Pol. J. Environ. Stud. Vol. 22, No. 4 (2013), 1251-1256

Short Communication

Estimation of Metallic Elements in Herbs and Spices Available on the Polish Market

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Received: 28 November 2012
Accepted: 5 March 2013

Abstract

Herbs and spices are commonly used in cuisine all over the world. They may contain many various substances beneficial for health, but also harmful (e.g. metallic) elements. Spices and herbal plants contain metal ions over a wide range of concentrations. Metals can have important positive or negative roles in human life.

The aim of this study was to estimate the trace metals content in select popular Polish herbs and spices available on the Polish market. Thirty samples of various herbs and spices (fennel, sage, oak bark, St. John's wort, linden inflorescence, mint, black pepper, garlic, marjoram, paprika, cinnamon, basil, oregano, herbs de Provence, and parsley) were analyzed. The contents of Cu, Ni, Fe, Zn, and Mn were determined using AAS method after sample mineralization with 65% nitric acid and 30% hydrogen peroxide. Metals contents were compared in spices from different manufacturers. The chemometric techniques were used to evaluate similarity with respect to herb and spice metal contents.

Keywords: herbs, spices, metallic elements, cluster analysis

Introduction

Herbs and spices have been used since ancient times. Today they are popular in most cuisines all over the world. In the last few decades there has been an increasing interest in herbs, spices, and medicinal plants [1-3].

Herbs and spices grow in various regions of the world. Spices are dried products of plants that have been used as diet components often to improve aroma, taste, and acceptability of food. They consist of rhizomes, barks, leaves, fruits, seeds, and other plant parts. Fragrance and aroma characterize them. Although herbs and spices have no nutritive properties, they can improve taste and smell of food. Moreover, they are supposed to have medical properties such as antioxidant and antimicrobial action or antidiabetic potential. On the other hand, herbs and spices can contain some harmful component like pesticides, micotoxines, and metals [2, 4-8].

Plants may be easily contaminated during growing and processing. They can contain metals from their presence in the soil, water, or air. Plants also are an important link in the transfer of trace elements from soil to man. Some trace elements are essential for normal growth and functioning of living organisms, but only at low concentrations. They catalyze many biochemical reactions occurring in the organisms involved in the formation of red blood cells, hormones, and vitamins, as well as take part in the processes of photosynthesis and the creation of pigments, respiration, oxidation, and reduction. Some of these elements are important in metabolism, are part of the bone and tissues of living organisms, and participate in the functioning of neural systems. But in too high doses these metals can be toxic [1, 5, 9, 10].

Materials and Methods

Studied material consisted of 30 herb and spice samples commonly used in households: fennel (*Foeniculum vulgare*), sage (*Salvia officinalis*), oak bark (*Quercus cortex*),

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St. John's wort (*Hypericum perforatum*), linden inflorescence (*Tilia vulgaris*), mint (*Mentha piperita*), black pepper (*Piper nigrum*), garlic (*Allium sativum*), marjoram (*Origanum majorana*), paprika (*Capiscum* sp.), cinnamon (*Cinnamomum zeylanicum*), basil (*Ocimum basilicum*), oregano (*Origanum vulgare*), herbs de Provence (mixed herbs), and parsley (*Petroselinum crispum*). The research of this paper were Herbapol's herbs and spices of three leading brands available on the Polish market: Prymat, Kamis, and Galeo.

Studied samples of herbs and spices were purchased directly from local markets in the Pomorskie region. Packaging of studied samples were opened immediately prior to analysis and homogenized in an agate mortar.

In order to assay the total amount of metals, the samples were mineralized with 65% nitric acid and 30% hydrogen peroxide. For acid digestion, approximately 0.5 g of herbs and spices was weighed accurately into the pre-cleaned round-bottomed flask. Concentrated nitric acid (5 mL) was added, the flasks were covered, and the samples were left for 30 minutes. Then the flask was placed in a prepared wet mineralization system and boiled. During the digestion process the 2 mL of hydrogen peroxide was added three times. The whole process took approximately 2 h. until digestion was complete. The digested samples were allowed to cool before being transferred quantitatively into pre-cleaned 25 mL volumentric flasks. The samples were then diluted to volume by the addition of deionized water.

The total amount of Cu, Ni, Fe, Zn, and Mn was analyzed using the AAS method with acetylene-air flame (spectrometer AAnalyst 400, Perkin Elmer). The wavelengths for metals were: Cu 324.8 nm, Ni 232.0 nm, Fe 248.3 nm, Zn 213.9 nm, and Mn 279.5 nm as recommended by the manufacturer. The detection limit of the method, as expressed in milligrams per kilogram of dry herbs and spices, for every studied metal (Cu, Ni, Fe, Zn, and Mn) was 0.05.

All chemicals used were of analytical reagent grade. All laboratory ware used in the analysis was previously soaked in a nitric acid 4 mol/l solution for at least 24 h and rinsed with deionized water. All analyses were done in triplicate.

The accuracy and precision of the methods was assured by simultaneous analysis of certified reference material INCT-TL-1 (black tea leaves). Reference material was prepared and certified by the Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology (Warsaw, Poland).

Results

The contents of studied metals are expressed in $mg\cdot kg^{-1}$ of dry matter (d.m.) and presented in Table 1.

The lowest copper content in the tested herbs and spices was in oak bark (3.82±0.05 $mg\cdot kg^{-1}$) and granulated garlic (2.7-4.2 $mg\cdot kg^{-1}$), the highest in marjoram (15.6-17.1 $mg\cdot kg^{-1}$). The lowest concentration of nickel was measured in linden inflorescence (0.8 $mg\cdot kg^{-1}$), and highest in fennel (26.5 $mg\cdot kg^{-1}$). The lowest amount of iron was determined in sage (20 $mg\cdot kg^{-1}$) and the highest in marjoram (1,120 $mg\cdot kg^{-1}$). The lowest concentration of zinc was measured in black pepper (9.26-18 $mg\cdot kg^{-1}$) and the highest in St. John's wort (86 $mg\cdot kg^{-1}$). The lowest manganese content was observed in granulated garlic (9.41-11.0 $mg\cdot kg^{-1}$) and cinnamon (5.5-19 $mg\cdot kg^{-1}$), while the highest was in oak bark (802 $mg\cdot kg^{-1}$).

For every group of species the Student *t*-test at the significance level of α =0.05 was applied. The results showed that many cases are not statistically different. The content of the metal in a specified plant species was comparable regardless of manufacturer spices, e.g. marjoram, basil, and garlic. The exceptions were paprika and black pepper. The contents of particular metals in paprika samples were different in every manufacturer. The iron content in studied black pepper were significantly different for every producer.

Generally, in all available literature different elements in various spices and herbs were studied. The copper concentration in fennel, St. John's wort, pepper, and paprika was similar to that reported by Sekeroglu, Krejpcio, Abou-Arab, and Karadas [3, 4, 7, 10]. The authors found lower copper content in linden and mint than Kara, and in garlic and parsley than Sattar. Simultaneously, the authors found higher content of copper in marjoram than Abou-Arab and in cinnamon and basil than Krejpcio. The nickel content in studied herbs and spices was rather higher than those found by Abou-Arab, Basgel, Karadas, and Kara [7, 9-11]. In herbs authors found lower iron concentrations than those reported in literature [3, 7, 9], while in the spices it was higher [3, 5, 7, 10]. The zinc concentration in studied fennel, sage, and linden was lower than that found by Basgel [9], while in John's wort, garlic, and marjoram it was higher than reported by Sekeroglu, Krejpcio, Sattar, and Abou-Arab [3-5, 7]. In studied mint, pepper, and paprika the zinc concentration was similar to the literature results [3-5, 7, 9-11]. Manganese concentration found for all of the herbs and spices was higher than those reported in literature [3, 5, 7, 9-11].

Table 2 summarizes the analyzed concentrations of metals in the Certified Reference Materials. The Student t-test, which was applied for analyzed and certified values of certified reference material, showed that the results are not statistically different at the significance level of α=0.05. Analysis of the certified reference material confirmed the good quality of the research. The recovery percentages of individual elements ranged from 93 to 108%.

Correlation Analysis

Table 3 presents the correlation matrix for the element concentrations in herbs and spices.

The correlation coefficient is a measure of the linear relationship between two attributes or columns of data. The correlation coefficients can range from -1 to +1 and are independent of the units of measurement. The negative correlation coefficients show a negative correlation while the positive correlation coefficients show a positive correlation

Table 1. Content of Cu, Ni, Fe, Zn, and Mn in analyzed herbs and spices (average value ±standard deviation).

Herb/spice (Producer)	Cu	Ni	Fe	Zn	Mn
	[mg·kg^{-1} d.m.]				
Fennel (Herbapol)	11.5±0.1	26.5±0.3	78.9±0.9	56.3±0.9	188±3
Sage (Herbapol)	9.01±0.05	6.87±0.21	20.0±0.5	34.8±0.2	240±3
Oak bark (Herbapol)	3.82±0.05	2.04±0.01	29.2±0.6	21.4±0.1	802±11
St. John's wort (Herbapol)	9.68±0.02	1.97±0.26	53.8±0.5	86.0±0.4	127±1
Linden inflorescence (Herbapol)	6.09±0.10	0.845±0.16	55.5±0.1	25.0±0.3	38.8±0.2
Mint (Herbapol)	6.71±0.07	3.40±0.26	293±1	28.8±0.1	78.6±0.5
Black pepper (Galeo)	10.6±0.03	23.0±0.10	611±5	15.9±0.1	189±3
Black pepper (Prymat)	9.58±0.07	6.87±0.01	200±2	9.26±0.13	190±2
Black pepper (Kamis)	15.0±0.16	8.29±0.09	984±4	18.0±0.1	197±3
Garlic (Galeo)	3.17±0.01	2.78±0.11	59.4±0.5	24.7±0.1	11.0±0.07
Garlic (Prymat)	2.70±0.03	1.51±0.10	69.3±0.6	23.9±0.1	9.41±0.03
Garlic (Kamis)	4.24±0.03	1.94±0.12	54.6±0.5	22.0±0.1	10.1±0.2
Paprika (Galeo)	24.2±0.09	2.51±0.27	327±1	29.3±0.1	170±1
Paprika (Prymat)	12.6±0.05	1.29±0.14	659±1	27.4±0.4	57.1±0.6
Paprika (Kamis)	3.52±0.07	0.16±0.08	38.9±0.3	14.1±0.4	206±7
Marjoram (Galeo)	15.6±0.08	3.44±0.30	1280±7	32.8±0.2	62.8±0.2
Marjoram (Prymat)	16.6±0.02	3.85±0.06	1150±1	34.0±0.3	57.1±0.6
Marjoram (Kamis)	17.1±0.14	3.75±0.19	934±6	37.3±0.5	59.2±0.2
Basil (Galeo)	13.6±0.29	2.84±0.20	577±5	36.1±0.3	67.6±0.4
Basil (Prymat)	14.1±0.09	2.81±0.10	625±4	36.2±1.3	69.4±0.3
Basil (Kamis)	13.4±0.12	2.95±0.25	552±4	38.3±0.1	72.0±0.6
Oregano (Galeo)	13.7±0.10	9.01±0.15	459±8	20.0±0.2	43.6±0.4
Oregano (Kamis)	8.74±0.01	10.6±0.40	619±12	26.6±0.2	54.7±0.3
Herbs de Provence (Prymat)	13.8±0.02	2.64±0.06	473±6	32.9±0.3	63.5±0.2
Herbs de Provence (Kamis)	12.2±0.10	3.87±0.29	530±2	33.6±0.1	59.2±2.3
Parsley (Galeo)	7.42±0.07	2.21±0.04	381±2	31.9±0.2	62.8±3.5
Parsley (Kamis)	4.83±0.02	0.19±0.14	189±1	25.2±0.4	34.7±0.1
Cinnamon (Galeo)	8.87±0.07	1.82±0.32	336±3	25.6±0.2	19.0±0.1
Cinnamon (Prymat)	6.84±0.10	1.79±0.39	118±7	28.2±0.1	18.7±0.1
Cinnamon (Kamis)	6.58±0.05	11.3±0.20	152±4	26.7±0.1	5.50±0.12

between the two variables. A value near 0 indicates virtually no correlation exists between two attributes, whereas a value near +1 or -1 indicates a high level of correlation [10, 11].

Correlation analysis of total element contents (Table 3) shows that there are rather weak relationships between analyzed elements. Only between copper and iron is there positive correlation, and it equals 0.75.

Cluster Analysis

The cluster analysis technique is an unsupervised classification procedure that involves a measurement of the similarity between objects. Objects are grouped in clusters in terms of their nearness or similarity [10, 11]. The measurement of the similarity is based on the single linkage Euclidean distance.

Table 2. Quality control results obtained for the analysis of certified reference material.

Element	Analyzed value [mgMe·kg^{-1} d.m.]	Certified value [mgMe·kg^{-1} d.m.]	% Recovery
Cu	20.5±0.82	20.4±1.5	100
Ni	5.74±0.32	6.12±0.52	93.8
Fe	451±8	432*	104
Zn	37.4±1.0	34.7±2.7	108
Mn	1590±10	1570±11	101

*indicative value

Table 3. Correlation matrix for the element concentrations in herbs and spices.

	Cu	Ni	Fe	Zn	Mn
Cu	1.00				
Ni	0.26	1.00			
Fe	**0.75**	-0.03	1.00		
Zn	0.19	0.18	-0.22	1.00	
Mn	-0.29	0.05	-0.30	-0.08	1.00

The dendrogram of cluster analysis for obtained average results of every studied species are presented in Fig. 1.

Eight groupings of herbs and spices were obtained from cluster analysis for averaged results (Fig. 1.):

Group 1: oak bark
Group 2: St. John's wort
Group 3: marjoram
Group 4: herbs de Provance, basil, paprika
Group 5: oregano, black pepper
Group 6: cinnamon, parsley, mint, garlic, linden inflorescence
Group 7: sage
Group 8: fennel

Cluster analysis also was used to compare herbs and spices from different manufacturers (Fig. 2). There is similarity for black pepper, paprika and basil of producers Prymat and Galeo. Garlic of producer Kamis is similar to garlic of producer Galeo. Kamis and Prymat made comparable marjoram and cinnamon.

Conclusions

This study attempts to evaluate the contents of five select metals in herbs and spices available on the Polish market. The study allows for the following conclusions:

1. Concentrations of metals in the tested herbs and spices occurred in a wide range. The range levels of metals in the studied samples were:
   - copper – from 3.37 to 16.4 mgCu·kg^{-1}
   - nickel – from 0.84 to 26.5 mgNi·kg^{-1}
   - iron – from 20.0 to 1120 mgFe·kg^{-1}
   - zinc – from 14.4 to 86.0 mgZn·kg^{-1}
   - manganese – from 10.2 to 802 mgMn·kg^{-1}
2. The highest concentrations of the analyzed elements were determined in the fennel, and spices marjoram and oregano.
3. Excluding every studied metal in paprika and Fe in black pepper, metal content was rather comparable in spices from different manufacturers.
4. The herbs and spices were classified into eight groups by cluster analysis. The first group of herb was oak bark containing an incomparably higher concentration

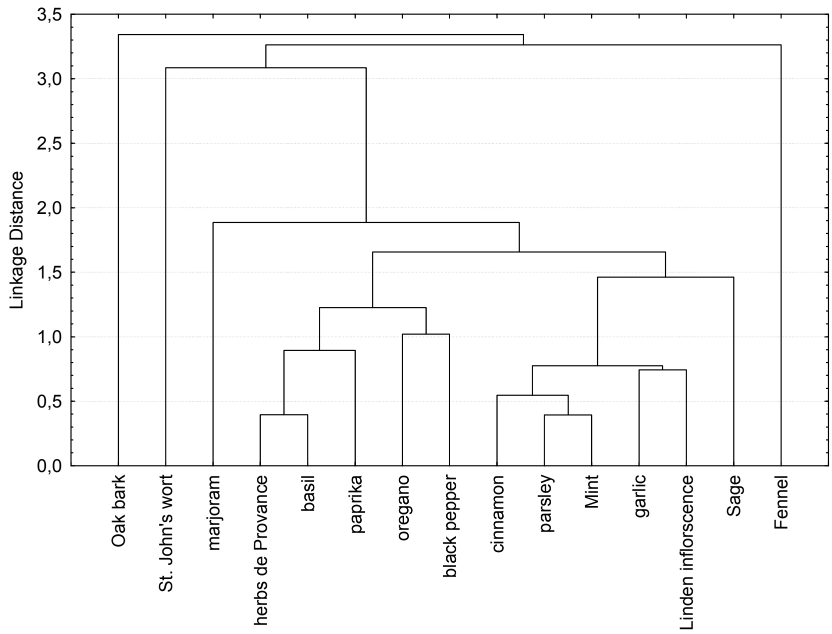

Fig. 1. Dendrogram of cluster analysis for average results.

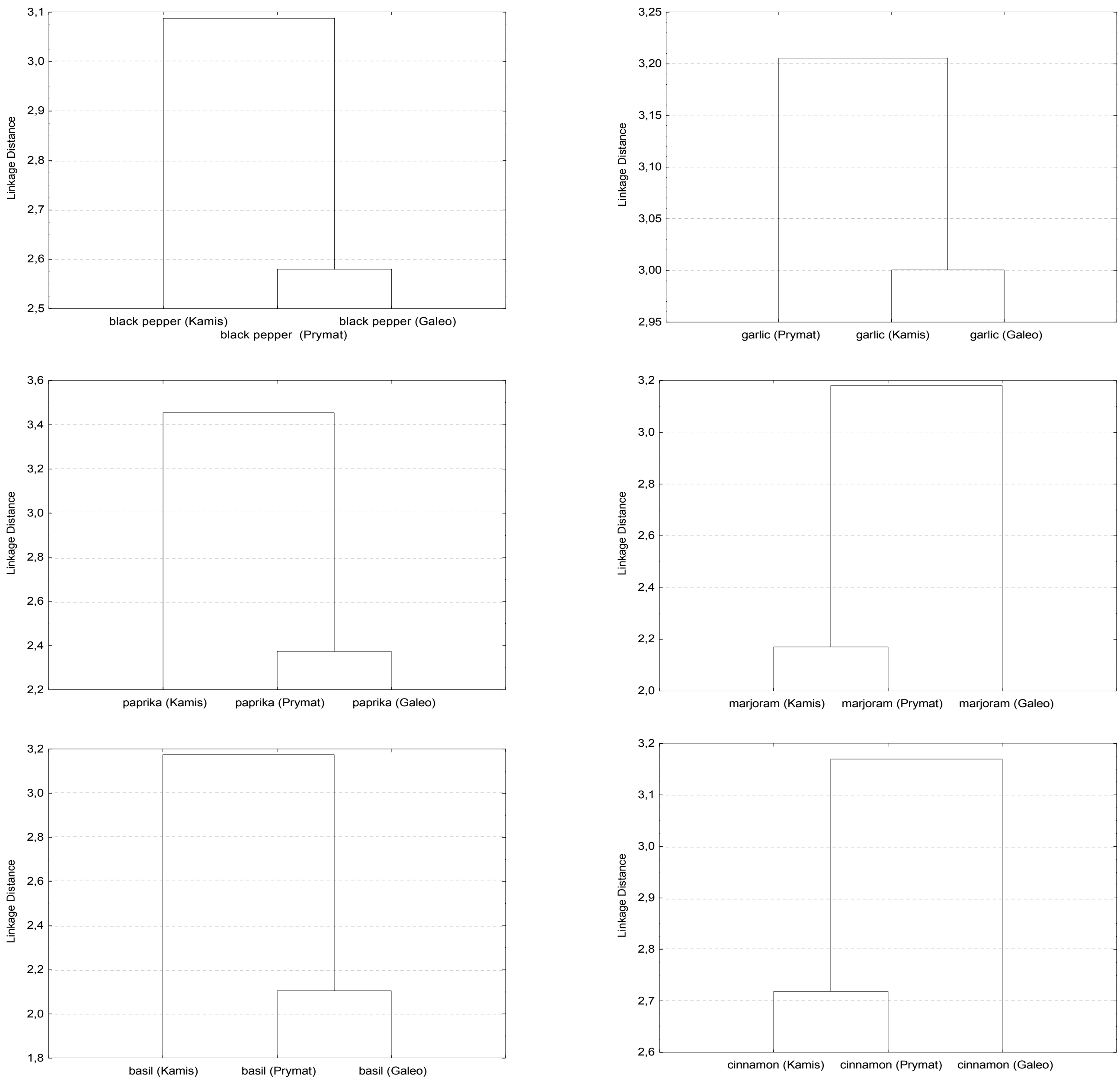

Fig. 2. Dendrogram of cluster analysis for herbs and spices from different manufacturers.

of Mn. The second group of herbs was St. John's wort and had the highest concentration of Zn. The third group of spices (marjoram) had the highest concentration of Fe. The fourth group of plants included herbs de Provence, basil, and paprika – all of which had similar concentrations of every studied metal. The fifth group of spices were oregano and black pepper. The largest group of plants was the sixth (cinnamon, parsley, mint, garlic, linden inflorescence), which had similar concentrations of Cu, Ni, and Zn. The seventh group included only sage and had a higher concentration of Mn and the lowest concentration of Fe. The last group of herb (fennel) had the highest concentration of Ni.

Acknowledgements

Financial support came from the University of Gdańsk, projects DS:530-8150-D199-12 and BNSRMN:538-8110-1062-12.

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