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ELEMENTAL ANALYSIS OF CULINARY HERBS AND SPICES BY ICP OES: CLASSIFICATION BY CHEMOMETRICS

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ABSTRACT. The inductively coupled plasma optical emission spectrometry method (ICP OES) was optimized and validated for the quantification of 21 elements in 88 samples of 23 types of culinary herbs and spices. All analyzed samples were low in Na, but rich in Ca, K and P. Among the microelements, the most abundant was Fe, followed by Cu, Zn, Cr, and Se. The concentrations of toxic elements (Cd and Pb) were below the permissible limits given by the World Health Organisation (WHO). Chemometrics was performed by the principal component analysis (PCA) and cluster analysis (CA). PCA generated two principal components that explained 43.82% of the total variance in the data and all samples were classified into six groups based on the element content. Also, PCA and CA allowed the differentiation and classification of culinary herbs and spices based on the concentration of five major elements.

Keywords: *culinary herbs, spices, macro and microelements, ICP OES, chemometrics, classification*

INTRODUCTION

Spices have been an irreplaceable part of traditional and modern cuisines since ancient times. Herbs are plants with aromatic leaves and represent a subset of spices [1]. Not only do spices give a specific flavour to food, but they also have a beneficial effect on human health. In a study conducted by Naveed et al. [2], essential oils from four Pakistani spices

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cumin, cinnamon, cardamom and clove showed the antibacterial activity against multi-drug resistant bacteria: *S. typhi, S. paratyphi, E. coli, S. aureus, P. fluorescens* and *B. licheniformis.* El-Ghorab et al. [3] pointed out the antioxidant properties of ginger and cumin. The use of essential oils and extracts from spices as preservatives in food protection has also been described [4, 5]. Sgorbini et al. [6] characterized and quantified biologically active markers in some herbs and species (clove, American peppertree, black pepper, white pepper, rosemary, sage and thyme) using separative (HS-SPME-GC-MS) and non-separative (HS-SPME-MS) approaches. They used aromatic markers, eugenol for cloves, carvacrol and thyme for thyme, and thujones for saga which were directly quantified on the solid matrix through the multiple headspace extraction-HS-SPME. Paleari et al. [7] characterized spices and aromatic herbs using GC/MS. They separated components which came from spices/aromatic herbs from the others which came from phenomena due to lipolytic endoenzymatic processes.

Apart from the importance of the organic components, the importance of major and trace elements in spices must not be neglected. The results obtained by Khan et al. [8] indicated that the essential trace elements that were found in aromatic spices have a good nutritional contribution. In contrast, the concentrations of toxic elements (As, Cd, Pb) were low and did not pose a threat to human health. Ghanjaoui et al. [9] have developed and validated the inductively coupled plasma optical emission spectrometry (ICP OES) method for the determination of trace elements in basil powder samples from Spain and Morocco. In a study conducted by Tahri et al. [10], 14 elements were determined by inductively coupled plasma atomic emission spectrometry (ICP AES) in rosemary samples collected in eastern Morocco. Özcan and Akbulut [11] have estimated the content of major and minor elements in medicinal and aromatic plants grown in Turkey which are used as spices, condiments and herbal tea by ICP AES, concluding that mineral content varied significantly depending on the species and location of the plant, while the content of heavy metals was very low in all of the samples. Kumaravel and Alagusundaram [12] reported 15 trace elements in five Indian spices, with the absence of As and Hg in all of the samples.

However, Abou-Arab and Abou Donia [13] noted that heavy metals present in some spices exceeded the permissible levels, which could be a consequence of the use of contaminated irrigation water, the addition of some fertilizers and herbicides, or the contamination from traffic. The mineral and trace elements content were determined in culinary herbs and spices in many studies. Some of these studies deal with the determination of a small number of elements in a specific type of fresh herbs or spices. Also, before any chemometric technique can be used, it is important to ensure that accurate analytical data are being obtained since the conclusions drawn from chemometric techniques can only be as reliable as the data. In this study, all samples were analysed under analytical control with the optimization of the operating parameters of the instrument and with the analysis of a certified reference material. Based on the lack of comprehensive studies of all well-known macro and microelements involving large number of culinary herb and spice samples, the aim of this work was to determine macro and microelements (Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Si, V, Zn) in 88 commercially available samples of culinary herbs and spices after the optimization and validation of the ICP OES method, as well as their classification using the principal component analysis (PCA) and cluster analysis (CA).

RESULTS AND DISCUSSION

Optimization of the Method

According to Mermet [14], the Mg II/Mg I line intensity ratio higher than 10 was selected to evaluate ICP operating conditions and the plasma robustness. The highest Mg II/Mg I ratio was obtained for RF power of 1150 W and nebulizer gas flow of 0.5 L/min. As in previous works [15, 16], the results showed a higher Mg II/Mg I ratio for the radially viewed configuration (Table S1).

A final selection of wavelength lines was taken into consideration after the study of ratio $slope_{cal}/slope_{sam}$ as well as the accuracy obtained for each line and spectral interferences. As can be seen in Table 1 the slopes of both kinds of lines were statistically comparable, which indicates the lack of matrix effects. ME data up to 7.6% indicates that the method of evaluation of the matrix effect generates reliable results.

Validation of the Method

The accuracy of the method was checked by analyzing the SRM. The recovery percentages for all elements were in the range 91-105% except for Na, Cd, Pb, Se and Si which were < 91%. The percent coefficient of variation (CV%) obtained for the precision evaluation for all analyte elements was ranged from 1.7% for Ca to 14.9% for Cr. Nevertheless, in all cases, the accuracy and precision were within the acceptable recoveries and CV percentages obtained from the Horwitz function [17-19] and the AOAC Peer-Verified Methods (PVM) program on the analyte level [20].

Table 1. The analyte line selected with the ratio $slope_{cal}/slope_{sam}$ and matrix effect (ME), as well as coefficient of determination (R^2), LOD and LOQ of the calibration for each element determination

Element	Wavelength (nm)	Plasma view mode	$Slope_{cal}/Slope_{sam}$	ME (%)	R^2	LOD (ng/g)	LOQ (ng/g)
Al	309.271	axial	0.976	-2.4	0.9990	77.5	260
B	249.773	axial	1.013	1.3	0.9982	8.00	26.6
Ba	455.403	axial	0.981	-1.9	1	0.50	1.90
Be	234.861	axial	0.968	-3.2	0.9998	0.80	2.40
Ca	393.366	radial	[a]	[a]	0.9984	0.10	0.50
Cd	226.502	axial	1.019	1.9	1	2.40	7.80
Co	228.616	axial	0.971	-2.9	1	4.10	13.6
Cr	283.563	axial	0.952	-4.8	0.9996	7.80	25.9
Cu	324.754	axial	0.988	-1.2	1	7.60	25.5
Fe	259.940	axial	1.009	0.9	1	7.50	25.1
K	766.490	radial	[a]	[a]	0.9990	6.60	22.1
Mg	279.553	radial	[a]	[a]	0.9990	0.20	0.60
Mn	257.610	axial	1.023	2.3	1	1.20	4.40
Na	589.592	radial	[a]	[a]	1	0.10	0.50
Ni	221.647	axial	1.054	5.4	0.9996	7.40	25.0
P	213.618	radial	[a]	[a]	1	49.0	163
Pb	220.353	axial	1.063	6.3	1	25.4	84.5
Se	196.090	axial	1.049	4.9	1	41.8	139
Si	251.611	axial	0.924	-7.6	0.9974	20.6	68.8
V	309.311	axial	0.988	-1.2	1	7.40	24.8
Zn	213.856	axial	1.044	4.4	0.9996	1.50	4.80

[a] It was not necessary to optimize $slope_{cal}/slope_{sam}$ and matrix effect for the major elements Ca, K, Mg, P and Na because of their relatively high concentration in the samples

Macro and Microelements in Culinary Herbs and Spice Samples

The results of the elemental analysis of spice and herb samples (Supplementary materials) indicate that Ca and K were the most abundant macro elements, followed by P, Mg, and Na. The mean concentrations of Ca are ranged from 0.6 mg/g in garlic to 17.4 mg/g in lovage, while the mean concentrations of K are ranged from 1.45 mg/g in cinnamon to 10.9 mg/g in parsley. The highest mean concentrations of P and Mg were found in white mustard and celery yielding 7.83 mg/g and 4.75 mg/g, respectively.

The lowest mean concentrations of P and Mg were found in cinnamon yielding 0.570 mg/g and 0.381 mg/g, respectively. The mean concentration of Na varied and ranged from 2.85 µg/g in chive to 138 µg/g in clove. All analyzed samples are low in Na, but rich in Ca, K and P. The macro element contents are in good agreement with the reported data on macro element content of spices and condiments used in Turkey, but lower for Na (1.16-16.45 mg/g Ca, 3.57-27.67 mg/g K, 0.48-4.31 mg/g Mg, 0.44-9.37 mg/g P, and 1.1-20.91 mg/g Na) [11].

Among the essential elements, Fe was the most abundant, followed by Cu, Zn, Cr and Se. The results obtained for these metal concentrations are in accordance with the literature data for aromatic spices [8] and medicinal herbs [21]. The mean content of Se, which has a role in the antioxidant defence system of the body, ranged from n.d. in thyme, basil, dill, parsnip, nutmeg, garlic, chive, rosemary and caraway to 0.255 µg/g in ginger. According to Aras and Ataman [22], the differences in the content of Se can be a consequence of the soil composition in which the food is grown.

The manganese, cobalt, silicon, nickel, boron and vanadium were detected in all samples and levels were among 9.51-249 µg/g, 0.076-0.813 µg/g, 7.68-936 µg/g, 0.843-4.89 µg/g, 2.57-30.1 µg/g and 1.05-19.9 µg/g, respectively. Boron is essential for plants and tends to accumulate in plant tissues. Rich sources of B are nuts, leafy vegetables and fruits [22]. According to WHO [23] the mean daily intake of B for adults is 1.2 mg per day.

In this study, the levels of Be and Ba were in the range of n.d.-0.077 µg/g and 3.98-314 µg/g, respectively. Ba was detected in all samples. When grown in Ba-rich soils, plants can accumulate higher levels of Ba, which further increases the potential dietary Ba intakes [24].

Lead and cadmium have no essential function in plants and at high concentrations are toxic for plants and animals as well as for humans. The uptake of Pb and Cd by plant roots depends on the concentration, the oxidation state of this metal in the solution, and the physical-chemical characteristics of the soils such as pH content of clay, minerals, and organic matter [25, 26]. The Joint FAO/WHO [27] provisionally recommends that the weekly intake of lead should not exceed 25 µg/kg of body weight per week and 7 µg/kg of body weight should be regarded, provisionally, as the maximum tolerable weekly intake of Cd. The results obtained for Pb (0.38-2.67 µg/g) and Cd (0.032-0.221 µg/g) are in accordance with the literature data [8,12] and below the limits given by the FAO/WHO [27].

Pearson's Correlation Analysis

In this study, the correlation analysis was performed at a 0.05 probability level to evaluate the relationship among the element concentrations. The results are included in Supplementary material (Table S2 (Supplementary material). According to Cohen, a strong correlation exists when $r \geq |0.5|$ [28]. Among the elements, K showed a positive correlation with Ca, Mg, B and V; P with Zn; Al with Ni and Si; Cr with Si; and Fe with Ni, Pb and Si.

The elements showing the significant positive correlation are Fe and Si (0.80), Al and Si (0.74) and Fe and Pb (0.73). Of all macro elements Mg shows a good correlation with V (0.84), B (0.74) and Ca (0.71). It is assumed that a good correlation indicates a similar origin of the elements in the tested plants [21]. There were some correlations which were very close to 0, for example, Na with Pb, K, Mg, Cu, Zn, B, Be with Al, Cd with Cr, Ni and Se, which indicates weak relations between these elements.

Chemometric Data Processing

PCA was used for extracting the data from variables and reducing the number of inter-correlated variables to uncorrelated variables (PC), thereby allowing a more accurate estimate [29]. The principal components are rotated so that the total sum of squares of the loading along each axis is maximised [30]. For this chemometric calculation, a data matrix (21×88) was constructed using 88 samples as rows and content of 21 metals as columns. Six principal components with eigenvalues > 1, as suggested by the Kaiser criterion [30], were extracted by PCA. These six components explained about 74.3% of the variation in the data. The first component (PC1) had the highest eigenvalue of 5.44 and explained 25.89% of the total variance. The eigenvalue of the second component (PC2) was 3.76 and explained 17.93% of the total variance in data. As the first two factors explain 43.82% of the total variations and the contributions of the third, fourth, fifth and sixth are considerably lower, PC1 and PC2 were used for a further analysis. Figure 1 shows the score plot for all 88 samples. The first group, in the lower right quadrant, consists of spices from the *Lauraceae* family (cinnamon and bay laurel). This group is extracted by the high concentrations of Cd and Be (Figure 2). The second group, the *Zingiberaceae* family (turmeric and ginger), is located on the negative side of PC1 and the negative side of PC2. This group is extracted by the high concentrations of Cr, Si and Pb. Next to these elements, Al, Ni, and Fe are grouped in the lower left quadrant with the significant positive correlation between Fe and Si (0.80), Al and Si (0.74) and Fe and Pb (0.73). Al and Si are highly present in the soil. Silicon gives strength to the cell wall and increases the resistance of the plant to insects and fungal diseases, while the available Al, despite its toxicity in plants [31], in some species such as *Camellia sinensis* and *Melastoma malabathricum* has a beneficial effect on plant growth [32]. The third group consists of spices from the *Lamiaceae* family (basil, one sample of marjoram, and one sample of oregano) is located in the negative side of PC1, and in the positive side of PC2. This group is extracted by the high concentrations of V and Zn, and relatively high concentrations of macroelements K, Ca, and Mg (Figure 2). Potassium and phosphorus (negative loadings on PC1 and positive loadings on PC2) in some spices probably originate from artificial fertilizers NPK [33]. Potassium, phosphorus and magnesium are grouped in the same quarter as the elements necessary for photosynthesis. The fourth group includes spices from the *Lamiaceae* family (Breckland thyme, thyme, marjoram, oregano, and rosemary) and it is located near zero of PC1 and PC2. The fifth group, *Apiaceae* (dill, parsley, coriander, caraway, celera, lovage, and parsnip), is between the two groups of *Lamiaceae* and this group is extracted by the high content of P (Figure 2). The sixth group is *Amaryllidaceae* (garlic and chive) and it is located on the positive side of PC1 and near zero of PC2. It can be seen that the samples from the *Brassicaceae* family (white mustard) do not belong to any group. The *Brassicaceae* family was reported as a hyperaccumulator of Cd, Zn and Ni [26, 34].

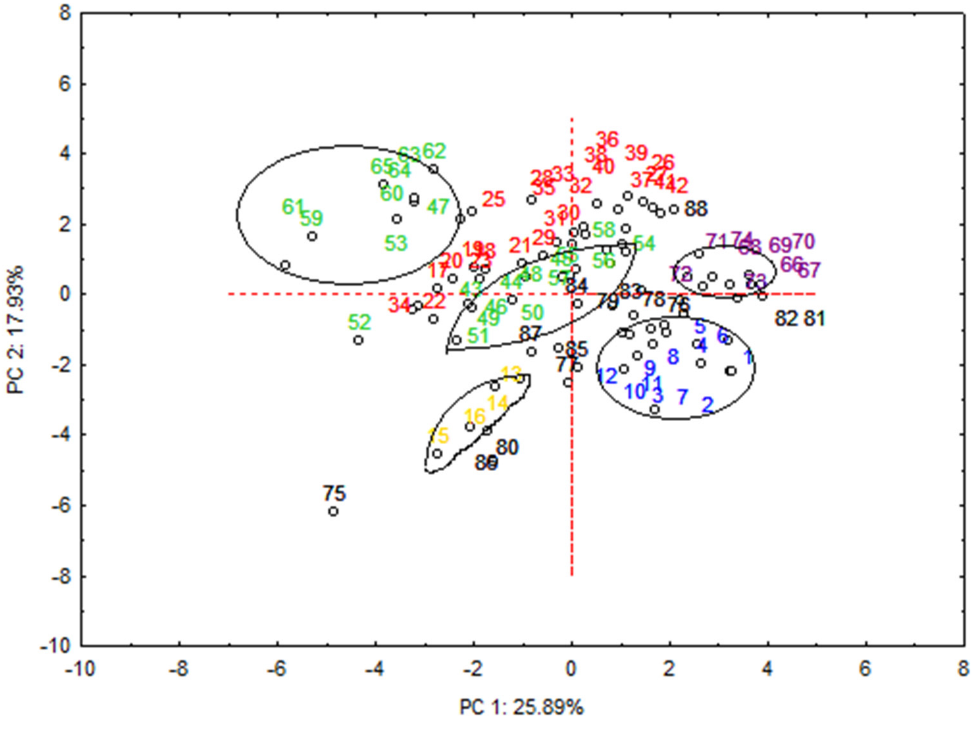

Figure 1. PCA score plot obtained for classification of culinary herbs and spices

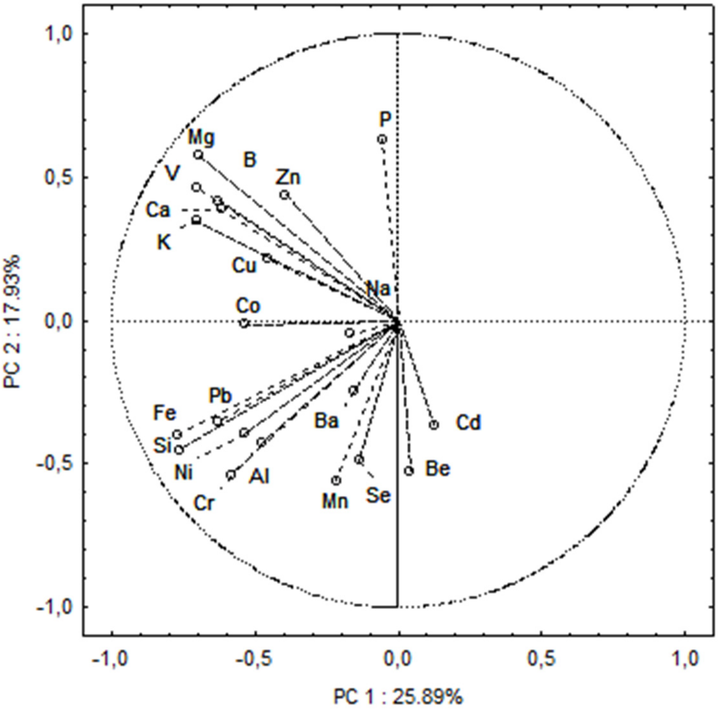

Figure 2. PCA loading plot of the elemental composition of culinary herbs and spices

When macro elements were considered as the elements with bigger loadings on PC1 and PC2, the scores of PC1 and PC2 in Figure 3 indicate that the macro elements affect the separation of the samples. The first and second components reported 48.65% and 21.58% variance, respectively. The first two components described 70.23% variances for all data. From the higher scores of the first principal component, it can be interpreted that the concentrations of Na on PC1 are higher for the samples from the *Myrtaceae* family (clove) and are lower for all other samples, the concentrations of Ca are similar and the concentrations of Na are high for the samples from the *Apiaceae* family (parsley, dill), the concentrations of Mg are higher for the samples from the *Apiaceae* family (lovage, celery) and the samples from the *Lamiaceae* family (basil). When the second principal component is interpreted, P concentrations on the PC2 loadings are higher for samples from the *Apiaceae* family (coriander, caraway) and for one sample from the *Brassicaceae family* (white mustard) and they are lower for all other samples. The cinnamon and bay laurel samples from the *Lauraceae* family have the lowest content of Mg, K and P. The turmeric and ginger samples from the *Zingiberaceae* family, the parsnip samples from the *Apiaceae* family, the garlic samples from the *Amaryllidaceae* family, the black pepper samples from the *Piperaceae* family and the nutmeg samples from the *Myristicaeae* family have the lowest content of Ca and K.

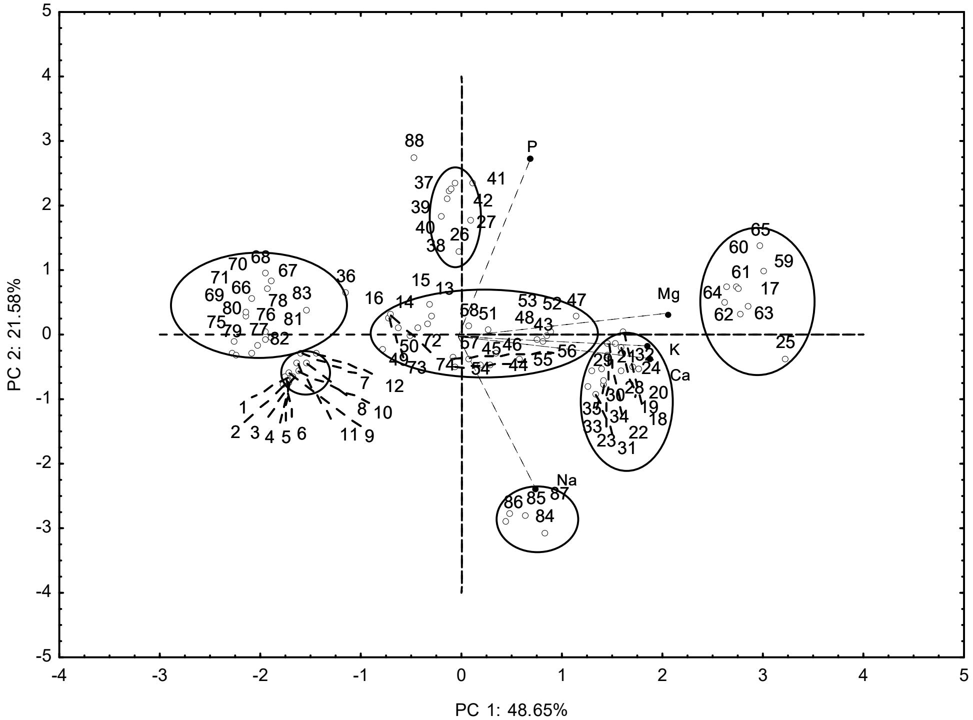

Figure 3. PCA score plot for classification of culinary herbs and spices based on macro element contents

The cluster analysis was performed using the same variables as in PCA, obtaining a second correct classification (Supplementary material) with six clusters. The first cluster on the right consists of samples from the *Lauraceae* family (cinnamon and bay laurel). The second cluster includes samples from the *Amaryllidaceae* (garlic), *Apiaceae* (parsnip), *Myristicaceae* (nutmeg) and Piperaceae (black paper) family. The third cluster consists of two subclusters. The first subcluster includes the samples from the *Myrtaceae* family (clove), the second subcluster contains the samples from the Apiaceae family (parsley, dill). The fourth cluster consists of the samples from the *Apiaceae* (25 celery and 17 lovage) and *Lamiaceae* (59-65 basil) family. The fifth cluster includes the samples from the *Zingiberaceae* (turmeric, ginger) *Lamiaceae* (oregano, Breckland thyme, thyme, marjoram, rosemary), Amaryllidaceae (chive) family.

The sixth cluster includes the samples from the *Apiaceae* family (coriander, caraway). White mustard from the Brassicaceae family is joined to this cluster. Based on the CA results, the samples from the Lamiaceae family are grouped in cluster five, the only base is in cluster four, the Apiaceae family samples are grouped in three clusters (three, four and six) which are next to each other, and this grouping of samples is in accordance with the results obtained from PCA.

CONCLUSIONS

This study contributes to the analysis of element concentrations in 88 culinary herb and spice samples. All of the analyzed samples were found to be high in Ca and K compared to other elements. Among microelements, Fe was the most abundant, followed by Cu, Zn, Cr and Se. The concentrations of toxic elements (Pb and Cd) were below the limits given by FAO/WHO [27]. The correlation analysis showed that strong positive correlations exist between Fe and Si, Al and Si and Fe and Pb. Of all macro elements, Mg showed a good correlation with V, B and Ca. The data analysis was done using chemometrics such as PCA and CA. According to PCA, all samples were classified into six groups. The first group consists of the spices from the family of *Lauraceae* (cinnamon and bay laurel), the second group includes the family of *Myrtaceae* (clove), the third group consists of the spices from the family of *Lamiaceae* (basil, Breckland thyme, thyme, marjoram, rosemary, and oregano), the fourth group includes the spices from the family of *Apiaceae* (dill, parsley, coriander, caraway) and *Amaryllidaceae* (chive), the fifth group is the *Zingiberaceae* family (turmeric and ginger) and the sixth group is the *Amaryllidaceae* family (garlic). The samples from the family of *Brassicaceae* (white mustard) do not belong to any group. CA confirms the results obtained by PCA. Also, the chemometric analysis allowed the classification of culinary herbs and spices based on the concentation of five major elements. Due to their simplicity, PCA and CA can be useful to classify culinary herbs and spices according to their species.

MATERIALS AND METHODS

Reagents

Ultra-scientific (USA) ICP multi-element standard solutions of about 20.00 ± 0.10 mg/L were used as a stock solution for calibration. The glass containers used for storing the samples were treated with a 20% nitric acid and washed with ultra-pure water 0.05 µS/cm (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) to avoid the contamination of the samples with traces of any metals. The nitric acid (65%) (Merck, Darmstadt, Germany) was of analytical grade.

Instrumentation

The entire analysis was carried out on an iCAP 6000 inductively coupled plasma optical emission spectrometer (Thermo Scientific, Cambridge, UK) which uses the Echelle optical design and a charge injection device solid-state detector. The nebulizer was glass concentric. An iTEVA software from Thermo Scientific (Cambridge, UK) was used to collect and analyze the data. The digestion was performed in a microwave digestion system ETHOS 1 (Milestone, Bergamo, Italy).

Samples

Eighty-eight commercially available samples of twenty-three different culinary herbs and spices were purchased at local markets in Serbia. All samples were bought as pulverized/ground and dried by the manufacturer. No further drying was applied. The English and botanical names of the analyzed culinary herbs and spices are listed in Table 4.

Sample Preparation

The samples were digested according to Khan et al. [8] with the following modifications: 1 g of each sample was accurately weighed and then 7 ml concentrated HNO_3 (70%) and 1 mL H_2O_2 were added and digested using the microwave system. The conditions were as follows: 500 W at 80 °C for 5 min; 500 W at 50 °C for 5 min; 500 W at 180 °C for 10 min, and 0 W for 30 min for cooling. After cooling the content of the tubes was transferred to 25 mL volumetric flask and diluted to 25 mL with a 0.5% HNO_3. The same procedure was carried out for a blank sample and SRM NCS ZC73036. All samples were analyzed in triplicates.

Optimization of the Method

Before the metal analysis, the operating parameters were conducted to check the instrument performance. Using a 27.12 MHz ICP, RF power, and nebulizer, the argon flow rate was varied under the constant values of other plasma conditions: flush pump-rate 100 min^{-1}, analysis pump-rate 50 min^{-1}, coolant gas flow-rate 12 L/min, auxiliary gas flow-rate 0.5 L/min, dual-viewed plasma mode (axial/radial) and sample uptake delay of 30 s.

The standard addition method was used to overcome the matrix effect [35, 36]. A ratio of two elemental signals was used to calculate the matrix effect [37]. The analytic lines were evaluated according to the ratio of the slope of the calibration curve and slope of the standard addition method line ($slope_{cal}/slope_{sam}$).

Table 4. Culinary herbs and spices studied

No	n[a]	English name	Species	Family
1-6	6	Cinnamon	*Cinnamomum verum* J.Presl	Lauraceae
7-12	6	Bay laurel	*Laurus nobilis* L.	Lauraceae
13-14	2	Turmeric	*Curcuma longa* L.	Zingiberaceae
15-16	2	Ginger	*Zingiber officinale* Roscoe	Zingiberaceae
17	1	Lovage	*Levistricum officinale* W.D.J. Koch	Apiaceae
18-24	7	Parsley	*Petroselinum crispum* (Mill.) Fuss	Apiaceae
25	1	Celery	*Apium graveolens* L.	Apiaceae
26-27	2	Coriander	*Coriandrum sativum* L.	Apiaceae
28-35	8	Dill	*Anethum graveolens* L.	Apiaceae
36	1	Parsnip	*Pastinaca sativa* L.	Apiaceae
37-42	6	Caraway	*Carum carvi* L.	Apiaceae
43-48	6	Oregano	*Origanum vulgare* L.	Lamiaceae
49-50	2	Breckland thyme	*Thymus serpyllum* L.	Lamiaceae
51	1	Thyme	*Thymus vulgaris* L.	Lamiaceae
52-53	2	Marjoram	*Origanum majorana* L.	Lamiaceae
54-58	5	Rosemary	*Rosmarinus officinalis* L.	Lamiaceae
59-65	7	Basil	*Ocimum basilicum* L.	Lamiaceae
66-71	6	Garlic	*Allium sativum* L.	Amaryllidaceae
72-74	3	Chive	*Allium schoenoprasum* L.	Amaryllidaceae
75-80	6	Black pepper	*Piper nigrum* L.	Piperaceae
81-83	3	Nutmeg	*Myristica fragans* Houtt.	Myristicaceae
84-87	4	Clove	*Syzygium aromaticum* L. Merrill & Perry	Myrtaceae
88	1	White mustard	*Sinapis alba* L.	Brassicaceae

[a] number of samples from each selected spice.

Validation

The validation process involved the linearity of the calibration curve which was tested from 0 to 5 mg/kg, detection (LOD) and quantification limit (LOQ). Both limits were expressed in ng/g. All calibration curves were prepared with four standard solutions, including the blank. The linearity was assessed by the coefficients of the determinations (R^2) of calibration curves. The certified reference material (green tea), supplied by The China National Analysis Center for Iron and Steel, Beijing, China (NCS ZC73036), was analyzed for the determination of B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Si, V and Zn in order to the check the accuracy of the method. The samples were handled according to the supplier's specifications.

Supplementary materials containing the standard reference material analysis results and cluster analysis dendrogram can be obtained upon request from the authors.

Data Analysis

All correlations (Pearson's correlation analysis) and chemometric analyses such as principal component analysis (PCA) and cluster analysis (CA) were performed using Statistica 8.0 (StartSoft, Tusla, Oklahoma, USA). PCA is a chemometric technique used to reduce the dimensionality of large datasets, with an increasing interpretability and minimization of data lost. The new PC variables are linear functions of the origin data. PCA is used to reduce solving an eigenvalue problem [38]. Cluster analysis, also called numerical taxonomy, is a chemometric technique used for grouping similar objects in the same clusters. Cluster analysis examines all relationships between variables and does not differentiate between dependent and independent variables [39]. The chemometric techniques are used to evaluate whether or not there is a relationship between the metal contents in different types of herbs which belong to the same family, as well as for grouping samples based on the metal contents.

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