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# Minerals in grain gluten-free products. The content of calcium, potassium, magnesium, sodium, copper, iron, manganese, and zinc

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ABSTRACT

The popularity of gluten-free (GF) products has significantly increased in recent years. Products with a Crossed Grain symbol are consumed not only by patients diagnosed with gluten-related diseases, but also by healthy individuals. This study is an attempt to determine the quality of grain GF products in the aspect of their mineral content. Fifty grain GF products (flours, breads, mixes for cooking, snacks, pasta, flakes and others) were selected and the content of eight minerals: calcium, potassium, magnesium, sodium, copper, iron, manganese, and zinc was determined. The content of analysed minerals in 100 g of the products was: Ca (<0.01–237 mg), K (17–1417 mg), Mg (7–223 mg), Na (<0.01–1512 mg), Cu (<0.01–1 mg), Fe (0.3–19 mg), Mn (<0.01–4.0 mg), and Zn (0.2–3.1 mg). In general, products from oats, millet, buckwheat, amaranth, quinoa, acorn, and teff contained more analysed minerals than products based on rice, corn, potato, and GF wheat starch.



## 1. Introduction

Gluten-free (GF) products are those with natural absence or acceptable level (<20 mg/kg) of gluten (EU 828/2014). These products can be signed with a Crossed Grain symbol. GF products are an important sector in food industry. Their global value in 2015 was estimated for 3.3 bln US$ and forecasts assume that market of GF products will be increasing at least until 2020 (Euromonitor International, 2015).

GF products are consumed not only by patients diagnosed with strictly gluten-related disorders: celiac disease (CD), Dühring's disease, gluten sensitivity, gluten or wheat allergy, but also with other diseases like autism, Hashimoto's disease, and irritable bowel syndrome (Ludvigsson et al., 2013; Lebwohl et al., 2015). Epidemiological studies indicate that approximately 1–2.5% of worldwide population suffers from CD – from 0.5% in Tunisia and Egypt, 1–3.5% in Western Europe to 5.6% in Algeria (Lohi et al., 2007; Mustalahti et al., 2010; Gujral et al., 2012; West et al., 2014). The prevalence of CD is rather constant and the growth of GF market is a result of society's interest in new eating habits. People search for alternative diets as a part of healthy life-style or to lose their body weight.

For patients with gluten-related diseases, only products with a sign of Crossed Grain are safe and should guarantee the absence of gluten. Even if product is made from GF raw material, there is a risk that it was contaminated with wheat/rye/barley during production process. However, the quality of GF products is determined not only by the lack of gluten, but also by other food quality indicators, like microbiological safety, sensory attributes, and nutritional value. For many years, producers and consumers attention was mainly focused on gluten absence and sensory properties of GF products, but lately also nutritional value has become an important aspect. Many studies indicate nutritional deficiencies in people on rigorous GF diet based on the most popular raw materials like corn or rice. Therefore, people search for less popular GF raw materials such as amaranth, quinoa, acorn, and teff, which can improve the nutritional quality of their diet. The most common mineral deficiencies indicated for GF diet are calcium, copper, iron, magnesium, and zinc (Botero-López et al., 2011; Caruso et al., 2013; Shepherd and Gibson, 2013; Wierdsma et al., 2013; Oxentenko and Murray, 2015).

To the best of our knowledge, the data concerning mineral content in various GF grain products, especially from less popular raw materials, are very limited. The data for more popular GF products, e.g. made from rice and corn can be found in the literature (Kunachowicz, 2001; Ragaee et al., 2006; Hager, 2013; Rybicka et al., 2015), whereas the mineral content in food products from amaranth, teff or quinoa is not well described (Hager et al.,

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2012; National Nutrient Database for Standard Reference, 2016). Most of the papers discuss raw materials or just selected products (Alvarez-Jubete et al., 2009; Arendt and Zannini, 2013; Gebremariam et al., 2014; Nascimento et al., 2014; Sarker et al., 2015; Bolaños et al., 2016). This lack of knowledge about the nutritional value of grain GF products is also highlighted by other researchers (Nowak et al., 2016).

The objective of the study was to assess the quality of a range of grain GF products available on the European market in the aspect of mineral content. The content of four macroelements: calcium (Ca), potassium (K), magnesium (Mg), sodium (Na) and four microelements: copper (Cu), iron (Fe), manganese (Mn), zinc (Zn) is described in this study. Due to the limited data on mineral content in these products, the obtained results are important part of their quality characteristics.

## 2. Materials and methods

### 2.1. Materials

GF products (50) available on the Polish market in 2011–2013 were purchased in the local stores. All products were from two production batches and were signed with a Crossed Grain symbol. Selected products included: breads (5), mixes for breads and cookies (6), flours (14), pastas (4), flakes (8), snacks (8), and others such as grouts or beverages (5).

Two certified reference materials (CRM), NCS ZC73009 Wheat and NCS ZC73010 Mealie (National Institute of Standards and Technology, Gaithersburg, USA), were selected to verify the accuracy of the analytical procedure.

### 2.2. Sample preparation

All analysed food products and CRMs were mineralized with nitric acid (Lendinez et al., 2011; Rybicka, 2015). Food samples were homogenized (ErgoMixx, Bosch, Munchen, Germany) and 5.0 g portion was mixed with 30 mL of 65% nitric acid (Emsure, Merck, Warsaw, Poland). The process of wet mineralization was carried out at 200 °C in the mineralization block (Model Q-439, BUSHI) until complete digestion of the sample. After cooling, samples were filtered to the certified polymethylpentene flasks and refilled to 50 mL with demineralized (Hydrolab System, Wiślina, Poland) and filtered water (Millipore HA filter 0.45 μm, Waters, Millford, Ma, USA).

Prepared samples were stored maximally up to 2 weeks at 4 °C in the dark until mineral determinations. All samples were prepared in six replicates (three replicates from each production batch).

The concentrations of Ca, K, Mg, Na, Cu, Fe, Mn, and Zn were determined using atomic absorption spectroscopy in the flame (F-AAS) (SpectrAA-800, Varian, USA). Conditions of measurements, as well as detection and quantification limits are indicated in Table 1 (Analytical Methods for Flame Atomic Absorption Spectrometry, 1989). For each determination, at least two 7-point calibration curves were prepared, each adjusted to the expected concentration of appropriate mineral in analysed sample.

### 2.3. Statistical analysis

Statistical analyses were performed using Statistica 12.0 program (StatSoft, Inc., 2000). Data are presented as mean ± SD of six measurements. All data were submitted to one-way analysis of variance (ANOVA). Analysis of variance has shown significant effect of the type of product on the content of tested minerals ($p < 0.05$). The significance of differences between means was determined by least significant differences (LSD) test at $\alpha = 0.05$.

## 3. Results and discussion

### 3.1. Accuracy verification of F-AAS method

To ensure the accuracy and precision of the F-AAS method, two CRMs (NCS ZC73009 Wheat and NCS ZC73010 Mealie) were analysed. The results of CRMs analysis are presented in Table 2.

**Table 1**
Parameters of Flame Atomic Absorption Spectroscopy (F-AAS) determinations of minerals.

| Mineral | λ [nm][a] | Concentrations range [μg/mL][b] | Gases | Detection limit [μg/mL] | Quantification limit [μg/mL] | Note |
|---|---|---|---|---|---|---|
| microelements | | | | | | |
| Cu | 324.7 | 0.03–10 | air/ acetylene | 0.014 | 0.042 | |
| Fe | 248.3 | 0.06–15 | air/ acetylene | 0.031 | 0.093 | |
| Mn | 279.5 | 0.02–5 | air/ acetylene | 0.007 | 0.021 | addition of potassium nitrate [2 mg/mL[c]] |
| Zn | 213.9 | 0.01–2 | air/ acetylene | 0.003 | 0.009 | |
| macroelements | | | | | | |
| Ca | 422.7 | 0.01–3 | air/ acetylene | 0.016 | 0.048 | addition of lanthanum [1 mg/mL[c]] |
| | 239.9 | 2–800 | air/ acetylene | 0.500 | 1.500 | |
| K | 769.9 | 1–6 | air/ acetylene | 0.007 | 0.021 | |
| | 404.4 | 0.15–20 | air/ acetylene | 1.000 | 3.000 | |
| Mg | 202.6 | 0.03–10 | air/ acetylene | 0.129 | 0.421 | addition of lanthanum [1 mg/mL[c]] |
| Na | 589.6 | 0.01–2 | air/ acetylene | 0.001 | 0.003 | |
| | 330.3 | 2–400 | air/ acetylene | 0.650 | 1.950 | |

[a] Analytical wavelength.
[b] Concentrations recommended for appropriate wavelength by the producer of F-AAS.
[c] Final concentration in a sample.