saccharides (glucose, fructose, sucrose), elemental analysis (selected elements were Ca, K, Mg, Na, Cu, Fe, P a Zn), ASTA color value and pH value of water extract. Average content of moisture in paprika was 10.7 ±1.7 %. Average content of ash in the paprika samples was 5.8 ±0.6. Average total lipid content in paprika was 10.6 ±3.3 %. Total content of nitrogen in paprika was 1.93 ±0.17 % in average. Content of fructose (316 ±92 $mg \cdot g^{-1}$), glucose (215 ±119 $mg \cdot g^{-1}$) and sucrose (92 ±41 $mg \cdot g^{-1}$) in ground paprika was measured by HPLC-ELSD. Elemental analysis has been performed by ICP-OES. Average content of individual elements was: Ca 27 ±7 $mg \cdot g^{-1}$, K 198 ±23 $mg \cdot g^{-1}$, Mg 23 ±4 $mg \cdot g^{-1}$, Na 20 ±4 $mg \cdot g^{-1}$, Cu 0.155 ±0.015 $mg \cdot g^{-1}$, Fe 1.2 ±0.4 $mg \cdot g^{-1}$, P 33 ±6 $mg \cdot g^{-1}$ and Zn 0.17 ±0.04 $mg \cdot g^{-1}$. Average ASTA color value of paprika samples was 119 ±31 ASTA. The pH value of paprika water extract was 5.13 ±0.12 in average. Obtained data were statistically processed with Analysis of Variance (ANOVA) on p <0.05 and with Principal Component Analysis (PCA). Statistical analysis of the data confirmed, that samples from more distant regions (Hungary, Spain, Turkey, Bulgaria) can be differentiated according to their different chemical composition, while samples from similar regions (Hungary, Slovakia, Romania) is more difficult to differentiate.

Keywords: paprika; *Capsicum anuum*; chemical analysis; geographical origin; PCA.

INTRODUCTION

Paprika as a spice are considered dried and ground fruits of certain plant varieties of *Capsicum anuum* var. *longum* L. Paprika *Capsicum* comes originally from Central America. It got to Europe thanks to Spanish travelers and was one of the first crops brought from America to Europe **(Peter et al., 2012)**. Today growing of paprika is spread all over the world. Paprika fruits after the harvest undergo some technological treatments which lead to spice product in kitchen used as a sweet paprika. Paprika is in cuisine mostly used for giving to meals taste and color **(Klimešová et al., 2015)**.

Paprika is a good source of many sensory and nutritionally significant compounds, such as compounds forming color pigment (capsanthin, capsorubin, cryptoxanthin, zeaxanthin etc.) **(Peter et al., 2012)**, flavor, pungent taste (capsaicin, dihydrocapsaicin) **(Popelka et al., 2017)**, antioxidant properties (ascorbic acid, tocopherol, polyphenols) **(Škrovánková et al., 2017)** and saccharides **(Márkus et al., 1999)**. Content of these different compounds in paprika depends mostly on geographical factors, such as geographical position, sea level, annual sum of rainfall, temperature during vegetation period, annual amount of sunlight and also composition of the soil **(Marschner, 1995)**. Other factors influencing chemical composition of paprika can be maturity of the fruits **(Peter et al., 2012)**, time of harvest **(Isidoro et al., 1995)** or ripening of the fruits after the harvest **(Kerek et al., 2015)**.

Chemical composition of ground paprika relates also to quality parameters of paprika. Quality of ground paprika, as a trade commodity, is judged also by ASTA value (from shortcut American Spice Trade Association). ASTA value is a number expressing amount of carotenoid colorants in acetone extract **(Isidoro et al., 1995)**.Content of carotenoids is important parameter which relates to quality and provenience of paprika. Other quality determining parameters are unit weight, paprika’s moisture, content of ash or content of lipids. European paprika of highest quality comes from Hungary and Spain and some of them have Protected Designation of Origin (PDO) mark. Nevertheless, the market offer also ground paprika which doesn’t reach the quality of the protected one. That is reason paprika becomes a commodity, where different producers put effort on its adulteration.

As an adulteration of food we may consider any inadequacy of food product with food law or intended deception of consumer in order to reach higher financial profit. The main mechanism is composition change of the food or stating false information on product's label **(Hong et al., 2017)**. In the case of paprika we can as a fraud or adulteration consider false declaration of geographical origin, misuse of PDO mark, forming mixtures of higher and lower quality paprika's, adding of oleoresin or inorganic dashes etc. As the number of food frauds grow, need for faster and more sensitive techniques revealing the adulteration grows as well.

Proving authenticity of particular food is important for whole chain from the farmer, through producer to the final consumer. It is vital to set comprehensive rules and conditions which help consumer not to be fooled, or worse, harmed on his health **(Čížková et al., 2012)**. There are many different analytical methods to be used for authentification of paprika geographical origin or country of origin adulteration. The analytical techniques are chosen according to concrete commodity, demands of methods speed, sensitivity and type of adulteration detection. Mostly used analytical techniques to reveal food fraud are spectroscopic methods (ICP-OES/ICP-MS/Sr-IR-ICP-MS/IR spectroscopy/ Raman spectroscopy/ NMR), chromatographic methods (LC/HPLC or GC/GC-MS), methods using analysis of DNA (RAPD-PCR/HRM-PCR), immune-chemical methods (ELISA, Biosensors) or electrochemical methods (CE/ FZCE) **(Hong et al., 2017, Doyle et al., 2017)**.

Hand by hand with analytical techniques go also statistical analysis methods and forming of statistical models describing particular commodity. The most important is having enough parameters basing the similarity or difference of particular products and its specificity. Among mostly used statistical methods belong Cluster and Hierarchic Cluster Analysis (CA, HCA), Discriminatory Analysis (DA, DPLS. PLS-DA), Linear Discriminatory Analysis (LDA), Artificial Neural Net (ANN), Soft Independent Modeling Class Analogy (SIMCA) and Support Vector Machines (SVM) **(Doyle et al., 2017)**.

Scientific hypothesis

Aim of this study was to test hypothesis, whether chemical composition of ground paprika can be affected by geographical origin of the paprika plant.

MATERIAL AND METHODOLOGY

Total of 11 samples (Table 1) of ground paprika with different proveniences have been chosen for the analysis. Five of the samples were provided with a mark of Protected Designation of Origin (PDO). All of the samples were obtained from market chains in Czech Republic.

Sample preparation

Samples used for determination of total nitrogen content were mineralized in Kjeldahl digestion unit (Kjeldaterm, C.Gerhardt GMBH, Germany). Total of 1 g of sample was mixed with 2 g of Weiniger catalyst (Lachema a.s., Czech Republic) and was digested for 24 hours.

For determination of saccharides 1 g of sample was extracted with 10 mL of extraction solution (ultrapure water and ethanol mixed in ration 4:1) in a 50 mL centrifugation tube placed on vertical shake table (GFL, Germany). After 1 h of extraction, samples were centrifuged for 4 min at 6000 rpm in centrifuge (EBA 21, Hettich, Germany); supernatant was filtered using filter with 0.45 μm pore size (Labicom, Czech Republic) and filled up to 50 mL in a volumetric flask with ultrapure water.

Sample for elemental analysis was prepared using wet ashing method in a microwave oven (Milestone 1200, Milestone, Italy). Total of 0.25 g sample matrix was decomposed in a mixture of nitric acid (6 mL) (Analytika Praha spol. s.r.o., Czech Republic) and hydrochloric acid (2 mL) (Analytika Praha spol. s.r.o., Czech Republic). After the decomposition sample was filtered using filter with 0.45 μm pore size and filled up to 25 mL in a volumetric flask with ultrapure water.

For determination of ASTA value 0.1 g samples were extracted by 20 mL of acetone (VWR International S.A.S, France) on vertical shake table for 3 hours. All the samples were diluted by acetone in volume ratio 1:5.

Chemical analysis

Moisture, ash and total lipid content was determined according to methods specified in ISO method (**ČSN ISO 7540, 2010**). Total nitrogen content was determined according to Kjeldahl method (**ČSN ISO 1871, 2009**). An Agilent Infinity 1260 liquid chromatograph (Agilent Technologies, USA) equipped with ELSD detector was used for determination of saccharides. As a stationary phase for analysis was used Prevail Carbohydrates ES column (250/4.6 mm). Mobile phase was formed by acetonitrile mixed with water in volume ratio 75:25. An elemental analysis was performed using ICP-OES (Ultima 2, Horiba Scientific, France) according to procedure described by **Diviš et al. (2015)**. ASTA value was determined according to ISO method (**ČSN ISO 7541, 1989**), using spectrophotometer Helios Gamma (Spectronic Unicam, USA). The pH value was measured using pH meter with combined electrodes (WTW, Germany).

Statistical analysis

All experimental data were statistically processed using software XLstat (Addinsoft, USA). Obtained data were pretreated by using Analysis of Variance (ANOVA) to find statistical significant differences between geographical groups. Tukey's comparative test on the level of importance p <0.05 has been performed for individual parameters among paprika samples.

The pretreated data were used as input parameters in Principal Component Analysis (PCA) to find correlation between the chemical composition of different samples and their geographical origin.

Table 1 Name of the samples, PDO mark, country of origin and producer.

Sample name	Sample description		
	PDO mark	Country of Origin	Producer
Pimentón de la Vera dulce	YES	Spain	Orencio Hoyo S.L.
Pimentón de la Vera picante	YES	Spain	Orencio Hoyo S.L.
Žitavská paprika sladká mletá	YES	Slovakia	Mäspoma spol. s.r.o.
Sweet paprika organic	NO	Bulgaria	Family Farm Tsar
Szegedi Paprika	YES	Hungary	Szegedi Paprika ZRt.
Kalocsai Édes	YES	Hungary	Édes ZRt.
Kirmizi Pulbiber	NO	Turkey	Karden Baharat Ltd.
Paprika sladká maďarská	NO	Hungary	Goldenway, s.r.o.
Paprika sladká španělská	NO	Spain	Goldenway, s.r.o.
Paprika sladká	NO	Romania	Opal a.s.
Magyar paprika	NO	Hungary	Thymosspol s.r.o.

RESULTS AND DISCUSSION

Moisture of ground paprika is a vital parameter which impacts stability of carotenoid dyes and microbial stability of the product. Low moisture enhances oxidation of nutritionally significant compounds (ascorbic acid, tocopherol, dyes). On the other hand, moisture content above 15 % helps to develop molds and other undesirable micro flora and breaking the safety of the food **(Chetti et al., 2014)**. High content of moisture also raises total weight of the product and helps producer to sell less product with higher profit. For ensuring the food safety and setting same conditions for all the producers all spice suppliers are obliged to comply demands on maximum moisture content in ground paprika, which is specified in Decree No. 162/2016. Czech legislation permits maximum moisture content in ground paprika to be 11 %.This condition has not been met at 3 samples: Kirmizi Pulbiber (Turkey), Szegedi Paprika (Hungary) and Sweet Paprika Organic (Bulgaria). Moisture content among samples varied between 8.7 ±0.1 % and 15.0 ±0.1 % **(Table 2)**. Lowest moisture content was measured in Hungarian paprika Kalocsai füszerpaprika örlemeny, the highest in Sweet Paprika Organic from Bulgaria. Average moisture content in analyzed paprika samples was10.7 ±1.7 %. Obtained results were compared to food databases and literature. American database **USDA (2015)** states moisture content in ground paprika to be 11.24 %, which is in the interval of the results obtained in this study, while Czech database **Nutridatabáze (2014)** states much lower moisture content in paprika, such as 7.9 %. Obtained results of moisture content comply with the results of **Duman et al. (2010)**, who measured paprika moisture content during different storage conditions. Results of **Duman et al. (2010)** varied from 9.68 ±0.31 % to 12.38 ±0.19 %.Moisture in paprika had been also investigated by **Zaki et al. (2013)**.Their average sample moisture was 9.5 ±0.9 %.

The ash content in sample determines amount of inorganic compounds in food. In the case of ground paprika the information of higher ash content can reveal mixing ground paprika with some inorganic dash **(Čížková et al., 2012)**. Maximum permitted ash content according to Czech legislation Decree No. 162/2016 is

Table 2 Content of moisture, ash, total lipids, total nitrogen and measured ASTA value at paprika samples.

Sample name	Parameters				
	Moisture (% ±SD)	Ash (% ±SD)	∑ Lipids (% ±SD)	∑ Nitrogen (% ±SD)	ASTA (- ±SD)
Pimentón de la Vera dulce	9.87 ±0.04^{cd}	4.96 ±0.02^{e}	11.5 ±0.2^{cd}	2.09 ±0.02^{ab}	115 ±1^{g}
Pimentón de la Vera picante	8.49 ±0.04^{a}	5.0 ±0.2^{e}	15.5 ±0.3^{a}	2.04 ±0.04^{bc}	111 ±1^{g}
Žitavská paprika sladká mletá	10.45 ±0.04^{de}	5.5 ±0.2^{d}	10.47 ±0.4^{de}	2.18 ±0.03^{a}	94 ±1^{g}
Sweet paprika organic	15.0 ±0.1^{a}	5.8 ±0.2^{bcd}	2.38 ±0.03^{g}	1.59 ±0.04^{f}	105 ±2^{f}
Szegedi Paprika	11.09 ±0.01^{c}	5.5 ±0.6^{d}	7.3 ±0.1^{f}	2.07 ±0.01^{abc}	127 ±1^{e}
Kalocsai Édes	8.7 ±0.1^{h}	7.04 ±0.03^{a}	10.6 ±0.3^{de}	1.76 ±0.03^{e}	84 ±1^{h}
Kirmizi Pul Biber	11.5 ±0.2^{b}	6.3 ±0.3^{b}	13.4 ±0.3^{b}	1.69 ±0.05^{ef}	82 ±1^{h}
Paprika sladká maďarská	10.2 ±0.1^{e}	6.2 ±0.2^{bc}	12.3 ±0.3^{bc}	1.96 ±0.07^{cd}	172 ±4^{a}
Paprika sladká španělská	9.9 ±0.2^{f}	6.2 ±0.4^{bc}	9.9 ±0.2^{e}	1.98 ±0.04^{bcd}	148 ±2^{c}
Paprika sladká	9.2 ±0.2^{g}	5.8 ±0.2^{bcd}	9.94 ±0.04^{de}	1.9 ±0.1^{d}	136 ±4^{d}
Magyar paprika	8.97 ±0.01^{gh}	5.56 ±0.04^{d}	12.6 ±0.1^{bc}	1.99 ±0.02^{bcd}	153 ±1^{b}

Note: *All samples were made in triplicates. **Values in the same column with different letters are significantly different at p <0.05.

Table 3 Content of saccharides and pH value of water extract of paprika samples.

Sample name	Parameters				
	Fructose ($mg.g^{-1}$ ±SD)	Glucose ($mg.g^{-1}$ ±SD)	Sucrose ($mg.g^{-1}$ ±SD)	∑ Saccharides ($mg.g^{-1}$ ±SD)	pH (- ±SD)
Pimentón de la Vera dulce	214 ±18^{c}	185 ±20^{bc}	45 ±4^{f}	444 ±74	4.94 ±0.05^{h}
Pimentón de la Vera picante	209 ±15^{c}	33 ±9^{e}	58 ±13^{def}	299 ±78	5.09 ±0.05^{ef}
Žitavská paprika sladká mletá	339 ±22^{b}	198 ±21^{bc}	127 ±11^{b}	664 ±88	5.01 ±0.05^{g}
Sweet paprika organic	565 ±24^{a}	541 ±33^{a}	177 ±9^{a}	1284 ±178	4.94 ±0.05^{h}
Szegedi Paprika	329 ±17^{b}	217 ±12^{bc}	127 ±7^{b}	673 ±83	5.10 ±0.05^{ef}
Kalocsai Édes	293 ±23^{b}	141 ±31^{cd}	52 ±4^{ef}	486 ±100	5.09 ±0.05^{f}
Kirmizi Pul Biber	209 ±16^{c}	74 ±25de	45 ±6^{f}	329 ±72	5.35 ±0.05^{a}
Paprika sladká maďarská	292 ±27^{b}	240 ±17^{d}	79 ±8^{cde}	611 ±91	5.14 ±0.05^{cd}
Paprika sladká španělská	307 ±18^{b}	236 ±21^{b}	87 ±9^{cd}	630 ±91	5.30 ±0.05^{b}
Paprika sladká	320 ±21^{b}	216 ±22^{bc}	66 ±7^{def}	603 ±104	5.13 ±0.05^{de}
Magyar paprika	361 ±12^{b}	258 ±26^{b}	139 ±8^{bc}	759 ±91	5.10 ±0.05^{ef}

Note: *All samples were made in triplicates. **Values in the same column with different letters are significantly different at p <0.05.

7.0 %. This condition has been met at all of the analyzed samples except Hungarian sample Kalocsai fűszerpaprika őrlemeny. The ash content varied from 5.5 ±0.2 % to 7.04 ±0.03 % **(Table 2)**. The highest content has been determined at sample Kalocsai fűszerpaprika őrlemeny, the lowest at samples Žitavská paprika (Slovakia) and Szegedi paprika (Hungary). Average content of ash of paprika samples was 5.8 ±0.6 %. Obtained results were compared with Czech food database and literature. Czech database **Nutridatabáze (2014)** states ash content in ground paprika to be 6.4 % hm. **Lee et al. (2017)** determined average ash content in paprika samples to be 5.14 %, **Zaki et al. (2013)** published average paprika ash content as to be 6.5 ±0.4 %.Results obtained in this study were in compliance with literature

Lipid content of ground paprika may help in revealing other type of food fraud. Higher content of total lipids in paprika might discover added lipophilic compounds (mostly oleoresins), which might help to rise ASTA value of the product **(Minguez-Mosquera et al., 1993)**. Lowest content of total lipids was determined at sample Sweet paprika organic from Bulgaria (2.38 ±0.03 %). The highest content of total lipids was determined at the sample Pimentón de la Vera picante from Spain (15.5 ±0.3 %). Total lipid content of each paprika sample is summarized in Table 2. Average content of total lipids was 10.6 ±3.3 %. Obtained data were compared with food databases and published literature. American database **USDA (2015)** determines total lipid content in paprika to be 12.89 % and Czech database **Nutridatabáze (2014)** determines total lipid content in paprika to be 13.8 %, which is close to the higher edge of results obtained in this study. **Zaki et al. (2013)** published total lipid content in paprika 8.4 ±2.6 %, which is in the range of results obtained in this study.

Kjeldahl method helps to get information about total nitrogen in sample, which can be recalculated as crude protein contained in food sample. Content of nitrogen depend on paprika variety, used agriculture technique and geographical origin **(Minguez-Mosquera et al., 1993)**.

Table 4 Content of macroelements in paprika samples.

Sample name	Macroelements			
	Ca ($mg.g^{-1}$ ±SD)	K ($mg.g^{-1}$ ±SD)	Na ($mg.g^{-1}$ ±SD)	Mg ($mg.g^{-1}$ ±SD)
Pimentón de la Vera dulce	29 ±3^{bc}	206 ±16^{b}	22±0.4^{f}	3.9 ±0.2^{g}
Pimentón de la Vera picante	29 ±2^{bc}	202 ±15^{bc}	25 ±0.4^{d}	5.2 ±0.3^{f}
Žitavská paprika sladká mletá	28 ±3^{bc}	178 ±13de	24 ±0.4^{e}	8.0 ±0.2^{c}
Sweet paprika organic	17 ±2^{d}	182 ±13de	17 ±0.3^{g}	3.4 ±0.4^{h}
Szegedi Paprika	37 ±3^{a}	189 ±10^{cd}	21 ±0.4^{f}	6.0 ±0.2^{e}
Kalocsai Édes	36 ±2^{a}	212 ±12^{b}	29 ±0.4^{a}	9.0 ±0.4^{b}
Kirmizi Pul Biber	30 ±3^{ab}	264 ±16^{a}	16 ±0.3^{h}	161 ±0.9^{a}
Paprika sladká maďarská	21 ±3^{cd}	186 ±13de	24 ±0.4^{e}	9.1 ±0.4^{b}
Paprika sladká španělská	26 ±3^{bc}	208 ±13^{b}	28 ±0.4^{b}	7.3 ±0.3^{d}
Paprika sladká	32 ±2^{ab}	175 ±17^{e}	27 ±0.4^{c}	7.5 ±0.3^{cd}
Magyar paprika	16 ±2^{d}	185 ±11de	17 ±0.3^{g}	3.4 ±0.2^{h}

Note: *All samples were made in triplicates. **Values in the same column with different letters are significantly different at p <0.05.

Table 5 Content of microelements in paprika samples.

Sample name	Microelements			
	Cu (mg.g^{-1} ±SD)	Fe (mg.g^{-1} ±SD)	P (mg.g^{-1} ±SD)	Zn (mg.g^{-1} ±SD)
Pimentón de la Vera dulce	0.15 ±0.05^{d}	0.97 ±0.02^{f}	36 ±2^{ab}	0.22 ±0.02^{a}
Pimentón de la Vera picante	0.15 ±0.05^{d}	1.69 ±0.03^{b}	38 ±2^{a}	0.20 ±0.02^{b}
Žitavská paprika sladká mletá	0.15 ±0.06^{d}	0.99 ±0.02^{f}	38 ±2^{a}	0.23 ±0.03^{a}
Sweet paprika organic	0.14 ±0.02^{e}	0.59 ±0.01^{i}	26 ±1^{d}	0.18 ±0.02^{c}
Szegedi Paprika	0.18 ±0.06^{b}	0.90 ±0.02^{g}	37 ±2^{a}	0.17 ±0.01^{cd}
Kalocsai Édes	0.15 ±0.05^{d}	1.68 ±0.04^{b}	37 ±2^{a}	0.13 ±0.01^{e}
Kirmizi Pul Biber	0.15 ±0.05^{d}	0.69 ±0.02^{h}	18 ±2^{e}	0.14 ±0.03^{e}
Paprika sladká maďarská	0.15 ±0.06^{d}	1.21 ±0.03^{d}	34 ±2^{c}	0.13 ±0.02^{e}
Paprika sladká španělská	0.04 ±0.03^{e}	1.32 ±0.03^{c}	37 ±2^{a}	0.10 ±0.02^{f}
Paprika sladká	0.16 ±0.02^{c}	1.82 ±0.04^{a}	35 ±2^{bc}	0.16 ±0.01^{d}
Magyar paprika	0.19 ±0.06^{a}	1.05 ±0.03^{e}	37 ±2^{a}	0.16 ±0.01^{d}

Note: *All samples were made in triplicates. **Values in the same column with different letters are significantly different at p <0.05.

Content of nitrogen varied among samples between 1.59 ±0.04 and 2.18 ±0.03 % **(Table 2)**. The lowest content of nitrogen was found in Bulgarian sample Sweet Paprika Organic, while the highest content of nitrogen contained Slovakian sample Žitavská paprika. Average content of nitrogen in samples was 1.93 ±0.17 %. Results were compared with food databases and with results of other authors. Czech database **Nutridatabáze (2014)** states total nitrogen content in ground paprika to be 2.4 %. **Giuffrida et al., (2013)** during investigation of different kinds of paprika came to similar results (1.91 ±0.14 %).

Saccharides impact the taste of paprika, but they are also important during pollen development **(Shaked et al., 2004)** and help seed to withstand stress from desiccation **(Demir et al., 2008)**. Observing amount of saccharides in paprika can describe development of ripening processes in paprika **(Asnin et al., 2014)**. The most abundant carbohydrate in paprika samples was fructose. Fructose content varied between 209 ±15 and 565 ±54 mg·g^{-1} **(Table 3)**.The lowest concentration has been measure at Spanish sample Pimentón de la Vera picante and highest at sample Sweet paprika organic from Bulgaria. Average content of fructose was 316 ±92 mg·g^{-1}. Second most abundant carbohydrate in paprika samples was glucose. Glucose content varied from 33 ±9 to 541 ±33 mg·g^{-1} **(Table 3)**.The lowest concentration was measured in Spanish sample Pimentón de la Vera picante and the highest in sample Sweet paprika organic from Bulgaria. Average glucose content was 215 ±119 mg·g^{-1}.The least abundant saccharide was sucrose. Average content of sucrose was 92 ±41 mg·g^{-1}. The lowest concentration was measured at sample Kirmizi Pulbiber from Turkey (45 ±6 mg·g^{-1}).The highest concentration of sucrose was determined at sample Sweet paprika organic from Bulgaria (177 ±9 mg·g^{-1}). Obtained data **(Table 3)** were compared with Czech food database **Nutridatabáze (2014)**, which states content of fructose to be 770 mg·g^{-1}, glucose 300 mg·g^{-1} and sucrose 70 mg·g^{-1}.Results measured in this study are in compliance with data published in database **Nutridatabáze (2014).**

Determination the mineral content of the sample is one of effective tools to consider origin of the paprika sample. Content of mineral compounds complies not only with the plant variety, but also with the soil and geographical location, where the paprika plant grows **(Brunner et al., 2014)**. Contents of calcium, potassium, magnesium, sodium, copper, iron, phosphorus and zinc were measured in this study (**Table 4, Table 5**). From all investigated elements most abundant was potassium with average concentration of 199 ±17 mg·g^{-1}. The least abundant elements were copper and zinc. Average concentration of copper was 0.155 ±0.006 mg·g^{-1} and average concentration of zinc was 0.165 ±0.015 mg·g^{-1}. The highest content of minerals has been found at Turkish sample Kirmizi Pulbiber. On the other hand the lowest content of minerals was found in sample Sweet Paprika Organic from Bulgaria. All obtained data are summarized in Table 4 and Table 5.

ASTA value is the basest qualitative parameter of ground paprika and describes content of carotenoid dyes. The content of carotenoid dyes depends on quality of the breed, freshness, storage conditions and other factors **(Peter et al., 2012)**. ASTA value varied in different samples between 82 ±1 and 172 ±4 ASTA **(Table 2)**. Average ASTA value in paprika samples was 119 ±31 ASTA. The highest ASTA value was measured at samples Paprika sladká maďarská (Hungary), Paprika sladká španělská (Spain) and Magyar paprika sladká (Hungary). Their average ASTA value was 158 ±1 ASTA. The lowest ASTA color was determined at samples Kirmizi Pulbiber (Turkey) and Kalocsai füszerpaprika örlemeny (Hungary), where average ASTA was measured to be 83 ±1 ASTA. Obtained results were in compliance with results of **Zaki et al. (2013)** and **Molnár et al. (2018)**. **Zaki et al. (2013)** measured ASTA at Moroccan paprika and resulted 125 ±12 ASTA. **Molnár et al. (2018)** determined ASTA in Peruvian paprika 140 ±35 ASTA and in Serbian paprika 101 ±28 ASTA.

The pH values of paprika samples varied in range from 4.94 ±0.05 to 5.35 ±0.05 **(Table 3)**. Average pH of all samples was 5.13 ±0.12. The lowest pH was determined at sample Sweet Paprika Organic from Bulgaria. The highest pH was determined at sample Kirmizi Pulbiber from Turkey. **Zaki et al. (2013)** and **Lee et al. (2017)**

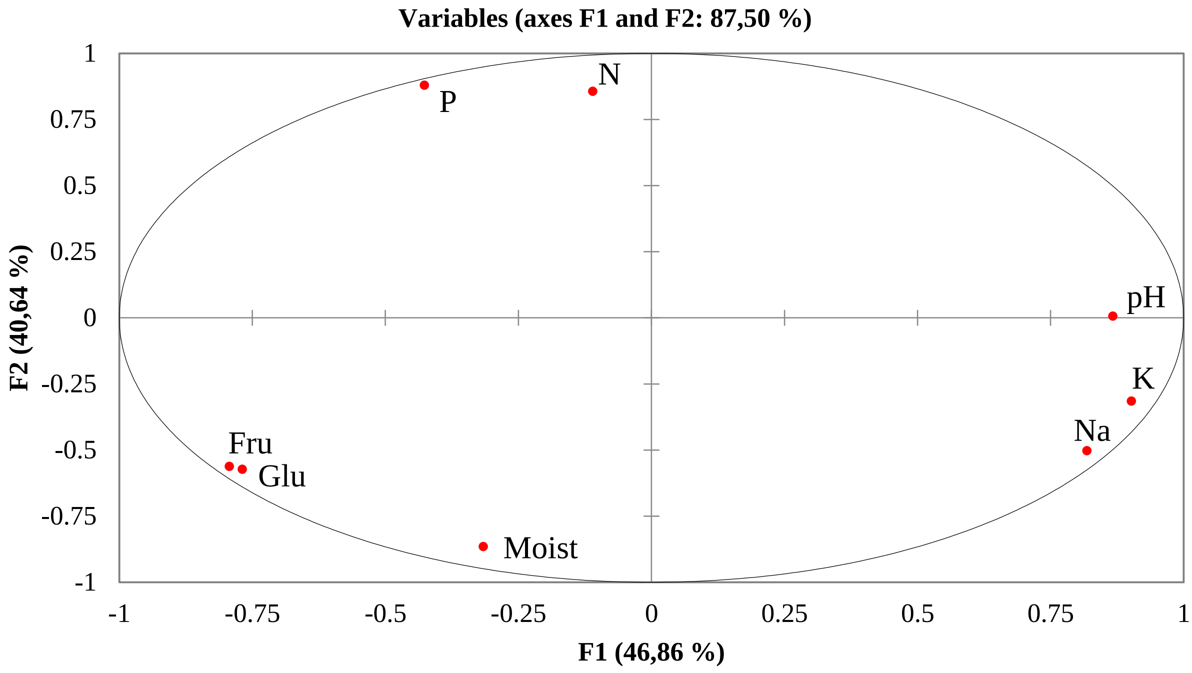

Figure 1 Projection of variables into the PCA factor plane of principal components F1 and F2 (Correlations between variables and factors).

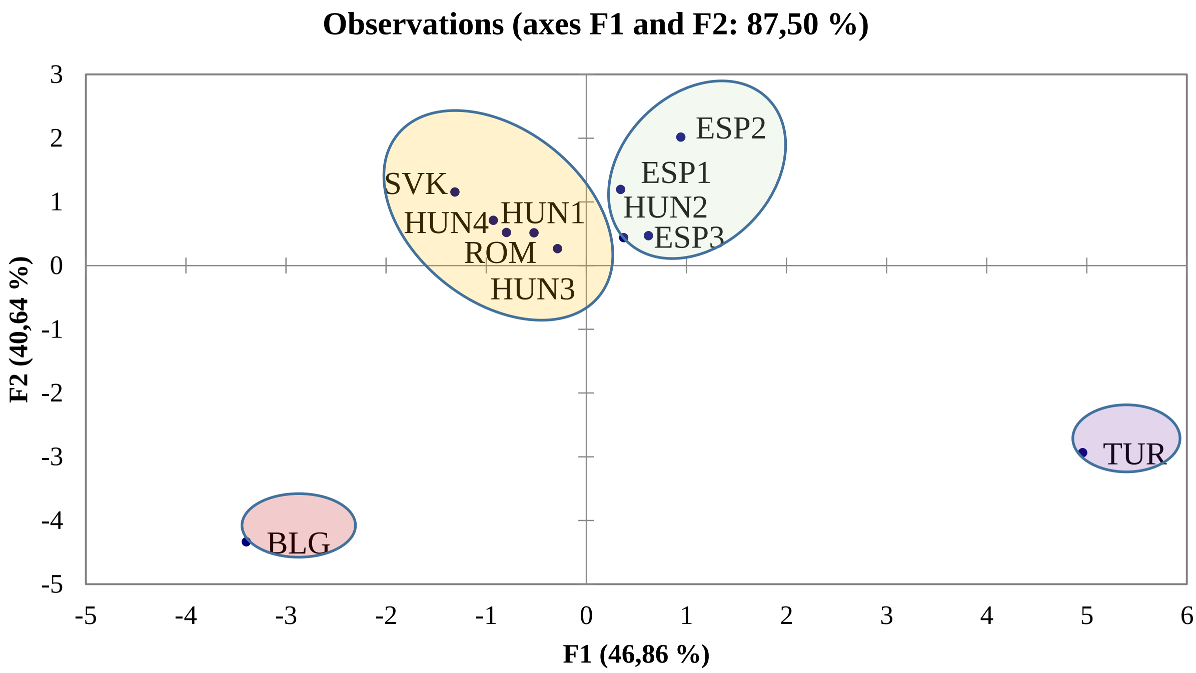

Figure 2 Projection of the PCA score of paprika geographical origin into the 2D factor plane of principal components F1 and F2. BLG – Bulgaria, ESP – Spain, HUN – Hungary, SVK – Slovakia, TUR – Turkey.

determined pH of paprika samples in the same range. **Zaki et al. (2013)** measured average pH of paprika samples to be 5.5 ±0.4, while **Lee et al. (2017)** determined average pH to be 5.05 ±0.02.

The data were processed by ANOVA and Tukey comparative test on the significance level 0.05. ANOVA was used for pretreatment of the data to find variables which exhibit statistical significant differences between the geographical groups of paprika. Statistical significant variables were sample moisture (F = 5.6537, *p* = 0.0401), concentration of fructose (F = 9.6446, *p* = 0.0132), potassium (F = 11.4762, *p* = 0.0090), sodium (F = 782.9995, *p* <0.0001) and phosphorus concentration (F = 43.1197, *p* = 0.0004). Other 3 variables, which were bordering with the significance level 0.05, were total content of nitrogen (F = 4.7834, *p* = 0.0555), concentration of glucose (F = 4.5750, *p* = 0.0603) and pH value (F = 4.5087, *p* = 0.0620).

After ANOVA pre-treatment of the data 8 input parameters have been selected into PCA. Obtained 8 input parameters have been reduced into 2 principal components with eigenvalue >1. According to the Kaiser criterion, components with eigenvalue less than one were excluded (F3, F4, F5, F6, F7, F8). Selected principal components F1 and F2 carried together 87.50 % of the variability of the original data set. Principal components were between each other more or less negatively or positively correlated with input variables **(Figure 1)**. Component F1 was strongly positively correlated with concentration of sodium and potassium and pH value. At the same time component F1 was strongly negatively correlated by concentration of glucose and fructose. Component F2 was strongly positively correlated by concentration of phosphorus and nitrogen. Strong negative correlation with component F2 have been observed with sample moisture and less negative correlation have been observed with amount of sodium, glucose and fructose.

The variables correlated also between each other. **(Figure 1)**. Intervariable correlations have been observed between sample moisture and concentration of glucose and fructose. Glucose and fructose are both monosaccharides participating in glycolysis. Correlation between moisture content and concentration of saccharides in ground paprika might depend on moisture, because stability of organic compounds in ground paprika depends (except other factors) also on sample moisture **(Chetti et al., 2014)**. Sample moisture showed a weak negative correlation with nitrogen content. On the other hand nitrogen content strongly positively correlated with content of phosphorus. Both of these elements belong among biogenic elements very abundant in living organisms. Weak negative correlation has been observed between nitrogen content and the rest of the parameters. As it was mentioned above, glucose and fructose content strongly positively correlated with each other and also with sample moisture. Fructose content showed strong negative correlation with pH value. Other parameters showed weak negative correlation with fructose and glucose. Another strong positive correlation has been observed between sodium and potassium content. These two elements form in living organisms' sodium-potassium pump. Content of these two elements strongly positively correlated with pH value. On the other hand has been observed strong negative correlation between sodium and potassium with phosphorus. Weak negative correlation has been observed with sodium and potassium in case of nitrogen. Phosphorous concentration had strong positive correlation with nitrogen. Strong negative correlation has been observed between concentration of phosphorus and concentration of sodium and potassium as well as sample moisture. Last observed parameter was pH value of the sample, which strongly positively correlated with sodium and potassium, but strongly negatively correlated with fructose content. Other parameters showed weak negative correlation with pH value.

Best possible graphical characterization of relations between paprika samples is dispersion of observations into the 2D factor plane of principal components F1 and F2 **(Figure 2)**. From the planar projection can be observed, with one exception, that samples have been divided into 2 clusters depending on their geographical origin. The first cluster includes samples from Hungary and geographically contiguous regions (Slovakia, Romania). The cluster is positioned in the first quadrant, which means positive correlation with component F2 and negative correlation with component F1. On the other hand the second cluster includes samples from Spain (with one exception, which is Hungarian sample from Kalocsai region). These samples forming the second cluster are positioned in second quadrant, which means positive correlation with both components F1 and F2. Sweet Paprika Organic (Bulgaria) and Kirmizi Pulbiber (Turkey) were projected separately from other samples forming clusters. Sweet Paprika Organic can be seen in third quadrant and Kirmizi Pulbiber in fourth quadrant.

Specifics of different combinations of observations, sample parameters and their variables can be visualized in 2D planar projection **(Figure 1 and Figure 2)**. Samples of paprika forming cluster in the first quadrant (samples from Hungary, Slovakia and Romania) have shown higher concentrations of phosphorous, nitrogen and saccharides. On the other hand samples forming the second cluster positioned in second quadrant (samples from Spain and Kalocsai sample) have shown lower content of saccharides, but higher content of sodium and potassium. Entirely different was sample Sweet Paprika Organic from Bulgaria, which in comparison to other samples had the highest content of saccharides, which led to projection this sample in the third quadrant. Similar observation was at Turkish sample Kirmizi Pulbiber, which differed from the other samples by the highest content of sodium and potassium, which led to projection this sample in the fourth quadrant.

CONCLUSION

Statistical analysis of obtained data confirmed hypothesis, that chemical content of paprika is influenced by geographical origin of the paprika plant. Samples from more distant regions (Hungary, Spain, Turkey, and Bulgaria) were, according to chemical analyses, successful to differentiate, while samples of paprika from similar regions (Hungary, Slovakia, Romania) were more difficult to differentiate. To separate samples of ground paprika only by their geographical origin, more complex analysis using other analytical method and obtaining more input data for multivariate analysis would be needed.

REFERENCES

Asnin, L., Park, S. W. 2014. Isolation and Analysis of Bioactive Compounds in Capsicum Peppers. *Critical Reviews in Food Science and Nutrition*, vol. 55, no. 2, p. 254-289. https://doi.org/10.1080/10408398.2011.652316

Brunner, M., Katona, R., Stefánka, Z., Prohaska, T. 2010. Determination of the geographical origin of processed spice using multielement and isotopic pattern on the example of Szegedi paprika. *European Food Research and Technology*, vol. 231, no. 4, p. 623-634.

Čížková, H., Ševčík, R., Rajchl, A., Pivoňka, J., Voldřich, M. 2012. Trendy v autenticitě potravin a v přístupech k detekci falšování. *Chemické listy*, vol. 106, no. 10, p. 903-910.

ČSN EN ISO 7540. 2010. *Ground paprika (Capsicum annuum* L.*) – Specification.*

ČSN EN ISO 1871. 2009. *Food and feed products – General guidelines for the determination of nitrogen by the Kjeldahl method.*

ČSN ISO 7541. 1989. *Ground (powdered) paprika – Determination of total natural colouring matter content.*

Demir, I., Teknin, A., Okmen, Z., Okcu, G. 2008 Seed Quality, and Fatty Acid and Sugar Contents of Pepper Seeds (*Capsicum annuum* L.) in Relation to Seed Development and Drying Temperatures. *Turkish Journal of Agriculture and Forestry*. vol. 32, p. 529-536.

Divis, P., Porizka, J., Vespalcova, M., Matejicek, A., Kaplan, J. 2015. Elemental composition of fruits from different black elder (*Sambucus nigra* L.) cultivars grown in the Czech Republic. *J. Elementol.*, vol. 20, p.549-557.

Doyle, N., Swain, D., Roberts, J. J., Cozzolino, D. 2017. The Use of Qualitative Analysis in Food Research and Technology: Considerations and Reflections from an Applied Point of View. *Food Analytical Methods*, vol. 10, p. 964-969. https://doi.org/10.1007/s12161-016-0654-8

Duman, A. D. 2010. Storage of red chili pepper under hermetically sealed or vacuum conditions for preservative of its quality and prevention of mycotoxine occurrence. *Journal of Stored Products Research*, vol. 46, p. 155-160. https://doi.org/10.1016/j.jspr.2010.02.002

Giuffrida, D., Dugo, P., Torre, G., Bignardi, C., Cavazza, A., Corradini, C., Dugo, G. 2013. Characterization of 12 Capsicum varieties by evaluation of their carotenoid profile and pungency determination. *Food Chemistry*, vol. 140, p. 794-802. https://doi.org/10.1016/j.foodchem.2012.09.060 PMid:23692768

Hong, E., Lee, S. Y., Jeong, J. Y., Park, J. M., Kim, B. H., Kwon, K., Chun, H. S. 2017. Modern analytical methods for the detection of food fraud and adulteration by food category. *Journal of the Science of Food and Agriculture*, vol. 97, p. 3877-3896. https://doi.org/10.1002/jsfa.8364 PMid:28397254

Chetti, M. B., Deepa, G. T., Antony, R. T., Khetagoudar, M. C., Uppar D. S., Navalgatti, C. M. 2014. Influence of vacuum packaging and long term storage on quality of whole chilli (*Capsicum annuum* L.). *Journal of Food Science and Technology*, vol. 51, p. 2827-2832. https://doi.org/10.1007/s13197-012-0763-3

Isidoro, E., Cotter, D. J., Fernandez, G. C. J., Southward, G. M. 1995. Color Retention in Red Chile Powder as Related to Delayed Harvest. *Journal of Food Science*, vol. 60, p. 1075-1077. https://doi.org/10.1111/j.1365-2621.1995.tb06295.x

Kerek, M., Ugróczy-Nagy, K., Mihály, M., Slezák, K., Jezdinský, A. 2015. The Effect of Postharvest Ripening Duration on Spice Pepper Powder Pigment and Sugar Content. *Acta Horticulturae*, vol. 1079, p. 619-625. https://doi.org/10.17660/ActaHortic.2015.1079.84

Klimešová, M., Horáček, J., Ondřej, M., Manga, I., Koláčková, I., Nejeschlebová, L., Ponížil, A. 2015. Microbial contamination of spices used in production of meat products. *Potravinarstvo*, vol. 9, p. 154-159. https://doi.org/10.5219/440

Lee, H. S., HONG, J. Y., CHOI, Y. J., Lee, Y. S., Seo, S. J., Shin, S. R. 2017. Characteristics in the components of the paprika by drying methods. *Korean Journal of Food Preservation*, vol. 24, 497-504. https://doi.org/10.11002/kjfp.2017.24.4.497

Márkus, F., Daood, H. G., Kapitány, J., Biacs, P. A. 1999. Change in the Carotenoid and Antioxidant Content of Spice Red Pepper (Paprika) as a Function of Ripening and Some Technological Factors. *Journal of Agricultural and Food Chemistry*, vol. 47, p. 100-107. https://doi.org/10.1021/jf980485z PMid:10563856

Marschner, H. 1995. *Mineral nutrition of higher plants*. 2nd ed. London, UK : AcademicPress, 889 p. ISBN 9780124735439.

Minguez-Mosquera, M. I., Hornero-Mendez, D. 1993. Separation and quantification of the carotenoid pigments in red peppers (*Capsicum annuum* L.), paprika, and oleoresin by reversed-phase HPLC. *Journal of Agricultural and Food Chemistry*, vol. 41, p. 1616-1620. https://doi.org/10.1021/jf00034a018

Molnár, H., Kónya, E., Zalán, Z., Bata-Vidács, I., Tömösközi-Farkas, R., Székács, A., Adányi, N. 2018. Chemical characteristics of spice paprika of different origins. *Food Control*, vol. 83, p. 54-60. https://doi.org/10.1016/j.foodcont.2017.04.028

Nutridatabáze, 2014. [online database], Available at: http://www.nutridatabaze.cz/potraviny/?id = 262.

Peter, K. V., 2012. *Handbook of herbs and spices*. 2nd ed. Oxford, UK: Woodhead. Woodhead Publishing series in food science, technology and nutrition. ISBN 978-0-85709-039-3.

Popelka, P., Jevinová, P., Šmejkal, K., Roba, P. 2017. Antibacterial activity of Capsicum extract against selected strains of bacteria and micromycetes. *Potravinarstvo Slovak Journal of Food Sciences*, vol. 11, p. 223-229. https://doi.org/10.5219/731

Shaked, R., Rosenfeld, K., Pressman, E. 2004. The effect of low night temperatures on carbohydrates metabolism in developing pollen grains of pepper in relation to their number and functioning. *Scientia Horticulturae*, vol. 102, p. 29-36. https://doi.org/10.1016/j.scienta.2003.12.007

Škrovánková, S., Mlček, J., Orsavová, J., Juríková, T., Dřímalová, P. 2017. Polyphenols content and antioxidant activity of paprika and pepper spices. *Potravinarstvo Slovak Journal of Food Sciences*, vol. 11, p. 52-57. https://doi.org/10.5219/695

USDA: United States Department of Agriculture, 2015. [online database], [cit. 2017-03-20]. Available at: https://ndb.nal.usda.gov/ndb/foods/show/278?manu = &fgcd = &ds = .

Zaki, N., Hakmaoui, A., Ouatmane, A., Fernandez-Trujillo, J. P. 2013. Quality characteristics of Moroccan sweet paprika (Capsicum annuum L.) at different sampling times. *Food Science and Technology (Campinas)*, vol. 33, p. 577-585. https://doi.org/10.1590/S0101-20612013005000072

Acknowledgments:

This work was financially supported by the project: Materials Research Centre at FCH BUT Sustainability and Development, REG LO1211, with financial support from the National Programme for Sustainability I.

Contact address:

Václav Štursa, Brno University of Technology, Faculty of Chemistry, Department of Food chemistry and Biotechnology, Purkyňova 118, 612 00 Brno, Czech Republic, E-mail: xcstursav@fch.vutbr.cz

Pavel Diviš, Brno University of Technology, Faculty of Chemistry, Department of Food chemistry and Biotechnology&Materials research centre, Purkyňova 118, 612 00 Brno, Czech Republic, E-mail: divis@fch.vutbr.cz

Jaromír Pořízka, Brno University of Technology, Faculty of Chemistry, Department of Food chemistry and Biotechnology&Materials research centre, Purkyňova 118, 612 00 Brno, Czech Republic, E-mail: porizka@fch.vut.cz