

**LEAD, MERCURY AND ARSENIC CONTENT IN SPICES:  
BLACK, WHITE AND GREEN PEPPER,  
BLACK CUMIN AND GINGER**

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**Abstract.** *In order to evaluate the safety of selected commercial spices brands, concentration of lead, mercury and arsenic, as well as moisture and mineral contents were analyzed in samples of dried black and white pepper powders, black, white and green peppercorns, black cumin seeds and ginger powder. Lead (Pb), mercury (Hg) and arsenic (As) concentrations in spice samples purchased from local markets in Belgrade were determined, after a microwave digestion of the samples, by atomic absorption spectrometry (AAS), using the graphite furnace AAS technique (Pb), cold vapor AAS technique (Hg) and hydride generation AAS technique (As). Trace levels of Pb, Hg and As in the selected dried spices samples were in the range 0.10 ppm – 0.79 ppm, 0.01 ppm – 0.10 ppm and 0.01 ppm – 0.51 ppm, respectively. The maximum Pb concentration was determined in the sample of ginger and it was 0.79 ppm, the maximum concentration of Hg was 0.10 ppm, determined in green peppercorns samples, while the maximum concentration of As in powdered black pepper sample was 0.51 ppm. The moisture and mineral contents in the different analyzed spices were in the range 1.70–13.10% and 3.40–6.50%, respectively. According to the obtained results, the concentrations of the analyzed toxic elements, as well as the moisture and mineral content in selected spices, were below the maximum permissible limits declared by the national legislations deemed safe for human consumption.*

**Key words:** *spices, heavy metals, arsenic, moisture and minerals contents, atomic absorption spectrometry*

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## 1. INTRODUCTION

Spices are defined as plant substances of indigenous or exotic origin, aromatic or with a strong taste, used to enhance the taste of foodstuff. Spices are dry parts of a plant such as roots, leaves and seeds, which are widely used as diet components, commonly to improve flavor, aroma, color, palatability and acceptability of foods. They are also used in beverages, liquors, pharmaceuticals, cosmetics and perfumery products (Farooqi et al., 2005). Many spices are sources of different bioactive compounds that can influence digestion and metabolism processes. Some spices such as black pepper, cumin and ginger have outstanding antioxidant and antimicrobial effects (El-Ghorab et al., 2010; Gülçin, 2005; Hinneburg et al., 2006; Shelef, 1984; Witkowska et al., 2013). In addition, it is known that some spices such as black pepper, chili, coriander and cumin show a significant antifungal activity (Thyagaraja and Hosono, 1996). On the other hand, they may contain some undesirable components such as mycotoxins, pesticides, polycyclic carbohydrates residues and heavy metals that may cause problems in human health.

Heavy metals are very harmful due to their non-biodegradable nature and potential to accumulate in different body parts, while most of these are extremely toxic due to their solubility in water. Some heavy metals, like Hg, Pb and As, are toxic at very low concentrations and cause adverse effects to people (Fergusson, 1990; Jarup, 2003). Lead is recognized as the most toxic environmental pollutant which reacts or complexes with many biomolecules; mercury is known as one of the most potent neurotoxins, while arsenic exposure is strongly associated with increased risks of both carcinogenic and systemic health effects. These toxic heavy metals have an adverse effect on gastrointestinal, immune, cardiovascular, reproductive, renal, and nervous systems (Bhan and Sarkar, 2005; Johnson, 1998; Tchounwou et al., 2003). Spices contain toxic heavy metals in a wide range of concentrations, and the content varies with the location and the type of soil for cultivation, fertilizers, herbicides and water resources used for irrigation, climate and environmental pollution levels. The industrial processing, packaging, transportation and storage conditions can play a significant role in elevating the contaminant levels of heavy metals content, which may affect the quality of plants and spices (Abou-Arab and Abou Donia, 2000; Angelova et al., 2005; Tsoumbaris and Tsoukali-Papadopoulou, 1994). Consumption of spices contaminated with traces of heavy metals may have serious adverse effects on human health due to their high toxicity. Distribution and accumulation of heavy metals among different plant parts depend on both plant species and the individual ability of a specific organ to accumulate metals (Angelova et al., 2005; Prasad and Freitas, 2003). Previous studies related to the determination of toxic metals such as Pb, As, Hg and Cd in pepper, ginger and black cumin – species analyzed in this paper – show that their content may vary significantly (Nkansah and Opoku Amoako, 2010; Darko and Voegborlo, 2014; Feryie, 2010; Krejpcio et al., 2007; Abou-Arab and Abou Donia, 2000; Esetlili et al., 2014; Huremović et al., 2014; Belay et al., 2014; Application Note 009754A\_01; Sharma et al., 2014; Soyak et al., 2004; Khan et al., 2014; Karadas and Kara, 2012; Aiwonegbe and Ikhuoria, 2007; Roychowdhury et al., 2002) and in many cases exceeds the maximum permissible limits regulated by different national legislations, EU legislations (Commission regulation (EC) No 149/2008 and No 629/2008) and recommendations by World Health Organization (WHO) (WHO guidelines for assessing quality of herbal medicines, 2007 and FAO/WHO Codex Alimentarius Commission CF/8 INF/1, 2014).

Aside from the level of heavy metals, moisture and mineral content are very important indices that illustrate purity, efficacy, quality and safety of spices. Insufficiently or improperly stored dried spices are subject to change which can lead to active components degradation, bacterial and fungal growth resulting in inadequate quality and safety of spices. Total ash makes a measure of the total amount of minerals present within a spice, indicating the inorganic residue remaining after total incineration of organic matter that is derived from plant tissue itself and specific inorganic components, often originating from environmental contamination. Analytical determination of heavy metals, moisture and mineral content in spices makes a part of permanent quality control, aimed to establish their purity, safety and efficacy.

Heavy metals can be determined by several analytical methods, but high selectivity and sensitivity spectroscopic methods are widely used in determination of toxic heavy metals (Blagojević et al., 2013; Caldas and Machado, 2003; Feryie, 2010; González et al., 2008; Ling et al., 2011; Long et al., 2004; Nkansah and Opoku Amoako, 2010; Ražić et al., 2006). Flame atomic absorption spectrometry, hydride generation atomic absorption spectrometry, cold vapor atomic absorption spectrometry and graphite furnace atomic absorption spectrometry are important and the most popular analytical methods for determination of heavy metals such as Pb, Hg and As in spices, medicinal herbs and food samples. (Blagojević et al., 2013; Caldas and Machado, 2003; Nkansah and Opoku Amoako, 2010; Ražić et al., 2006). These convenient and reliable methods are simple to use compared to other complicated spectroscopic methods such as inductively coupled plasma atomic emission spectrometry (Ling et al., 2011), inductively coupled plasma mass spectrometry (Feryie, 2010; Ling et al., 2011), inductively coupled plasma–optical emission spectrometry (González et al., 2008) and hydride generation atomic fluorescence spectrometry (Long et al., 2004). Many analytical methods, including atomic absorption spectrometry for trace element determination in plant samples, require digestion of the sample. Microwave digestion preparation is an efficient sample decomposition method, prior to determination of heavy metals (Yaling et al., 2004). Air–oven drying and dry ashing are widely used methods for determination of routine moisture and total ash in spices and food samples (AACCI Method 44–15.02, SRPS ISO 928:2001).

This study was conducted to evaluate the quality of commercial black, white and green pepper, black cumin and ginger dried spices available in Belgrade markets. The aim of the current study was to investigate the concentration of lead, mercury, including arsenic, moisture and mineral content in dried samples, as well as to analyze the safety of selected commercial spices brands.

## 2. MATERIAL AND METHODS

### 2.1. Spice materials and chemicals

Selected spice samples of black, green and white pepper (*Piper nigrum* L.), black cumin (*Cuminum cyminum* L.) and ginger (*Zingiber officinale* Roscoe) were purchased directly from local markets in Belgrade, in March 2015. A total of thirteen branded samples includes dried black and white pepper powder, black, white and green peppercorns (black, white and green pepper in grain), black cumin seeds and ginger powder packed by two different distributors and marked as brand name samples A and B. A white pepper powder sample packaged by brand name B was not available in Belgrade markets at the time of this study. All peppers and ginger spices used in this study were

produced in India, while the origin of black cumin was China. Five samples of each kind of the selected brand name spice were analyzed.

Three reference standard stock solutions containing lead, mercury and arsenic at a concentration of 1000 ppm were purchased from J. T. Baker (Avantor Performance Materials, U.S.A.) and used without further purification. Working standard solutions of the analyzed heavy metals were prepared by series dilution of their stock solutions immediately prior to use. Deionized water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ , Milli Q, Millipore) was used in all dilutions. All stock solutions and 12.1 M hydrochloric acid (HCl) (Merck, U.S.A.) used for analyses were of spectroscopic grades.

## 2.2. Methods

### 2.2.1. Microwave digestion of spice samples

The dried spices were digested using a modified microwave digestion procedure ((Blagojević et al., 2013) based on Milestone Microwave Laboratory Systems, Start E (User manual). Prior to heating in a Microwave digestion (MWD) system (Milestone Start E) with Teflon digestion vessels and high pressure supports, 10.0 g of dried spice sample were weighed into the Teflon digestion vessel, and 15 ml of concentrated 12.1 M HCl were added. The vessels were capped to 16.3 N m using the Milestone system. The microwave digestion treatments lasted for 30 minutes at 600 W power; microwave frequency was 2450 Hz. After completion of MWD treatments, samples were removed and allowed to cool and there upon filtered. Filtered samples were quantitatively transferred to a 25 mL glass volumetric flask class A and completed to the mark with deionized water, prior to metal analysis by AAS method.

### 2.2.2. Sample analysis by AAS

Digested samples were analyzed on Pb, Hg and As concentrations, using the graphite furnace absorption technique, the cold vapor atomic absorption technique and the hydride generation technique, respectively. Atomic absorption measurements were performed using an atomic absorption double beam spectrophotometer (GBC Scientific Equipment Ltd., Victoria, Australia), with a deuterium lamp for background correction and hollow cathode lamps. Flame (GBC-SensAA-Dual) and nebulizer gas flow rate  $5 \text{ L min}^{-1}$  were used for determination of As and Hg. Estimation of Pb in digested spices samples was completed by a GBC-SensAA-Dual-graphite furnace system, equipped with a deuterium lamp for background correction. The instrumental conditions during the analysis of certain heavy metals are listed in Table 1.

Quantification of heavy metals was achieved by using a calibration curve that was fitted by the least square method. The standard deviation of the response (SD) and the slope of the calibration curve (S) were used to calculate the limit of detection (LOD) and limit of quantification (LOQ) by using the equations  $\text{LOD} = 3.3(\text{SD}/\text{S})$  and  $\text{LOQ} = 10(\text{SD}/\text{S})$ , respectively. The obtained coefficients of determination ( $r^2$ ), LOD and LOQ values and linearity for each of the element are presented in Table 1.

**Table 1** Instrumental conditions for determination of heavy metals by AAS

Parameter	Heavy metals		
	Pb	Hg	As
AAS technique	Graphite furnace	Cold vapor	Hydride generation
Lamp	HLC <sup>a</sup>	HLC <sup>b</sup>	HLC <sup>c</sup>
Wavelength (nm)	217.0	253.7	193.7
Slit width (nm)	0.5	0.5	0.5
Flame		Air/acetylene	Air/acetylene
r <sup>2</sup>	0.9990	0.9998	0.9991
LOD (ppb)	1.09	0.91	1.32
LOQ (ppb)	3.30	2.76	3.67
Linearity (ppb)	3.40 – 350.0	2.8 – 150.0	4.0 – 300.0

Abbreviations: Hollow cathode lamp for Pb<sup>a</sup>, Hg<sup>b</sup> and As<sup>c</sup>

Measurement uncertainty was determined on the basis of 32 measurements on 0.1 ppm solution and expressed as relative standard deviation (RSD). RSD was below 6.5%, for all elements. The precision of the method was established by a spike recovery test. The recovery was tested by samples spiked with each of the metals at concentration levels ranged between 20 and 30 ppb. The spiked samples were digested and analyzed in a similar condition as non-spiked. The recoveries of Pb, As and Hg in the spiked spice samples were 96.5%, 97.5% and 101.8%, respectively.

### 2.2.3. Air-oven drying and dry ashing methods

Moisture and total ash determination of the spices samples were performed by air-oven drying and dry ashing methods, respectively.

Based on AACC Method 44-15A, moisture was determined by drying the spices samples for 16 hours at 105 °C in an oven. Ovens should be thermally regulated to 105.0 °C ± 0.5 °C and have minimal temperature variations (< 3 °C) within the oven.

According to the standard dry ashing method SRPS ISO 928:2001 for determination of total ashing, 2 g of selected dried spices samples were kept in a furnace for 5 hours at 550 °C to 600 °C to oxidize all organic materials without flaming, and the results were obtained gravimetrically.

## 3. RESULTS AND DISCUSSION

### 3.1. Determination of the heavy metals concentrations

Concentrations of certain heavy metals in the analyzed dried samples of black, green and white pepper, black cumin and ginger are presented in Table 2. The obtained results of the determination of toxic heavy metals for different brand name samples, commercially available in Belgrade markets, are presented as a mean value ± standard deviation (SD) in five determinations.

**Table 2** Heavy metal concentrations in selected spices

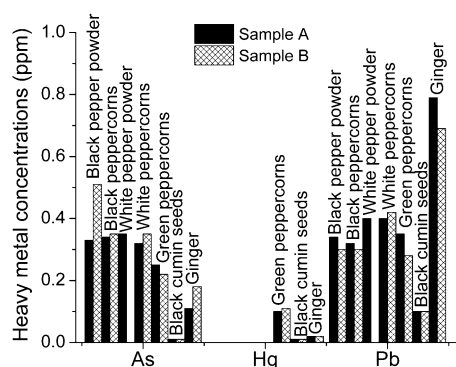
Heavy metal concentrations (ppm)				
(mean value $\pm$ SD)				
Spices	Sample	Pb	Hg	As
Black pepper powder	A	0.34 $\pm$ 0.02	ND <sup>b</sup>	0.33 $\pm$ 0.02
	B	0.30 $\pm$ 0.01	ND	0.51 $\pm$ 0.03
White pepper powder	A	0.40 $\pm$ 0.02	ND	0.35 $\pm$ 0.02
	B	NA	NA	NA
Black peppercorns (Black pepper in grain)	A	0.32 $\pm$ 0.02	ND	0.34 $\pm$ 0.02
	B	0.35 $\pm$ 0.02	ND	0.35 $\pm$ 0.02
White peppercorns (White pepper in grain)	A	0.40 $\pm$ 0.02	ND	0.32 $\pm$ 0.02
	B	0.42 $\pm$ 0.02	ND	0.35 $\pm$ 0.02
Green peppercorns (Green pepper in grain)	A	0.35 $\pm$ 0.02	0.102 $\pm$ 0.005	0.25 $\pm$ 0.01
	B	0.28 $\pm$ 0.01	0.104 $\pm$ 0.005	0.22 $\pm$ 0.01
Black cumin seeds	A	0.101 $\pm$ 0.005	0.0102 $\pm$ 0.0005	0.0106 $\pm$ 0.0005
	B	0.103 $\pm$ 0.005	0.0110 $\pm$ 0.0005	0.0102 $\pm$ 0.0005
Ginger powder	A	0.79 $\pm$ 0.04	0.021 $\pm$ 0.001	0.110 $\pm$ 0.006
	B	0.69 $\pm$ 0.04	0.020 $\pm$ 0.001	0.18 $\pm$ 0.01

Abbreviations: <sup>a</sup>NA – Not available.<sup>b</sup>ND – Not detected (levels were below detection limit)

The data in Table 2 show a significant variation in concentration of Pb, Hg and As for the analyzed spice samples, and indicate the presence of lead and arsenic at different levels in all spices samples, collected at the local markets in Belgrade. Besides, it was found that all tested samples of black and white pepper are free from mercury; the rest of the analyzed spices samples contained significantly variable content of mercury, ranging from 0.01 ppm – 0.10 ppm. However, there was no statistically significant difference ( $p > 0.05$ ) in Hg content between different brands of a single space type.

The concentrations of Pb in different analyzed spices were in the range 0.10 ppm – 0.79 ppm. The lowest and the same lead concentrations were detected in both brand name samples of black cumin, while maximum concentrations were determined in both ginger samples. The increased levels of Pb in both samples of ginger spices indicate that this plant presumably is inclinable to accumulate lead from the environment or during technical processing, packaging, transportation and storage conditions. Between different brands there were no significant differences ( $p > 0.05$ ) in concentration of Pb for both type black and white pepper and cumin. For green pepper and ginger, a significant difference ( $p < 0.05$ ) in Pb concentration between different brands was observed.

As can be seen from Table 2, the content of As significantly varied within the examined plant species, in the range 0.01 ppm – 0.51 ppm. The highest mean value of As was found in black paper powder (brand name B), while the same and very low concentration of As was determined in both black cumin samples. For black pepper powder and ginger, a significant difference ( $p < 0.05$ ) in As concentration between different brands was observed. Figure 1 presents multiple comparisons for all heavy metal concentrations in different spices collected from local markets in Belgrade.



**Fig. 1** Heavy metal concentrations in various spices samples

A comparison of the concentrations of Pb, Hg and As in selected spices determined in this study with that previously reported is presented in Table 3. The analyzed spices purchased from local markets in Belgrade had a lower level of Pb and Hg than samples which were produced and collected in different regions in Asia, Europe and Africa. The levels of As in both brands of ginger samples were in agreement with data reported in the literature. In comparison with the previous studies, the content of As in green peppercorns samples is significantly lower, but in black pepper powder of brand B is slightly higher. The obtained wide variations

in metal contents could be attributed to the differences in the geographical origin of spices (location and type of soil for cultivation) and environmental pollution levels, but contamination could occur during industrial processing, packaging, transportation and storage.

Spices belong to a group of condiments; therefore, the levels of heavy metals were compared with appropriate safety standards, as determined by maximum permissible limits (MPL) that were established by national legislation (Pravilnik – Službeni list SRJ br. 5/92, 11/92 – ispr. i 32/2002). Subject to the national legislation, the maximum permissible limits for arsenic and lead in herbal species are 1 ppm and 2 ppm, respectively. The maximum permissible mercury concentration in herbal spices is not regulated by national legislation, but maximum limits of both mercury and lead according to the different regulations and WHO recommendation is presented in Table 4.

**Table 3** Comparison of heavy metals concentrations in this study with previous studies

Spices	Heavy metal concentrations (ppm)		
	Pb	Hg	As
Black pepper <sup>a</sup>	0.01–20.35 <sup>1,4,5,7,8,9,11</sup> 0.30; 0.35 <sup>b</sup>	0.02–0.10 <sup>1,10</sup> ND <sup>c</sup>	0.049–0.440 <sup>3,9</sup> 0.332; 0.510 <sup>b</sup>
White pepper <sup>a</sup>	0.978 <sup>1</sup> 0.40; 0.42 <sup>b</sup>	0.0042 <sup>1</sup> ND <sup>c</sup>	/ 0.32; 0.35 <sup>b</sup>
Green peppercorns	0.13–1.4 <sup>2,15</sup> 0.28; 0.35 <sup>b</sup>	/ 0.01 <sup>b</sup>	9.30 <sup>14</sup> 0.20; 0.25 <sup>b</sup>
Black cumin	0.02–1.70 <sup>5,6,8,11,12</sup> 0.10 <sup>b</sup>	0.174 <sup>13</sup> 0.010; 0.011 <sup>b</sup>	0.063–0.723 <sup>3,12</sup> 0.010 <sup>b</sup>
Ginger	0.21–1.80 <sup>1,2,4,6,8,9</sup> 0.69; 0.79 <sup>b</sup>	0.00123 <sup>1</sup> 0.020; 0.021 <sup>b</sup>	0.047–0.209 <sup>9,15</sup> 0.11; 0.18 <sup>b</sup>

Abbreviations: <sup>a</sup>Powder and peppercorns; <sup>b</sup>This study (brand A and B); <sup>c</sup>Not detected.

<sup>1</sup>Nkansah and Opoku Amoako, 2010; <sup>2</sup>Darko and Voegborlo, 2014; <sup>3</sup>Feryie, 2010; <sup>4</sup>Krejpcio et al., 2007;

<sup>5</sup>Abou–Arab and Abou Donia, 2000; <sup>6</sup>Esetlili et al., 2014; <sup>7</sup>Huremović et al., 2014; <sup>8</sup>Belay, et al., 2014;

<sup>9</sup>Application Note 009754A\_01; <sup>10</sup>Sharma et al., 2014; <sup>11</sup>Soylak et al., 2004; <sup>12</sup>Khan et al., 2014;

<sup>13</sup>Karadas and Kara, 2012; <sup>14</sup>Aiwonegbe et al., 2007; <sup>15</sup>Roychowdhury et al., 2002.

**Table 4** Maximum limits for lead, arsenic and mercury in different EU regulations and WHO recommendations

	Maximum Limits (ppm)			Comments
	Pb	As	Hg	
Commission regulation (EC) No 629/2008	3.0 0.3	NE <sup>a</sup>	0.1	In food supplements In leafy vegetables
Commission regulation (EC) No 149/2008		NE	0.02	In herbal infusions and spices
WHO guidelines	10	NR <sup>b</sup>	NR <sup>b</sup>	In herbal medicines and products
FAO/WHO	10 – 20 <sup>c</sup>	2.0 – 5.0 <sup>c</sup>	0.2 – 0.5 <sup>c</sup>	
Codex Alimentarius Commission CF/8 INF/1	0.3	NR	NR	In leafy vegetables

Abbreviations: <sup>a</sup>NE – Not established; <sup>b</sup>NR – Not recommended by WHO; <sup>c</sup>Different national limits

Previous studies (Table 3) have shown that in analyzed spices the concentration of Pb, Hg and As in many cases exceeded the accepted permissible limits. According to the obtained results, the concentrations of Pb and As in all selected spices, and Hg in the black cumin and ginger spices were below MPL declared by the national legislations and EC regulations. Although the concentration of Hg in green peppercorn samples reaches the maximum permissible limits declared by the EC regulations, generally all spices samples are safe for human consumption.

### 3.2. Determination of moisture content

The results of the determination of moisture content in black, white and green peppercorns, black and white powder, black cumin and ginger samples were presented in Table 5, as mean value  $\pm$  standard deviation (SD), obtained for five determinations. The obtained results of moisture content were compared with safety standards established by national legislation (NL) (Pravilnik – Sl. list SFRJ, br. 4/85 i 84/87, Sl. list SCG, br.56/2003 – dr. Pravilnik i 4/2004 – dr. pravilnik i Sl. glasnik RS, br. 43/2013 – dr. pravilnik) and European Spice Association (ESA) limits of water content in these dried products (European Spice Association Quality Minima Document, 2011), presented in Table 5.

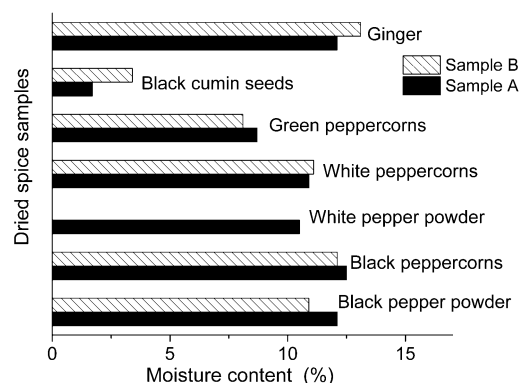
**Table 5** Moisture content in dried spices samples

Spices	Moisture content (%) (mean value $\pm$ SD)			
	MPL (%)		Sample brand name	
	NL <sup>a</sup>	ESA <sup>b</sup>	A	B
Black pepper powder		12.0	12.1 $\pm$ 0.3	10.9 $\pm$ 0.2
Black peppercorns	14.0	12.0	12.5 $\pm$ 0.3	12.1 $\pm$ 0.3
White pepper powder		12.0	10.5 $\pm$ 0.2	NA <sup>c</sup>
White peppercorns	15.0	12.0	10.9 $\pm$ 0.2	11.1 $\pm$ 0.2
Green peppercorns	NR <sup>d</sup>	13.0	8.7 $\pm$ 0.2	8.1 $\pm$ 0.1
Black cumin seeds	14.0	12.0	1.7 $\pm$ 0.1	3.4 $\pm$ 0.1
Ginger powder	14.0	12.0	12.1 $\pm$ 0.3	13.1 $\pm$ 0.3

Abbreviations: <sup>a</sup>bMaximum permissible limit (MPL) of the total ash in the examined spices, according to NL<sup>a</sup> ESA<sup>b</sup>. <sup>c</sup>NA – Not available. <sup>d</sup>NR – Not regulated by NL.



The moisture content for different brand name samples of the analyzed spices were in the range 1.7% – 12.5% (samples A) and 3.4% – 13.1% (samples B) and depended significantly on the plant species. Table 6 data demonstrate that the moisture content in all dried spices samples is in accordance with the NL limit. The moisture content in black pepper powder sample A, both samples of black peppercorns and a sample of ginger (brand name A) was found to be slightly above the ESA limit. Although the maximum permissible water content limit in green peppercorns is not regulated by the national legislation, the moisture content in green peppercorns was found to be below the ESA limit. The percentage of moisture in black cumin samples, although significantly lower when compared to the previously presented data (Mollazade et al., 2009; Gharib-Zahedi et al., 2010), may increase the shelf life of these spices during packaging and storage and also limit fungal and contamination effects. Figure 2 shows multiple comparisons for all moisture content in different spices collected from local markets in Belgrade.



**Fig. 2** Multiple comparisons for all moisture content in different spices

### 3.3. Determination of total ash content

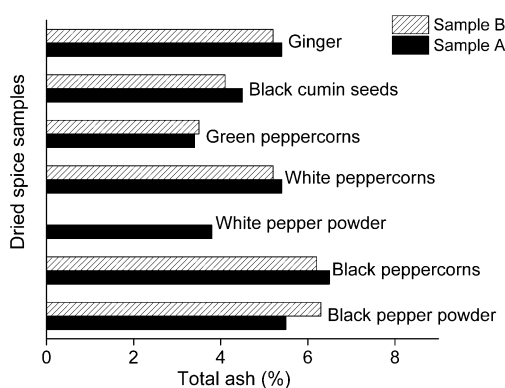
The results of total ash determination in the analyzed spices are presented in Table 6 as the mean value of total ash  $\pm$  standard deviation (SD) for five determinations, compared with maximum permissible limits of total ash in those dried products, established by the national legislation (Pravilnik – Sl. list SFRJ, br. 4/85 i 84/87 i Sl. list SCG, br.56/2003 – dr. pravilnik, 4/2004 – dr. Pravilnik i Sl. glasnik RS, br. 43/2013 – dr. pravilnik 30) and ESA (European Spice Association Quality Minima Document, 2011).

**Table 6** Total ash in dried spices samples

Spices	Total ash (%)			
	(mean value $\pm$ SD)			
	MPL (%)		Sample brand name	
	NI <sup>a</sup>	ESA <sup>b</sup>	A	B
Black pepper powder		7.0	5.5 $\pm$ 0.1	6.3 $\pm$ 0.2
Black peppercorns	7.0	7.0	6.5 $\pm$ 0.2	6.2 $\pm$ 0.2
White pepper powder	4.0	3.5	3.8 $\pm$ 0.1	NA <sup>c</sup>
White peppercorns		3.5	5.4 $\pm$ 0.2	5.2 $\pm$ 0.2
Green peppercorns	NR <sup>d</sup>	3.0	3.4 $\pm$ 0.1	3.5 $\pm$ 0.1
Black cumin seeds	8.0	14.0	4.5 $\pm$ 0.1	4.1 $\pm$ 0.1
Ginger powder	7.0	8.0	5.4 $\pm$ 0.2	5.2 $\pm$ 0.2

Abbreviations: <sup>a</sup>bMaximum permissible limit of the total ash in the examined spices, according to the NL<sup>a</sup> and ESA<sup>b</sup>. <sup>c</sup>NA – Not available. <sup>d</sup>NR – Not regulated by NL.

A comparison between total amounts of mineral components in all analyzed dried spices samples and the maximum permissible limit, recommended by the national legislation and ESA, indicates that the total ash content in both white peppercorn samples are above the national legislation limit and ESA limit. The maximum permissible total ash limit in green peppercorns is not regulated by the national legislation, but the total ash content in white pepper powder sample and both green peppercorn samples were found to be above the ESA limit. Figure 3 shows multiple comparisons for all total ash content in different spices, collected from local markets in Belgrade.



**Fig. 3** Multiple comparisons for all total ash content in different spices

Generally, the obtained results of moisture and total ash content are in agreement with data reported in the literature (Martin, 1979; Belay et al., 2012) and indicate a generally good quality and high purity of the examined spices.

#### 4. CONCLUSION

In this study, the concentrations of selected heavy metals (lead, mercury and arsenic), moisture content and total amount of minerals in black, white and green pepper, black cumin and ginger obtained in local markets in Belgrade were determined. The overall results indicated that lead and arsenic were present in all spices samples, while mercury was not detected in black and white pepper samples at the time of this study. Maximum concentrations of Pb (0.79 ppm), Hg (0.11 ppm) and As (0.51 ppm) were determined in the samples of ginger, green peppercorns and black peppercorns, respectively. The maximum moisture content (13.1%) and total ash content (6.5%) were determined in the ginger and black peppercorn samples, respectively. Heavy metal, moisture and total ash content in the selected commercial spices varied within plant species but, generally, were below maximum permissible limits established by the national legislation. Moreover, the current study showed that selected black, white and green pepper, black cumin and ginger are characterized by low heavy metal content and may safely be used for consumption without any hazardous effect on human health.

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## SADRŽAJ OLOVA, ŽIVE I ARSENA U ZAČINIMA: CRNI, BELI I ZELENI BIBER, CRNI KIM I ĐUMBIR

*U ovom radu, u cilju utvrđivanja bezbednosti odabranih komercijalnih začina, analizirane su koncentracije teških metala, kao i sadržaj vlage i ukupnih mineralnih materija, u uzorcima sušenog crnog i belog bibera u prahu, crnog, belog i zelenog bibera u zrnu, semena crnog kima i đumbira u prahu. Koncentracije olova (Pb), žive (Hg) i arsena (As) u uzorcima začina iz lokalnih prodavnica u Beogradu, određene su nakon mikrotalasne digestije atomskom apsorpcionom spektrometrijom (AAS), primenom tehnike grafitne peći (Pb), tehnike hladne pare (Hg) i hidridne tehnike (As). Određene koncentracije Pb, Hg i As u uzorcima sušenih začina su u opsegu 0,10 ppm – 0,79 ppm, 0,01 ppm – 0,10 ppm i 0,01 ppm – 0,51 ppm, redom. Maksimalna koncentracija Pb od 0,79 ppm određena je u uzorku đumbira, maksimalna koncentracija Hg od 0,10 ppm u uzorcima zelenog bibera u zrnu, dok je maksimalna koncentracija As određena u uzorku crnog bibera u prahu i iznosila je 0,51 ppm. U uzorcima ispitivanih začina sadržaj vlage i mineralnih materija je u opsegu 1,70–13,10% i 3,40–6,50%, redom. Dobijeni rezultati pokazuju da su koncentracije ispitivanih teških metala, kao i sadržaj vlage i mineralnih materija ispod maksimalno dozvoljenih vrednosti propisanih zakonskom regulativom Republike Srbije, kao i da su ispitivani uzorci crnog, belog i zelenog bibera u prahu i zrnu, crnog kima u zrnu i đumbira u prahu propisanog kvaliteta u ovom smislu.*

Ključne reči: začini, teški metali, arsen, sadržaj vlage i minerala, atomska apsorpciona spektrometrija