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QUALITY AND SAFETY OF SOME COMMERCIAL SPICES BRANDS

Slavica M. Blagojević[a]*, *Stevan N. Blagojević*[b], *Nataša D. Pejić*[a],
Biljana A. Begović[b] and *Spasenka P. Gajinov*[b]

[a] University of Belgrade, Faculty of Pharmacy, Department of Physical Chemistry and Instrumental Methods, Vojvode Stepe 450, 11221 Belgrade, Serbia
[b] Institute of General and Physical Chemistry, POB 45, 11158 Belgrade, Serbia

In this study, in order to evaluate the quality and safety of selected commercial spices brands, contents of moisture and minerals, as well as the concentration of certain heavy metals (*As, Hg and Pb*) *were determined in oregano, sweet basil, parsley and celery. The spice samples were subjected to microwave digestion, and were analyzed by atomic absorption spectrometry (AAS), using hydride generation AAS technique, cold vapor AAS technique, and graphite furnace AAS technique for determination of As, Hg and Pb, respectively. Maximum concentrations of As and Pb were determined in the same brand sample of celery, and are 0.75 ppm and 0.40 ppm, respectively, while the maximum concentration of Hg in various brands sweet basil samples is 0.05 ppm. According to the results, the contents of moisture and minerals, as well as the concentrations of heavy metals in all selected spices were below the maximum permissible limits declared by the national legislations, and are safe for human consumption.*

KEY WORDS: spices, heavy metals, moisture, minerals content, atomic absorption spectrometry

INTRODUCTION

Spices are dried parts of plants which have been used to improve color, flavor, and acceptability of foods. Most of these are fragrant and aromatic, and include many bioactive compounds that can influence digestion and metabolism processes. Many common spices have outstanding antioxidant and antimicrobial effects, while some others have a preservative effect (1,2). Yet, they can cause human health problems since they may contain some undesirable components like micotoxins, pesticides, organic compounds with diverse functional groups and heavy metals. Some heavy metals (Cu, Zn Cr, Fe, and Co) are essential, and required in very small quantities for proper functioning of human body (3), while some heavy metals like Pb, As, and Hg are toxic as they produce harmful effects upon exposure, even at very low concentrations (4).

* Corresponding author: Slavica M. Blagojević, University of Belgrade, Faculty of Pharmacy, Department of Physical Chemistry and Instrumental Methods, e-mail: slavica.blagojevic@pharmacy.bg.ac.rs

The content of heavy metals in plants may be influenced by geochemical characteristics of the soil in which the plants are cultivated (5), environmental pollution levels (5,6), and it varies depending on both the plant species, and parts which accumulate heavy metals (7). Also, industrial processing, packaging, transportation and storage conditions can play a significant role in elevating the contaminant levels of heavy metals, which may affect the quality and safety of plants and spices (8). Generally, the addition of spices that may be contaminated with trace and heavy metals to foods can lead to a serious consequences for human health, because most heavy metals are not biodegradable and have the potential for accumulation in different human body organs (9). The prolonged heavy metals exposure through foods may lead to the chronic accumulation of heavy metals in the kidney and liver of humans, leading to diseases of cardiovascular, reproductive, skin, nervous, kidney, bone, gastrointestinal, immune, skeletal, and muscular systems (4,9).

Because of the high toxicity of heavy metals and their tendency to accumulate in spices (10), the analytical determination of heavy metals in spices that are to be used for medical purposes and for improving the taste of food, is a part of permanent quality control in order to establish their purity, safety and efficacy. The most popular analytical methods for the determination of toxic heavy metals like As, Hg and Pb in spices samples are high sensitivity and selectivity spectroscopic methods such as: flame atomic absorption spectrometry, hydride generation atomic absorption spectrometry, and cold vapor atomic absorption spectrometry (7,11,12); graphite furnace atomic absorption spectrometry (13); inductively coupled plasma atomic emmision spectrometry (14); cold vapor generation atomic fluorescence spectrometry (15); inductively coupled plasma mass spectrometry (16), and inductively coupled plasma–optical emission spectrometry (17).

The contents of moisture and minerals are important indicators to illustrate the quality, as well as purity of spices. The water content is very important. Insufficiently or improperly stored dried spices are subject to change which can lead to the degradation of the active components, bacterial and fungal growth resulting in the inadequate quality and safety of spices. Total ash is a measure of the total amount of minerals present within a spice, and it refers to the inorganic residue remaining after total incineration of organic matter which is derived from plant tissue itself, and to the specific inorganic components that often originated from environmental contaminations.

The aim of the present study was to investigate the contents of moisture and minerals and the concentration of As, Hg and Pb in oregano, sweet basil, parsley and celery samples, and to analyze the quality and safety of commercial spices brands in the Belgrade markets.

EXPERIMENTAL

Sample materials

Oregano (*Origanum vulgare*), sweet basil (*Ocimum basilicum*), parsley (*Petroselinum crispum*) and celery (*Apium graveolens*), collected in May 2012, directly from local markets in Belgrade, were used as spice samples. A total of fifteen marked samples represent dried oregano, sweet basil, parsley and celery, packed by four different distributors whose brand names were hidden, and marked from A to D. Dried celery sample packaged by brand name D was not available in the Belgrade market at the time of this study.

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Air-oven drying method

It is one of the most common and widely used methods for routine moisture determination (18). The ovens should be thermally regulated to 105°C ± 0.5°C, and have minimal temperature variations (< 3°C) within the oven.

Total ash

Dry ashing is the standard method for determining the total ash of a food sample (19). For ashing, samples were kept in a furnace for 5 hours at 550°C - 600°C, to oxidize all organic materials without flaming, and the results were obtained gravimetrically.

Microwave digestion preparation

In this study we used microwave digestion as the efficient method for sample decomposition prior to the determination of heavy metals (20). The samples of dried spieces were digested using the Microwave digestion (MWD) system (Milestone Start E), with Teflon digestion vessels and high pressure supports. Prior to heating in the MWD, 10.5 g of dried sample were weighed into the teflon digestion vessel, and 15 ml of concentrated 12.1 M HCl (spectroscopic grade) were added; the vessels were capped to 16.3 N m. After the MWD tretments (30 min at 600 W power), the samples were removed, allowed to cool, and then filtered prior to being analyzed by the method descibed above.

Sample analysis

Digested samples were analyzed using hydride generation technique for As (11), cold vapor atomic absorption technique for Hg (11,12), and graphite furnace absorption technique for Pb determination (13). Atomic absorption measurements were made using Atomic absorption spectrophotometer (GBC-Australia), with a deuterium lamp for background correction and hollow cathode lamps. Air-acetylene flame (GBC-SensAA-Dual) and nebulizer gas flow rate 5 L min^{-1} were used for the determination of As and Hg. A GBC-SensAA-Dual-graphite furnace, equipped with a deuterium lamp for background correction, was used for the determination of Pb. Measurements were made using a hollow cathode lamp for As, Hg and Pb at wavelengths of 193.7 nm, 253.7 nm and 217.0 nm, respectively.

Quantification of heavy metals was achieved by using a calibration curve that was fitted by the least squares method. Measurement uncertainty was determined on the basis of 32 measurements on 0.1 ppm solution and expressed as relative standard deviation (RSD). RSD was 5%, for all elements. The standard deviation of the response (SD) and slope of the calibration curve (S) were used to calculate the limit of detection (LOD) by using the equation LOD = 3.3 (SD/S). The obtained LOD for As, Pb and Hg were 10 ppb, 1 ppb and 10 ppb, respectively.

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RESULTS AND DISSCUSION

Moisture content and total ash

The results of the determination of moisture and total ash in dried oregano, sweet basil, parsley and celery samples, collected in Belgrade markets are presented in Table 1. The obtained results were presented as mean value ± SD for five determinations.

The data in Table 1 show that the moisture contents in oregano (10.3% - 11.1%), sweet basil (9.5% - 11.0%), and celery (9.3% - 9.6%) samples are in accordance with the maximum permissible national legislation (Nl) (21) and European Spice Association (ESA) (22) limits of water content in those dried products. The moisture content in the parsley samples (10. 3% - 10.9%) was found to be below the national legislation limit, but above the ESA limit.

It was found that total ash in oregano (5.5% - 7.5%) and sweet basil samples (7.8% - 9.5%) varies for the different brand name, while the lowest ash was determined in oregano sample (brand name A) and the highest one in sweet basil sample (brand name B). On the other hand, the values of total ash in different samples of parsley (7.1% - 7.7%) and celery (6.1% - 6.5%) are close. However, the total amounts of mineral components in all dried spices samples are below the national legislation and ESA limit. Those results indicate good quality and high purity of the examined spices.

Table 1. Moisture content and total ash in dried spices samples

Moisture content (%) (mean value ± SD)						
Spice	Nl[a]	ESA[b]	A	B	C	D
Oregano	12.5	12.0	10.7 ± 0.3	10.3 ± 0.3	10.5 ± 0.3	11.1 ± 0.3
Sweet basil	12.5	12.5	10.5 ± 0.3	9.5 ± 0.3	10.8 ± 0.3	11.0 ± 0.2
Parsley	12.0	7.5	10.5 ± 0.2	10.9 ± 0.2	10.6 ± 0.3	10.3 ± 0.2
Celery	12.0	11.0	9.6 ± 0.2	9.3 ± 0.3	9.5 ± 0.3	NA[c]
Total ash (%)						
Spice	Nl	ESA	A	B	C	D
Oregano	8.0	10.0	5.5 ± 0.1	7.5 ± 0.1	6.8 ± 0.2	7.2 ± 0.2
Sweet basil	12.0	16.0	7.8 ± 0.1	9.5 ± 0.2	9.1 ± 0.2	8.2 ± 0.2
Parsley	8.0	14.0	7.5 ± 0.2	7.7 ± 0.2	7.1 ± 0.2	7.2 ± 0.1
Celery	8.0	12.0	6.5 ± 0.1	6.2 ± 0.2	6.1 ± 0.1	NA[c]

[a,b] Maximum permissible limit of the moisture content and total ash in the examined spices, according to the national legislation (Nl)[a] and European Spice Association (ESA)[b]. [c]NA - Not available.

Concentrations of heavy metals in spice samples

The results of the determination of toxic heavy metals in oregano, sweet basil, parsley and celery dried samples, for different brand name commercially available in Belgrade markets, were presented as mean value ± SD for five determinations are given in Table 2.

Table 2. Heavy metal concentrations in the selected spices

Heavy metal concentrations (ppm) (mean value ± SD)				
Spices	Sample	As	Hg	Pb
Oregano	A	0.05 ± 0.006	0.01 ± 0.001	0.34 ± 0.03
	B	0.02 ± 0.003	0.01 ± 0.001	0.36 ± 0.04
	C	0.05 ± 0.005	0.01 ± 0.002	0.30 ± 0.03
	D	0.04 ± 0.005	0.01 ± 0.002	0.28 ± 0.02
Sweet basil	A	0.35 ± 0.04	0.05 ± 0.004	0.12 ± 0.01
	B	0.45 ± 0.03	0.04 ± 0.005	0.13 ± 0.01
	C	0.44 ± 0.04	0.05 ± 0.005	0.15 ± 0.01
	D	0.42 ± 0.03	0.05 ± 0.004	0.11 ± 0.01
Parsley	A	0.05 ± 0.004	ND[b]	0.29 ± 0.03
	B	0.06 ± 0.005	ND	0.35 ± 0.03
	C	0.05 ± 0.004	ND	0.33 ± 0.03
	D	0.07 ± 0.006	ND	0.30 ± 0.02
Celery	A	0.60 ± 0.07	ND	0.34 ± 0.03
	B	0.75 ± 0.08	ND	0.40 ± 0.04
	C	0.70 ± 0.05	ND	0.35 ± 0.04
	D	NA[a]	NA	NA

[a] NA - Not available. [b]ND - Not detected. Levels were below the detection limit.

The concentrations of As and Pb in different oregano brands name were in the range from 0.02 to 0.05 ppm and from 0.28 to 0.36 ppm, respectively. On the other hand, in all the examined oregano products, the Hg concentration was the same (0.01 ppm), and considerably below the maximum permissible limit. The levels of heavy metals were compared with the appropriate safety standards as established by the national legislation (23). According to the national legislation, the maximum permissible limits for As and Pb in herbal species are 1 ppm and 2 ppm. The maximum permissible Hg concentration in herbal spices is not regulated by the national legislation, but according to the Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) and recommendation for general limits of Hg in food additive is 1 ppm (24). All the dried oregano samples were found to contain As, Hg and Pb in the concentrations that are lower than the maximum permissible limit.

The As and Pb concentrations in sweet basil samples ranged from 0.35 to 0.45 ppm, and from 0.11 to 0.15 ppm, respectively. The concentrations of Hg were comparable in different sweet basil samples with a range of of 0.04 - 0.05 ppm. The contents of the examined toxic heavy metals in dried basil samples were all below the maximum permissible limits by the national legislation (23).

The lowest and highest values of As concentration in the studied parsley samples were found to be 0.05 ppm and 0.07 ppm. The concentrations of Pb were comparable in all parsley samples, being in the range 0.29 ppm - 0.35 ppm. The Hg concentrations in parsley samples were found to be within the detection limit of the cold vapor AAS technique. As shown in Table 2, the comparison between the concentration of As and Pb in all parsley samples and the permissible levels recommended by the national legislation (23), indicates that the concentrations of these elements in all dried parsley samples were below the maximum permissible limits.

In the case of celery, the highest mean concentration of As was found to be 0.75 ppm for celery sample B, and the lowest 0.6 ppm for sample A. The concentration of lead is noticeably low, and it ranged from 0.40 ppm (sample B) to 0.34 ppm (sample A). In the samples of celery, Hg was not detected. The results presented in Table 2 show that the concentrations of As and Pb in dried celery samples were below the maximum permissible limits.

Figure 1 represents the multiple comparisons for all heavy metal content in different spices collected from local markets in Belgrade.

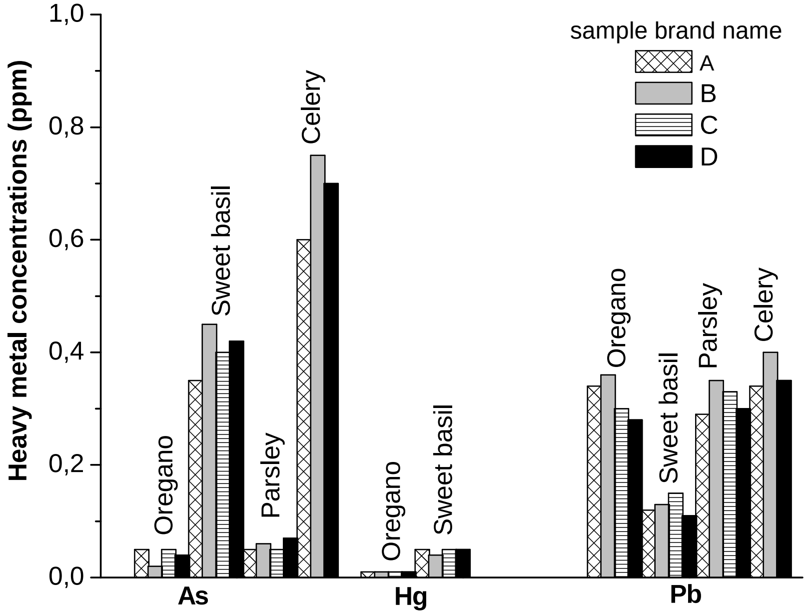

Figure 1. Contents of heavy metals in the samples of different spices

The concentrations of all three measured heavy metals in the oregano, sweet basil, parsley and celery samples were found to be at different levels. The highest mean level of As concentration (0.75 ppm) was found in celery samples (brand name B), while the lowest value of As (0.02 ppm) was found in oregano sample (brand name B). The concentrations of As were comparable in the oregano and parsley samples, being within the range of 0.02 - 0.07 ppm. The concentration of Hg was very low (0.01 ppm) and were the same in all the examined oregano products. On the other hand, the highest mean levels of Hg (0.05 ppm) were detected in sweet basil samples. In basil samples, the concentrations of Hg were similar (0.04 - 0.05 ppm), but five times higher than in the samples of oregano. Hg was not detected in any of the analyzed parsley and celery samples at the time of this study. The level of Pb in the examined plant spices ranged from 0.11 to 0.40 ppm, with the highest mean value found for celery (brand name B), and the lowest mean concentration in sweet basil (brand name D).

The overall results indicated clearly that As, Hg and Pb were present in spices collected in local markets in Belgrade, but the contents of these metals were found to be generally low, and they all meet the requirements of the corresponding safety standards.

CONCLUSION

The work presents the results of the determination of moisture content, total amount of minerals as well as concentrations of As, Hg and Pb in oregano, sweet basil, parsley and celery, spices that are widely used in Serbian cuisine. The moisture content, total ash and the examined toxic heavy metals in selected herbal spices depended on plant species, but generally were below the concentrations allowed by the national legislations. The results obtained in our study indicate that selected popular spices, available on the local markets in Belgrade, are of high quality, and safe for consumption, as far as moisture content and total inorganic compounds as well as As, Hg and Pb concentrations are concerned.

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REFERENCES

1. Hinneburg, I., Damien-Dorman, H.J. and Hiltunen, R.: Antioxidant activities of extracts from selected culinary herbs and spices. Food Chem. **97** (2006) 122-129.
2. Shelef, L.A.: Antimicrobial effect of spices. J. Food Safety **6** (1983) 29-44.
3. Divrikli, U., Horzum, N., Soylak, M. and Elci, L.: Trace heavy metal contents of some spices and herbal plants from western Anatolia, Turkey. Int. J. Food Sci. Technol. **41** (2006) 712-716.
4. Fergusson, J.E.: The Heavy elements: Chemistry, Environmental Impact and Health Effects. Eds. Pergamin Press, Oxford (1990) pp. 382-399.
5. Abu-Darwish, M.S., Abu-Dieyeh, Z.M., Batarseh, M., Al-Tawaha A.R.M. and Al-Dalain, S.Y.A.: Trace element contents and essential oil yields from wild thyme plant (*Thymus serpyllum* L.) grown at different natural variable environments, Jordan. J. Food Agric. Environ. **7** (2009b) 920-924.
6. Angelova, V., Ivanov, K. and Ivanov, R.: Heavy metal content in plants from family Lamiaceae cultivated in an industrially polluted region. J. Herbs, Spices & Med. Plants. **11** (2005) 37-46.
7. Prasad, M.N.V. and Freitas, H.M.: Metal hyper accumulation in plants. Biodiv. Prospect. Phytoremed. Technol. **6** (1990) 285-321.

8. Tsoumbaris, P. and Tsuokali-Papadopoulou, H.: Heavy metal in common foodstuffs: Quantitative analysis. Bull. Environ. Contam. Toxicol. **53,** 1 (1994) 61-66.
9. Jarup, L.: Hazards of heavy metal contamination. Br. Med. Bull. **68** (2003) 167-182.
10. Brooks, R.R.: Plants that hyperaccumulate heavy metals, in phytochemistry of hyper-accumulators. Eds. CAB International, Wallingford (1998) pp.15-53.
11. Garg, M. and Singh, J.: Quantitative AAS Estimation of heavy metals and trace elements in marketed ayurvedic churna preparations in India. Int. J. Pharm. Sci. Res. **3,** 5 (2012) 1331-1336.
12. Caldasa, E.D. and Machado, L.L.: Cadmium, mercury and lead in medicinal herbs in Brazil. Food Chem.Toxicol. **42** (2004) 599-603.
13. Ramezani, Z., Aghel, N. and Amirabedin, N.: Determination of Pb and Cd in garlic herb (*Allium sativum*) planted in Gilan and Khuzestan provinces using graphite furnace atomic absorption spectrometry. Nat. Pharm. Prod. **7** (2012) 41-44.
14. Ling, H.J., Yi, L. and Yu, Z.: Determination of the major metal elements including heavy metals in Saffron from Tibet and Henan by ICPAES or ICPMS. J. Chin. Pharm. Sci. **20** (2011) 297-301.
15. Yijian, C., Xuechang, D., Yun, D., Qiufen, H. and Hong, Y.: Determination of trace mercury in Chinese herbal medicine by cold vapour generation-atomic fluorescence spectrometry. Asian J. Chem. **20**, 6 (2008) 4639-4646.
16. Feryie, Ş.: Determination of arsenic, selenium and cadmium in some Turkish spices by inductively coupled plasma mass spectrometry, M. Sc. Thesis, Middle East Technical University, Ankara, 2010.
17. Gonzálvez, A., Armenta, S. and Guardia, M.: Trace elemental composition of curry by inductively coupled plasma optical emission spectrometry (ICP-OES). Food Addit. Contam.: Part B-Sur. **1** (2008) 114-121.
18. AACCI Method 44-15.02 Moisture-Air-Oven Methods, http://methods.aaccnet.org (accessed 6 september 2013).
19. SRPS ISO 928:2001, Spices and condiments-Determination of total ash, Institute for Standardization of Serbia.
20. Yaling, Y., Yan, G. and Qiang, L.: Determination of Heavy Metal Ions in Chinese Herbal Medicine by Microwave Digestion and RP-HPLC with UV-Vis Detection. Microchim. Acta **144**, 4 (2004) 297-302.
21. Pravilnik o kvalitetu začina, ekstrakata začina i mešavina začina ("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).
22. European Spice Association Quality Minima Document, 2011. http://www.esa-spices.org (accessed 28 februar 2013).
23. Pravilnik o količinama pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i drugih supstancija koje se mogu nalaziti u namirnicama, Službeni list SRJ br. 5/92, 11/92 - ispr. i 32/2002.
24. Joint FAO/WHO Expert committee on food additives, 2002. http://www.fao.org (accessed 28 februar 2013).

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КВАЛИТЕТ И БЕЗБЕДНОСТ НЕКИХ КОМЕРЦИЈАЛНИХ ЗАЧИНА

Славица М. Благојевић[а], *Стеван Н. Благојевић*[б], *Наташа Д. Пејић*[б], *Биљана А. Беговић*[б] *и Спасенка П. Гајинов*[б]

[а] Универзитет у Београду, Фармацеутски факултет, Катедра за физичку хемију и инструменталне методе, Војводе Степе 450, 11221 Београд, Србија
[б] Институт за општу и физичку хемију, ПОБ 45, 11158 Београд, Србија

У овом раду, у циљу одређивања квалитета и безбедности изабраних зачина, одређен је садржај влаге и укупних минералних материја, као и концентрације арсена (As), живе (Hg) и олова (Pb) у узорцима оригана, босиљка, першуна и целера. Концентрације тешких метала As, Hg и Pb, након микроталасне дигестије, одређене су различитим аналитичким техникама атомске апсорционе спектрометрије, применом хидридне технике (As), технике хладне паре (Hg) и технике графитне пећи (Pb). Максималне концентрације As и Pb одређене су у истом узорку целера и износе 0,75 ppm и 0,40 ppm, респективно, док је максимална концентрација Hg одређена у узорцима босиљка и износи 0,05 ppm. У узорцима зачина, вредности садржаја влаге, минерала и концентрације испитиваних тешких метала су испод максимално дозвољених вредности прописаних законском регулативом Републике Србије.

Кључне речи: зачини, тешки метали, влага, садржај минерала, атомска апсорпциона спектрометрија

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