# COMPOSITION OF GLUTEN-FREE FLOURS WITH SPECIAL REFERENCE TO MINERAL SUBSTANCES

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Abstract: The aim of this paper is to investigate the composition of gluten free flours, with particular reference to the minerals content (As, Ag, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Tl, Zn, Si, and P). The following types of gluten-free flours were analyzed: palenta, gluten-free mix fluor, gluten-free palenta, flax flour, white buckwheat flour, corn white flour, as well as gluten flours with the purpose of comparison: flour for integral bread and wheat flour type 400. The samples were prepared by wet digestion process and then subjected to an ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) analysis. Based on the results, it can be concluded that the mineral composition of gluten and gluten free flours is different. In terms of nutritive value, the flour which proved to be the richest in term of higher content of macro (K - 7373,215  $\mu$ g g<sup>-1</sup>, Na - 1978,009  $\mu$ g g<sup>-1</sup> and Mg - 1818,141  $\mu$ g g<sup>-1</sup>) and micro essential elements (Zn - 46,001  $\mu$ g g<sup>-1</sup> and Cu-4,110  $\mu$ g g<sup>-1</sup>) is a flax non-gluten-free flour. The lead content detected in white buckwheat (0.518  $\mu$ g g<sup>-1</sup>) and white corn flour (0.534  $\mu$ g g<sup>-1</sup>) is beyond the permitted amount, which limits their use in daily human diet.

**Key words**: gluten, mineral, flour, toxic elements, ICP-OES

#### Introduction

Gluten is a composite protein composed of gluteline and gliadin that occurs in the endosperm of wheat. The ratio of gluteline and gliadin in the protein mixture is about 1:1. Gliadin, has been identified as poisonous gluten component (Rathi and Zanwar, 2006). Celiac disease (CD) is a chronic systemic autoimmune disorder caused by permanent intolerance to gluten proteins in genetically sensitive individuals. CD was a rare disease with a prevalence of about 0.02%, however, recent studies conducted in Europe, India, South America, Australia and the United States indicate that the prevalence may range from 0.33-1.06% in children and between 0.18-1.2% in adults (Saturni et al., 2010). So far, the only used CD treatment is a strict diet that involves the use of non-gluten foods. Although gluten-free alternatives are available, finding gluten-free quality products is a challenge for itself. Also, the complete characterization of the nutritional properties of such foods is of major importance in order to form a non-glutenous diet that will satisfy the daily needs of the organism.

Flours that have no gluten are rice, buckwheat, millet, teff corn, flax, sesame, quinoa, amarante, and flour of nuts, such as almonds, flour of legumes, brine or soy. Oatmeal also does not contain gluten. The problem with the non-glutinous wheat flour is that forms the dough which has semi-liquid consistency and cannot keep the gases produced by fermentation, that resulting in a bread of compact and crumbly structure,

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undesirable color and flavor. For this reason, the production of gluten free bread is quite demanding. In the production of non-gluten-free products, as a substitute for wheat flour, most commonly are used different hydrocolloids, enzymes, starch, cereals, glutenfree cereals (millet, corn, rice) or pseudogrules (quinoa, buckwheat), protein sources (Paylović, 2017). The flour properties, as well as its composition depend on the origin and the type of grain itself and from the grinding method (Araujo et al. 2008). In terms of mineral composition of flour, the most common constituents are calcium, magnesium, phosphorus, potassium, zinc, iron, copper and manganese, while the other elements are present in trace quantities. Grain cereal generally contains very small amounts of calcium and phosphorus that are important for the functioning of the human organism. The content of mineral matters in the grain is about 2%, and the content of mineral matters in the flour that ranges from 0.45% to 2.00% and depend on grinding process (Rajković et al., 2012). Previous studies have indicated the average concentrations of these minerals in the range of 0.89-7.15 mg g<sup>-1</sup> for phosphorus, 0.76-3.16 mg  $g^{-1}$  for potassium, 0.19-0.51 mg  $g^{-1}$  for magnesium and 0.11-1.96 mg  $g^{-1}$  for calcium (Hadžić, 2013). Micronutrients such as copper, iron, manganese and zinc have the average content in flour of 1.00-2.80, 10.5-146.6, 3.9-14.7 and 5.1-13.9  $\mu g^{-1}$ respectively (Hadžić, 2013).

The subject of this paper is the determination of the mineral composition of various flours, in order to compare the mineral composition (macro, micro and trace elements) of flours with and without gluten. The results of this paper can be used as basis for further researches on the potential nutritional properties of flour present in the consumer market in Serbia.

#### Material and methods

The quantitative analysis of all samples was performed on ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry, ARCOS FHE12, SPECTRO, Germany), according to the manufacturer's instructions. Preparation of analysis samples was carried out by wet digestion. Before ICP-OES analysis all samples were diluted with distilled water purified by Fisher Chemical (HPLC grade) and filtrated (0.45  $\mu m$ ).

#### Results and discussion

In Table 1 are presented summary results of: As, Ag, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Tl, Zn, Si and P content in the flour samples. The results are shown in µg g<sup>-1</sup> of flour weight.

Calcium (Ca), potassium (K), phosphorus (P), sodium (Na) and magnesium (Mg) are macroelements that have been analyzed in flour samples. Calcium is the most prevalent microelement in the human body. The organism daily need is 1000 mg (Carruthers and Smith, 1979). In the sample of flax flour calcium was not detected, until flour for integral bread proved to be the richest in term of calcium content -1207.042  $\mu g$   $g^{-1}$ , which represents a value three times higher compared to other analyzed flours.

Table 1. Minerals content in tested flour samples,  $\mu g g^{-1}$ 

| Elements, µg g <sup>-1</sup> | Wheat flour type 400 | Flour for integral bread | Gluten-free mix fluor | Gluten-free palenta | Flax fluor | White buckwheat<br>flour | Corn white flour | Palenta  |
|------------------------------|----------------------|--------------------------|-----------------------|---------------------|------------|--------------------------|------------------|----------|
| 4                            | Gluten flours        |                          | Gluten-free flours    |                     |            |                          |                  |          |
| As                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Ag<br>B                      | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Bi                           | 30.275               | 23.239                   | 30.630                | 32.380              | 31.046     | 27.586                   | 32.673           | 17,525   |
| Ca                           | 390.825              | 1207.042                 | 359.459               | 433.333             | 0          | 861.206                  | 498.019          | 238.144  |
| Cd                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Co                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Cr                           | 14.678               | 12.676                   | 14.414                | 16.190              | 17.234     | 11.206                   | 19.801           | 8.247    |
| Си                           | 0                    | 0                        | 0                     | 0                   | 4.110      | 0.862                    | 0                | 0        |
| Fe                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| K                            | 1666.055             | 2592.254                 | 723.423               | 2670.476            | 7373.216   | 3455.172                 | 2882.178         | 1242.268 |
| Li                           | 3.669                | 2.816                    | 3.603                 | 3.809               | 4.104      | 3.448                    | 3.960            | 2.061    |
| Mg                           | 29.357               | 355.633                  | 0                     | 236.190             | 1818.141   | 937.931                  | 364.356          | 98.453   |
| Mn                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Na                           | 1549.541             | 1280.986                 | 2227.027              | 1702.857            | 1978.009   | 1515.517                 | 1686.139         | 858.247  |
| Ni                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Pb                           | 0.246                | 0.235                    | 0.282                 | 0.401               | 0.442      | 0.518                    | 0.534            | 0        |
| Tl                           | 0                    | 0                        | 0                     | 0                   | 0          | 0                        | 0                | 0        |
| Zn                           | 25.688               | 26.056                   | 24.324                | 28.571              | 46.001     | 34.482                   | 29.702           | 14.948   |
| Si                           | 344.954              | 237.323                  | 345.045               | 335.238             | 346.065    | 370.689                  | 300.990          | 169.587  |
| P                            | 1257.798             | 2978.873                 | 558.558               | 2262.857            | 9054.384   | 5305.172                 | 3356.436         | 1054.639 |

Besides calcium, potassium and sodium concentrations were significant. Minimum daily intake of potassium is 2000 mg (Carruthers and Smith, 1979). Lowest potassium concentration was detected for gluten free mix flour – 723.423  $\mu g \, g^{-1}$ , while the highest concentration of 7373.215  $\mu g \, g^{-1}$ , was detected in sample of flax flour. The minimum physiological requirement for sodium in humans is 500 mg per day, but the recommended intake is 2-3 g per day. Our analysis showed the highest sodium concentration in gluten-free mix. Magnesium as a very important mineral is a cofactor for over 300 enzymatic reactions, especially those that participate in the metabolism of food components and the creation of new molecules that are important for human health. The average daily intake of magnesium in the body is 350 mg. The magnesium concentrations in flours ranged from 29.357  $\mu g \, g^{-1}$  to 1818.141  $\mu g \, g^{-1}$ . The drastically

higher Mg concentration is detected in flax flour. The highest concentration of phosphorus is also detected at sample of flax flour - 9054.384 µg g<sup>-1</sup>. Phosphorus is involved in bone building, protein synthesis, growth, maintenance and healing of cells and tissues, muscle contraction, kidney function, regulation of heart rhythm, genetic material production, maintenance of normal acid-base balance in the organism, etc., and its average daily intake is 800 mg. Based on this overall it can be concluded that flax flour is the richest in term of the content of macroelements, namely Mg, K and P.

From the examined microelements (silver, boron, bismuth, cobalt, chromium, copper, iron, lithium, manganese thallium, zinc, and silicon), silver, boron, cobalt, iron, manganese, nickel and thallium were not detected. Copper is considered as one of the essential microelements with the greatest concentration in liver, brain, kidneys and heart. Copper is also very important in creating an immune response to infections. Allowed daily intake of this mineral is 1.5 - 3 mg (Carruthers and Smith, 1979). Not all analyzed samples have shown copper presence. Only flax flour and white buckwheat flour contained copper in 4.110 µg g<sup>-1</sup> and 0.862 µg g<sup>-1</sup>, respectively. Besides copper, second most important microelement for organism functioning is zinc. Zinc participates in over 200 enzymatic reactions in the body. It plays a key role in the synthesis and stabilization of genetic material. It is necessary for cell division, as well as for the structure and normal functioning of cell membranes, for the formation of antibodies, leukocytes, thyroid gland and the functioning of hormones. The average daily intake of this mineral in the body is 15 mg. The zinc concentration in the analyzed samples ranged from 14.948 μg g<sup>-1</sup> in palenta to 46.001 µg g<sup>-1</sup> in flax flour. Other microelements that have been detected in analyzed samples (Table 1) are not specifically discussed about.

Heavy metals that usually contaminate foods are lead, mercury, cadmium and arsenic (Carruthers and Smith, 1979), thus further analysis has been focused on lead, cadmium and arsenic presence determination. In analyzed samples, cadmium and arsenic were not detected even in traces, while most of the samples contained lead. According to the rules (Regulation, 1992), allowed concentration of lead, cadmium and arsenic in flours are 0.4  $\mu g \, g^{-1}$ , 0.1  $\mu g \, g^{-1}$  and 0.5  $\mu g \, g^{-1}$ , respectively. Lead is stored mostly in bones and concentration that human body can tolerate is not more than 1-2 mg. Lead poisoning affects the function of the brain and nervous system, reducing the level of intelligence, the power of perception and in worst cases can cause death. The World Health Organization (WHO) considers daily toxic amounts of 7  $\mu g$  per kg of bodyweight (Hadžić, 2013). In analyzed samples lead was not detected only in palenta flour. In the allowed concentration the lead was detected in wheat flour type 400, flour for integral bread and gluten-free palenta. The detected concentrations in the samples of white buckwheat flour and corn white flour were above permitted values prescribed by the rules. In sample of flax flour a detected lead concentration represents the limit value prescribed by the regulation.

#### Conclusion

Based on the presented results, it can be concluded that the mineral composition of gluten and gluten free flours is different. In terms of nutritive value, the flour which proved to be the richest in terms of the higher content of macro elements (K, Na and Mg) and micro essential elements (Zn and Cu) is flax gluten free flour. The lead

detected in white buckwheat and white corn flour is not negligible and indicates the need for limited and strictly controlled use in nutrition.

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#### References

- Rathi P.M., Zanwar V.G. (2016). Non-celiac Gluten Sensitivity (NCGS). Journal of The Association of Physicians of India. 64: 46-55.
- Saturni L., Ferretti G., Bacchetti T. (2010). The gluten-free diet: safety and nutritional quality. Nutrients. 2(1): 16-34.
- Pavlović M., (2017). Fizikalno-kemijska karakterizacija pšeničnog brašna. PhD thesis. Polytehnic in Pozega. Biotechnical department.
- Araujo R.G., Macedo S.M., Korn M.D.G.A., Pimentel M.F., Bruns R.E., Ferreira S.L. (2008). Mineral composition of wheat flour consumed in Brazilian cities. Journal of the Brazilian Chemical Society. 19(5): 935-942.
- Hadžić A. (2013). Minerali u ishrani. Univerzitet u Sarajevu, Sarajevo.
- Regulation S. (1992). Pravilnik o količinama pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutiku, anabolika i drugih supstancija koje se mogu nalaziti u namirnicama (Content of pesticides, metals, metalloids and other toxic substances in foods). Službeni list SRJ, broj, 5.
- Carruthers M., Smith B. (1979). Evidence of cadmium toxicity in a population living in a zinc- mining area: pilot survey of Shipham residents. The Lancet. 313(8121): 845-847.
- Rajković M., Stojanović M., Glamočlija Đ., Tošković D., Miletić V., Stefanović V., Lačnjevac Č. (2012). Wheat samples and heavy metals. Journal of engineering & Processing Management. 4(1): 85-126.

## SASTAV BEZGLUTENSKOG BRAŠNA SA POSEBNIM OSVRTOM NA MINERALNE MATERIJE

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#### Abstract

U ovom radu ispitivan je sastav bezglutenskog brašna u cilju određivanja sadržaja mineralnih materija (As, Ag, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Tl, Zn, Si i P). Analizirane su sledeće vrste brašna: palenta, bezglutenski mix, glutenfree palenta, laneno, belo heljdino brašno, projino kukuruzno belo brašno kao i glutenska brašna u cilju komparacije: brašno za integralni hleb i pšenično brašno-tip 400. Uzorci su najpre pripremljeni postupkom mokre digestije a potom podvrgavani ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) analizi. Na osnovu prikazanih rezultata može se zaključiti da se mineralni sastav bezglutenskih i glutenskih brašana razlikuje. U pogledu nutritivne vrednosti, brašno koje se pokazalo najbogatije u smislu većeg sadržaja makro (K - 7373,215 μg g<sup>-1</sup>, Na - 1978,009 μg g<sup>-1</sup> i Mg - 1818,141 μg g<sup>-1</sup>) i mikro esencijalnih elemenata (Zn - 46,001 μg/g i Cu-4,110 μg g<sup>-1</sup>) je laneno bezglutensko brašno. Sadržaj olova detektovan kod belog heljdinog (0,518 μg g<sup>-1</sup>) i belog kukuruznog brašna (0,534 μg g<sup>-1</sup>) je izvan granica dozvoljene količine olova u brašnima, što ograničava njihovu upotrebu u ishrani.

Key words: gluten, brašno, minerali, toksični elementi, ICP-OES

523

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