Mineral components analysis of selected dried herbs

G.Zaguła ,A. Fabisiak ,M. Bajcar ,M. Czernicka ,B. Saletnik,C.Puchalski

University of Rzeszow, Department of Bioenergy Technologies; e-mail: g_zagula@ur.edu.pl

Received April 12 2016: accepted June 07 2016

Abstract. This study includes the content of water, ash and volatiles in dried herbs like Oregano, Basil and de Provance. Moreover, amounts of H, N and C, and their calorific value were measured. The content of the following elements (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, Zn) in the tested herbs were established using the ICP-OES method. Basil leaves had the highest nitrogen and ash content at the level 4.5% and 15,9%. These herbs were characterized by a darker color as compared to oregano. Basil contained the richest source of Ca, K, Mg and P, while the lowest was found in herbs de Provence. The best source of Ca, K, Mg and P was basil, while their lowest amount was found in herbs de Provence (containing a mixture of different herbs), which mostly likely was the reason for the low amount of macro- and micro-components.

Key words: physical parameters, de Provence, Basil and Oregano herbs, caloric value, color, minerals, ICP-OES.

INTRODUCTION

From the earliest times medicinal plants were the primary source of drugs, and the knowledge of their operation and application has been passed on to future generations [14]. In Western Europe, the art of plant treatment originated from medieval herbalism. Herbs first gave proper taste and aroma to dishes and an additional function was also the preservation of food. They have also been used as drugs for a number of medical conditions. Many species of herbal plants have medicinal properties that beneficially impact the process of digestion and assimilation of nutrients. They became less significant as drugs when their place was taken by chemistry, in particular antibiotics.

According to Kaiser et al. [2] marjoram extract contains 78% polyphenols. Most rosemary acid is contained by thyme and rosemary herbs, respectively 157 mg/g d.w. and 84 mg / g d.w., while oregano is rich in caffeic acid- 12.6 mg/g d.w. [18].

The primary source of minerals for humans is food, and pharmaceutical preparations should complement the deficiency of certain elements [11]. Plant materials can be a valuable source of many micronutrients present in herbs. An additional asset for herbs is their bioavailability [18]. Heavy metals are a threat that affect processed and unprocessed food. According to the RASFF - Rapid Alert System for Food and Feed [12] they concern mainly lead, cadmium and mercury (more than 50% of reported alerts). The high-concentration of heavy metals in plants is a well-known problem.

According to studies, it is difficult to clearly determine the primary source of pollution, in particular since (in the case of herbs) heavy metals accumulate both in leaves and roots. The influence of heavy metals and other elements should be controlled so as not to exceed the recommended values given by WHO [19]. This is of particular importance not only in the case of herbs used in medicine, where the concentration of heavy metals is a major criterion in the production of the drug, but also in foods which partly consist of herbs. In the case of food, the acceptable level of micronutrients does not harm health.

According to Łozak et al. [5] a good source of iron can be found in infusions of mint and nettle (227 and 107 mg/kg). In contrast, fennel leaves are rich in compounds of potassium (29%) [16]. Rosemary herbs contain a significant amount of calcium, iron and potassium [8].Basil is one of the most valued and most used spices and the aromatic fresh or dried herb is used as an additive to many dishes. In the *Ocimum basilicum* L. type, large variations can be observed not only in the content and composition of essential oil [6, 10]. Basil herb contains 0.5-2.5% essential oil with a variable chemical composition [1]. Apart from the above, Basil contains 16% protein, 4.7% fat, 12% fiber, 5% of tannins, vitamin C and E and carotenoids and chlorophyll pigments and minerals. Oregano, aromatic and rich in taste *(Organum vulgare)* contains antioxidants (8%) and tannins (2%). This herb also contains vitamins C, A, beta-carotene and minerals. Many authors have reported that oregano is not harmful to health. One of the most popular spice mixtures are Herbes de Provence. The blend includes herbs such as basil, thyme, sage, peppermint, summer savory, marjoram and basil. The richness of the mixture sees it used in salt-free diet. An objective of this paper was to define the active ingredients and the assessment of cumulative elements in popular herbs.

Methods

The materials consisted of herbs of basil, oregano and de Provence herbs purchased at the market. Each time 3 samples were taken to measure average values with standard deviation. In the study, the content of ash, moisture and volatile substances in the herbs was determined by the LECO TGA 701 camera. The moisture content was performed at 105°C, and the ash at 600°C under nitrogen 0.01% comparator. The herbs' calorific value was determined using an AC 500 camera.

For this purpose, the homogenized material was dried in the oven at 105°C and then small tablets were made using the Lormann press.

The calorific value was determined by the sample's combustion in the oxygen atmosphere in a bomb calorimeter placed in water. The content of sulfur, carbon, hydrogen and nitrogen were determined using an S module and CHN TrueSpecTM camera. The measurements of Carbon, Hydrogen and Nitrogen were carried out in an oven at 950°C and Sulphur at 1350°C.

The color of the samples was measured using the UltraScan VIS spectrophotometer Hunter Lab. The white plate standard was taken to establish the optical white parametres values of L*=100.000, a*= 0.005, b*= -0.010. The differences in energetics distance (between standard and each herb sample) measured in the Lab color scale were expressed as:

$$\Delta E = \sqrt{\left(\Delta L^2\right) + \left(\Delta a^2\right) + \left(\Delta b^2\right)}, \quad (1)$$

where: ΔE is the difference in energetic distance,
Δ L, Δ a, Δ b - the difference in energetic distance in the space for the parametres, respectively, L, a, b between the optical plate parameter and sample.

The content of elements in the tested herbs was determined by the ICP-OES method. The samples of the studied herbs were mineralized in nitric acid 65% HNO_3 (V) using the Milestone Spectro-Lab.

Standard solutions were prepared by diluting polycyclic (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, S, Zn) (Merck Millipore) standard solutions at the concentrations of 1000ppm (mg/l). For the preparation of standard solutions deionized water was used. In order to determine the calibration curve, standard solutions at the range of concentrations from (0.001-1 ppm) were used. The study used the analytical lines of highest intensity.

Samples of the test material (5 g) containing 8 ml of HNO_3 were mineralized in accordance with the following program: 5 minutes in temperature 150°C; 10 minutes in temperature 150°C; 20 minutes in temperature 200°C; 30 minutes in temperature 50°C. An analysis of samples for the presence of elements was carried out using an optical emission spectrometer with the inductively coupled plasma (ICP-OES). The operating conditions for ICP-OES are shown in Table 1.

Table 1. ICP-OES operating conditions for the determination of some elements in the herbs

Rf powers (W)	1150
Gas flow rate (ml/min)	5
Coolant gas	12
Auxiliary gas	0,7
Nebuliser gas	0,4
Sample uptake rate (ml/min)	1
Pump rate (rpn)	70
Read time (s)	5

One-way analysis of variance (ANOVA) was performed at the significance level of p = 0.05, n = 3 in the test herbs for the mean values of water content, ash content, volatile components, caloric value, C, H, N, and measurement of color. The results were subjected to statistical analysis in the Statgraphics Plus 4.1. program, using the Student's t-test and Duncan's test at p = 0.05, n = 3. The principal component analysis of minerals and the correlation matrix of macro-and microelements were determined using the Statistica software package (Statistica 6.0).

RESULTS AND DISCUSSION

Biologically active ingredients present in herbs are important for the quality of herbal raw materials and products, which are an additional component of the herbs [15, 20].

Physicochemical parameters of the tested herbs

Table 2 shows the water, volatility, and ash content in the tested herbs. The water content changed from 7,80 to 9,59% depending on the type of herbs.

Table 2. Identified parameters for herbs

Identified parameters for herbs	Type herbs		
	De Provence	Basil	Oregano
	$\bar{x}$ ±SD	$\bar{x}$ ±SD	$\bar{x}$ ±SD
Humidity (%)	$8,72 \pm 0,7^{b}$	$9,59 \pm 3,5^{c}$	$7,80 \pm 4,9^{a}$
Ash (%)	$9,83 \pm 0,7^{e}$	$15,9 \pm 0,8^{f}$	$7,81 \pm 3,0^{d}$
Volatiles (%)	$22,2 \pm 0,9^{g}$	$22,6 \pm 0,8^{g}$	$22,4 \pm 1,5^{g}$
Nitrogen, N (%)	$2,8 \pm 0,7^{B}$	$4,5 \pm 3,1^{C}$	$1,5 \pm 0,6^{A}$
Carbon, C (%)	$48,6 \pm 1,7^{F}$	$43,4 \pm 0,7^{D}$	$47,3 \pm 1,1^{E}$
Hydrogen, H (%)	$5,8 \pm 0,4^{G}$	$5,3 \pm 0,6^{G}$	$5,4 \pm 0,5^{G}$
Calorics (MJ/kg dry weight)	$21382 \pm 105^{\underline{b}}$	$17846 \pm 150^{\underline{a}}$	$24015 \pm 104^{\underline{c}}$

Explanatory notes:

Values are means with standard deviation.

a-g; A-I; a-c- (the same letters denote no statistically significant differences at p = 0.05)

Dried herbs of different species did not significantly influence the amount of volatile compounds. On the other hand, the difference in ash content was significant. The amount of ash in basil was 2 times higher than in oregano. According to Kaloustian et al. [3], the value of ash is closely related to the species of dried herbs. The ash content of the tested herbs ranged from 7.8-15.9%. Similar results were obtained by Santos et al. [13].

The results of the analysis of nitrogen, carbon and hydrogen were different (Table 3). The highest content of nitrogen at the level of 4.5% was reported in basil herbs, while oregano contained only 1.5% of this element. The contents of carbon and hydrogen, according to the tested herbs, ranged respectively from 43.4-48.6% and 5.3-5.8%.

The highest energy content with value of 24015 MJ/kg d.w. was found in oregano, while the lowest one was obtained for basil, in which it amounted to 17 846 MJ/kg d.w.

The parametres of the dried herbs colors are shown in Table 3. Type of herb significantly affected the L* parameter. Colors of the tested herbs were characterized by lightness with ΔL value in the average of 50 (mid gray), greenness with negative Δa from -2.55 to -1.76 and yellowness refereed by positive Δb value from 10.9 to 14.1.

Table 3. Color assessment of herbs de Provence, basil and oregano

Identified color parameters	Type of herbs		
	Herbs de Provence	Basil	Oregano
	$\bar{x}$ ±SD	$\bar{x}$ ±SD	$\bar{x}$ ±SD
ΔL	46,9 ± 0,01^{a}	50,3 ± 0,04^{b}	52,3 ± 0,02^{c}
Δa	-2,55 ± 0,02^{d}	-2,52 ± 0,01^{d}	-1,76 ± 0,01^{e}
Δb	10,9 ± 0,32^{f}	12,8 ± 0,35^{g}	14,1 ± 0,13^{h}
Δ E	6,56 ± 0,09^{B}	3,88 ± 0,03^{A}	3,75 ± 0,07^{A}

Explanatory notes:

Values are means with standard deviation.

a-h; A-I (the same letters denote no statistically significant differences at p = 0.05)

In his studies Alibas [1] proved that the loss of color (L*, a*, b*) nettles was the result, among others, of thermal degradation. Changes in the content of parameters a* and b* influenced the saturation of color in the tested herbs. The total color difference (ΔE) between the standard and sample was 3.75 for oregano, similar for basil (3.88) and amounted to 6.56 for de Provence herbs.

Mineral components

Content of mineral significantly depends on macro- and microelements. The threshold of measurement for ICP-OES methods was above 0.001mg/g. Table 4 shows the mineral content of basil, de Provence and oregano herbs. The content of macro-and microelements was significantly different in the tested herbs, with the exception of copper for all herbs and chromium for basil and oregano. Herbs de Provence constitute a mixture of herbs with a similar amount of mineral components compared to oregano (Table 4). In the case of basil the content of elements was two times higher. Basil herbs contain 25.1 mg/g Ca, 33.2 K, 9.59 mg/g Mg and 4.38 mg/g P. Similar results were obtained by Pachkore and Markandeya [9], with reference to potassium. In the study conducted by Özcan et al. [7, 8] chromium and manganese, for the same varieties of basil, amounted to 0.068 mg/g and 0.17 mg/g.

In the studied spices, there was a high content of Mg (2.92-9.59 mg/g), for which the range was similar to herbal medicinal products tested by Ulewicz-Magulską and Wesolowski [17].

In the case of herbs, the degree of accumulation of minerals in leaves which are eaten directly or subjected to drying methods, is of significant meaning. The analyzed herbal plants differ in macronutrient content due to differences in species.

Table 4. Concentrations of elements in tested herbs

Minerals [mg/g]	Type of herbs		
	Herbs de Provence	Basil	Oregano
	$\bar{x}$ ±SD	$\bar{x}$ ±SD	$\bar{x}$ ±SD
Al	0,32 ± 0,27^{a}	0,44 ± 0,06^{c}	0,35 ± 0,17^{b}
Ba	0,019 ± 0,05^{d}	0,023 ± 0,04^{e}	0,026 ± 0,03^{f}
Ca	15,3 ± 0,31^{g}	25,1 ± 0,42^{i}	16,3 ± 0,47^{h}
Cr	b.t.m.	b.t.m.	b.t.m.
Cu	b.t.m.	b.t.m.	b.t.m.
Fe	0,43 ± 0,10 ^{B}	0,74 ± 0,18^{C}	0,41 ± 0,70^{A}
K	18,1 ± 0,07^{E}	33,2 ± 0,12^{F}	13,4 ± 0,39^{D}
Mg	5,07 ± 0,02^{H}	9,59 ± 1,39^{I}	2,92 ± 0,02^{G}
Mn	0,08 ± 0,08$^{\underline{a}}$	0,07 ± 0,02$^{\underline{a}}$	0,05 ± 0,03$^{\underline{a}}$
Na	0,21 ± 0,09$^{\underline{c}}$	0,66 ± 0,03$^{\underline{d}}$	0,07 ± 0,02$^{\underline{b}}$
Ni	b.t.m.	b.t.m.	b.t.m.
P	2,94 ± 0,12$^{\underline{B}}$	4,38 ± 1,21$^{\underline{C}}$	2,07 ± 0,01$^{\underline{A}}$
Pb	b.t.m.	b.t.m.	b.t.m.
S	3,32 ± 0,31$^{\underline{E}}$	4,19 ± 1,03$^{\underline{E}}$	2,22 ± 0,05$^{\underline{D}}$
Sr	0,080 ± 0,003$^{\underline{H}}$	0,180 ± 0,007$^{\underline{I}}$	0,020 ± 0,002$^{\underline{G}}$
Zn	0,026 ± 0,005$^{\underline{K}}$	0,033 ± 0,001$^{\underline{L}}$	0,017 ± 0,003$^{\underline{J}}$

Explanatory notes:

Values are means with standard deviation.

a-k; A-J; a-I; A-J; *A-F* (the same letters denote no statistically significant differences at p = 0.05)

b.t.m. - below the threshold of measurability

An analysis of the major components (Ca, Mg, K, P) of the tested herbs showed the formation of two groups. The dendrogram in Figure 2 shows the first focus, which includes herbs de Provence and oregano, and the second bond (basil, herbs de Provence, and oregano). The distances of the first and second bond were 5.3 and 22.2, respectively.

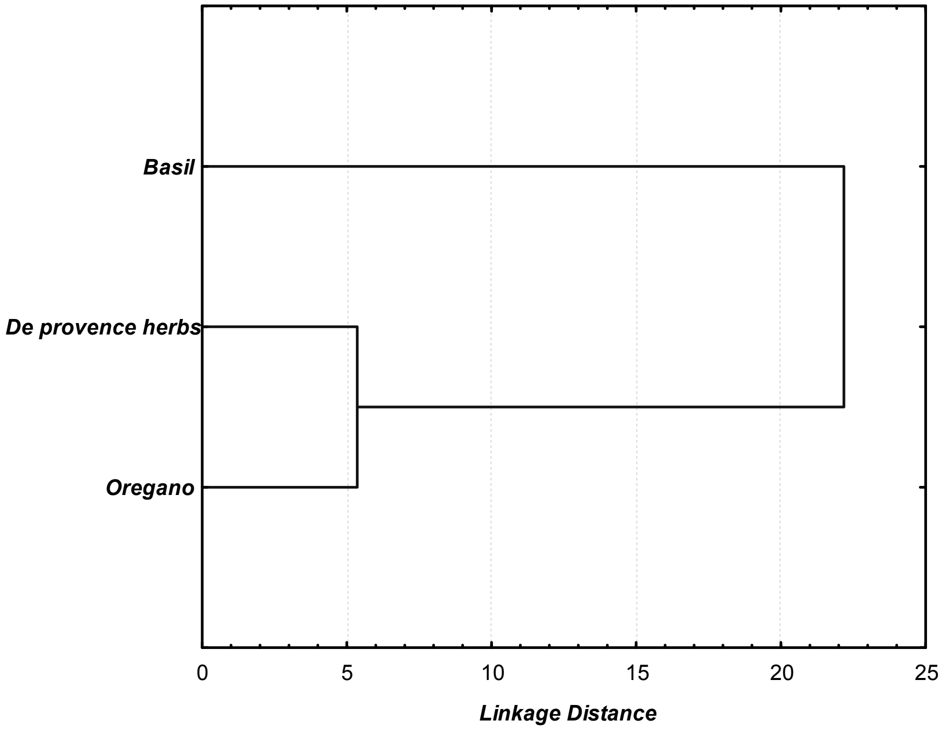

Fig. 1. Dendrogram of cluster analysis

A correlation analysis is shown in Table 5. The correlation coefficient, which is a measure of linear dependence, can range from -1 to +1. The correlation coefficients shown in Table 5 indicate a powerful relationship between the elements in the tested herbs. This may attest to the fact that to a large extent, the correlation coefficient between the elements is higher than 0.5. Similarly, high correlation coefficient elements were obtained in the research of Karadaş i Kara [4] analyzing selected herbs and spices.

This study showed significant correlations between Ca, K, Mg, P. The elements which most often performed in the correlation to other components were aluminum and calcium. Generally herbs matrix was characterized by a high propensity to the prevalence of high positive correlation.

Table 5. Correlation matrix for the elements in dried herbs

	Al	Ba	Ca	Fe	K	Mg	Mn	Na	P	S	Sr	Zn
Al	1,00											
Ba	-0,18	1,00										
Ca	0,98	0,02	1,00									
Fe	0,94	0,16	0,99	1,00								
K	0,87	0,33	0,95	0,98	1,00							
Mg	0,82	0,42	0,92	0,96	1,00	1,00						
Mn	-0,08	0,99	0,13	0,27	0,43	0,51	1,00					
Na	0,87	0,34	0,95	0,98	1,00	1,00	0,43	1,00				
P	0,78	0,47	0,89	0,95	0,99	1,00	0,56	0,99	1,00			
S	0,64	0,64	0,78	0,86	0,94	0,96	0,72	0,94	0,98	1,00		
Sr	0,79	0,45	0,90	0,95	0,99	1,00	0,55	0,99	1,00	0,97	1,00	
Zn	0,65	0,63	0,79	0,87	0,94	0,97	0,71	0,94	0,98	1,00	0,98	1,00

CONCLUSIONS

Dried herbs are still high in biologically active compounds. The highest value of total color difference (ΔE) between the sample and standard was found for herbs de Provence. Physicochemical properties of herbs depended on the type of the herb. Generally, high contents of nitrogen and ash were found in dried leaves of basil. Oregano herbs had the higher caloric value up to 35% compared to basil.

Mineral content varied and was strictly correlated with the grade of herbs. The best source of Ca, K, Mg and P was basil, while their lowest amount was found in herbs de Provence (containing a mixture of different herbs), which mostly likely was the reason for the low amount of macro- and micro-components.

REFERENCES

1. **Alibas I., 2010**: Determination of drying parameters, ascorbic acid contents and color characteristics of nettle leaves during microwave-, air- and combined microwave-air –drying. Journal of Food Process Engineering, 33, Pp. 213-233.
2. **Kaiser A., Carle R., Kammerer D.K., 2013**: Effects of blanching on polyphenol stability of innovative paste-like parsley *(Petroselium crispum (Mill.) Nym ex A.W.Hill)* and marjoram *(Origanum majorana L.)* products. Food Chemistry, 138, Pp. 1648-1656.
3. **Kaloustian J., Portugal H., Pauli A.M., Pastor J., 2002**: Chemical, chromatographic and thermal analysis of rosemary *(Rosmarinus officinalis)*. Journal of Applied Polymer Science, 83, Pp. 747-756.
4. **Karadaş C., Kara D., 2012**: Chemometric approach to evaluate trace metal concentrations in some spices and herbs. Food Chemistry, 130, Pp.196-202.
5. **Łozak A., Sołtyk K., Ostapczuk P. Fijałek Z., 2002**: Determination of selected trace elements in herbs and their infusions. Science of the Total Environment, 289, Pp.33-40.
6. **Miele M., Dondero R., Ciarallo G., Mazzei M., 2001**: Methyleugenol in *Ocimum basilicum* L. Cv. Genovese Gigante. J. Agriculture and Food Chemistry, 49, Pp.517–521.
7. **Özcan M., Arslan D., Űnver A., 2005**: Effect of drying methods on the mineral content of basil *(Ocimum basillcum L.)*. J Food Enginering., 69, Pp.375-379.
8. **Őzcan M.,** 2004: Mineral contents of some plants used as condiments in Turkey. Food Chemistry, 84, Pp.437-440.
9. **Pachkore G.L., Markandeya S.K., 2010**: Effect of drying on the essentials oil and the mineral contents of basil *(Ocimum basilicum L.).* The IUP Journal of Life Sciences, 4,Pp. 39-43.
10. **Purkayastha J., Nath S.C., 2006**: Composition of the camphor-rich essential oil of *Ocimum basilicum* L. native to Northeast India. Journal Essential Oil Research, 18, Pp. 332–334.
11. **Pytlakowska K., Kita A., Janowska P., Połowniak M., Kozik V., 2012**: Multi-element analysis of mineral and trace elements in medical herbs. Food Chemistry, 135,Pp. 494-501.
12. **RASFF Raport,** Rapid Alert System for Food and Feed, 2008.
13. **Santos J., Herro M., Mendiola J.A., Oliva-Teles M.T., Ibáñez E., Delerue-Matos C., Oliveira M.B.P.P., 2014**: Fresh –cut aromatic herbs: nutritional quality stability during shelf-life. LTW-Food Science and Technology, (In Press).
14. **Seidler-Łożykowska K., Koziak A., Golcz A., Mieloszyk E., 2006**: Macroelements and Essentials oil content in the raw material of the selected medicinal plant species from organic cultivation. Journal of Research and Applications in Agricultural Engineering, 51,Pp. 1160-163.
15. **Sharma, G. P., Prasad, S., 2004**: Effective moisture diffusivity of garlic cloves undergoing microwave-convective drying. Journal of Food Engineering, 65, Pp. 609–617.
16. **Słupski J., Lisiewska Z., Kmiecik.,** 2005: Contents of macro and microelements in fresk and frozen dill *(Anethum graveolens L.)* Food Chemistry, 91,Pp. 737-743.
17. **Ulewicz-Magulska B., Wesołowski M., 2012**: Analiza porównawcza zawartości wybranych biopierwiastków w ziołach o właściwościach leczniczych i przyprawowych. Bromatologia i Chemia Toksykologiczna, 1, Pp. 5-11.
18. **Vallverdu-Queralt** A., **Regueiro J., Martinez-Huelamo M., Alvarenga J.F., Leal L.N., Lamuela-Raventos R.M., 2014**: A comprehensive study on the phenolic profile of widely used culinary herbs and spices: Rosemary, thyme, oregano, cinnamon, cumin and bay. Food Chemistry, 154,Pp. 299-307.
19. **WHO, 2002**: Traditional medicine strategy 2002-2005. Geneva.

20. **Yongsawatdigul**, **J., Gunasekaran, S., 1996**: Microwave-vacuum drying of cranberries: Part II, Quality evaluation. Journal of Food Processing and Preservation, 20, Pp.145–156.

21. **Piotrowski K., Wiltowski T., Mondal K**., **2004**: Biomasa – kłopotliwe pozostałości czy strategiczne rezerwy czystej energii? Cz. 1, CzystaEnergia [Biomass – problematic remains or strategic reserves of pure energy? P. 1, Pure Energy], no. 10, Pp. 16-19.

22. **Saletnik B., Bajcar M., Zaguła G., Czernicka M., PuchalskiCz**., **2015**: Optimization of Physicochemical Properties of Torrefied Products Obtained by Thermal Processing of Oat Straw. TEKA.Commission of Motorization and Power Industry in Agriculture, 15, 4, Pp.155-160.