FLAME ATOMIC ABSORPTION SPECTROSCOPY IN MINERAL ANALYSIS OF BARLEY FROM BANAT AREA

Mirela Ahmadi[1], Dorel Dronca[2], Cornelia Milovanov[3], Camelia Tulcan[1], Oana-Maria Boldura[1], Călin Mircu[4], Ioan Huţu[3], Ion Violeta[5], Mihaela Scurtu[5]

[1]*Department of Chemistry and Biochemistry, Banat University of Agriculture Sciences and Veterinary Medicine "King Michael I of Romania" from Timisoara (USAMVB), Timisoara – 300645, Calea Aradului 119, România.*
[2]*Department of Animal and Plant Genetic Improvement, USAMVB, Calea Aradului 119, Timişoara – 300645, România.*
[3]*Department Animal Production and Veterinary Public Health, USAMVB, Calea Aradului 119, Timişoara – 300645, România.*
[4]*Department of Genetically Engineering, USAMVB, Calea Aradului 119, Timişoara – 300645, România.*
[5] *S.C. Scient CromatecPlus – Research Development Innovation Centre for Instrumental Analysis S.R.L., Str. Petre Ispirescu, nr 1, Sat Tancabesti, Com. Snagov, Ilfov – 077167, România.*
e-mail: ddronca@animalsci-tm.ro

Abstract
Barley as a cereal grain is very important for animal and human nutrition, being also used in food products technology for fermented or distillated beverages. It has very good nutritional properties for animals and human, being the forth ranks in cultivation and quantity production in the world. The flame atomic absorption spectroscopy (FAAS) is an analysis method for metals, but the laboratory procedure is essential for the final result. Our goal was to analysis the barley content from Banat area with FAAS method using direct determination from the solution after digestion and using a diluted solution. The direct determination for copper content in barley (in mg/Kg, presented as mean and SD) was 4.146±0.205; iron content was 25.657±0.583; manganese determination was 10.391±0.192 and zinc content was 17.911±0.565. The quantity of metals (in mg/Kg, presented as mean and SD) from diluted (5x) samples for copper was 4.463±0.403; for iron was 26.821±1.083; for manganese was 11.136±0.444; for zinc was 18.731±0.665. Comparative evaluation of the mineral content for copper, iron, manganese and zinc showed that the quantitative analysis of five times diluted samples present higher values for all analyzed minerals comparative with direct determination.

Introduction
Barley is a cereal grain, part of the grass family, and it is also known as *Hordeum vulgare*. The importance of barley (cereal grain) is provided by the content of dietary fiber (especially □-glucan) and other complex carbohydrates, well balance of amino acids (tryptophan) and proteins, low lipids, and good source of enzymes, minerals (selenium, copper, manganese, phosphorus, magnesium) and vitamins (thiamine, niacin, especially tocopherols). The mineral content of barley is very important for animal diet and also in beer technology, but this is correlated with the soil and water characteristics from cultivation area (Aldughpassi et al., 2016).
Diabetes people depend on a healthy diet, rich in fibers and characterized by low glycemic index. Naked barley (*Hordeum vulgare*) is a low glycemic index grain, which contains soluble fibre of ß-glucan in higher quantities compared to hulled barley. Naked barley and naked oats were tested for glycemic index, and naked barley presented significant lower glycemic index comparative

with oats (Steele et al., 2013).
The nutraceutical products based on ß-glucan depends very much of the carbohydrate structure. Thus, the chemical structure, the size and the viscosity are characteristics that could be influenced by the germination stage and the processing method (ex. Microwave). Ahmad in 2016, demonstrated experimentally that in germinated barley for ß-glucan was lower compared to ß-glucan obtained from microwave processed barley or from unprocessed barley (Ahmadi, 2016).
Barley is used in. the morning meal for human, because brings fibers and manganese – which is great for nervous system. The regularly consumption of barley can modulate the blood sugar, helps in weight loss – reducing the visceral fat tissue, reduces the blood pressure and cholesterol, reduce the risk of cancer disease and heart diseases, reduce the symptoms of arthritis, has anti-aging properties (Baik and Ullrich, 2008; Olson 2016; Sheikh, 2016; Stanca et al., 2016).

Experimental

Our aim was to analyze the barley cultivated in Timis County, with flame atomic absorption spectroscopy, and to evaluate if the dilution influences the final result.
First stage was to harvest barley from the Timis County field, more precisely from Libling. Then, for flame atomic absorption spectroscopy we made a digestion for every single sample, using azotic acid 65% (15.8mol/l), Merck and Milli-Q water, and then we made the quantitative analyze for copper, iron, manganese and zinc. The analytical determination for minerals was conducted into two directions: the direct analyze and the analyze from dilution (five times dilution). For reading the concentration of copper, iron, manganese and zinc with worked with a Flame Atomic Absorption Spectroscopy and then we calculate the final concentration depending to the quantity of barley took as initial sample for digestion. The accuracy, precision, repeatability and also stability were the results were presented comparatively, and the unit was mg of metal to kg barley. The results were presented as mean (average) and standard deviation (SD).

Results and discussion

Different method of minerals analysis are presented in the literature, referring to different temperature program for digestion, different concentration of azotic acid or even different acid, and of course various analytical equipment. The results of our study are presented in figure 1.

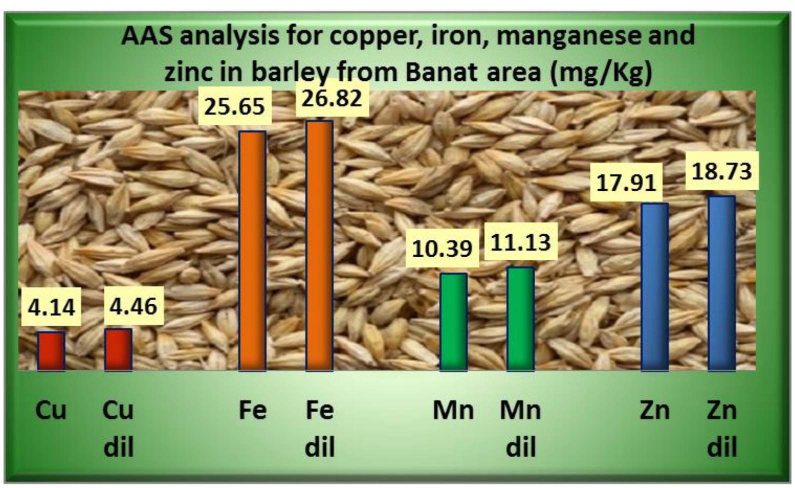

Figure 1. Copper, iron, manganese and zinc AAS analysis in hole barley (*Hordeum vulgare*) from Banat area (direct and 5 times dilluted determination)

All concentrations determination for copper, iron, manganese and zinc, were similar after direct or 5 times diluted determination. Concentrations were calculated as mean (average) and standard deviation in mg/kg, and for direct determination in barley the concentration was: copper content 4.146±0.205; iron 25.657±0.583; manganese 10.391±0.192 and zinc 17.911±0.565; but for diluted (five times) samples for copper was 4.463±0.403; iron was 26.821±1.083; manganese was 11.136±0.444; zinc was 18.731±0.665.
Our results for copper, iron, manganese and zinc concentration from barley were similar with the results presented by other authors in the literature data, even if some condition were not the same (the variety of the barley, the soil composition, the analytical equipment).
The mineral content of different cereals was studied from long time ago, because the chemical mineral composition of cereals is important for the animal and human diet, for the characterization of the soil, and for the fermented and distilled products using barley as substrate.
Thus, Liu and other collaborators presented in 1974 a report of mineral components in milled barley from United States Department of Agriculture, Wisconsin. The results presented 4.0mg/kg copper, 28.0mg/kg iron, 11.0mg/kg manganese, 22.8mg/kg zinc, 257mg/kg calcium, 138mg/kg sodium, 10.2mg/kg aluminum, 0.37mg/kg molybdenum, 1,290mg/kg magnesium, 4,390mg/kg potassium and 2,970mg/kg phosphorus, determined from whole kernel of Atlas barley (Liu et al., 1974). Also, Liu and Zhang in 2010 determined the content of some minerals from hulled barley by ultraviolet and flame atomic absorption spectrometry and the results presented K > S > Mg > Ca > Fe > Na > Zn > Mn > Cu.
There are different methods for investigation of mineral content from grains. Energy dispersive X-ray analysis and neutron activation analysis can also be used for calcium, magnesium, phosphorus and potassium content from different anatomical parts of grains. Thereby, using energy dispersive X-ray method it was investigated the content of calcium related to phosphorus, magnesium and potassium from aleurone cells protein of barley. The results demonstrated that calcium is found in very small quantities compared to P, Mg and K in endosperm. But if the endosperm was used for seedling, the new barley seedlings took over some minerals from endosperm to develop in a new plant (Stewart et al., 1988).
Not only the biomineral plants are important for grain, but heavy metals are also evaluated because the physiology of the plant, crop quality and production is negatively affected; and the quality of cereals are absolutely involved in the quality of food or beverages having the cereals as ingredients. So, heavy metals are contaminants that could be present in the soil and water due to the pollution. Thus, it is very easy for plants to cumulate toxic metals during growing from soil and water. Advanced technologies and analysis techniques involve transcription factors (transcriptomics), metabolites (metabolomics), stress in proteins (proteomics) and mineral elements (ionomics), for evaluate the stress induced by pollution, and also to evaluate the heavy metals tolerance with economic consequences (Singh et al., 2015).
Genetic engineering tries to find new ways to modify the gene of barley, to provide all the nutrients for an optimal growth. Generally, the cereals require macronutrients (nitrogen, phosphorus, potassium, calcium, magnesium, sulphur) and micronutrients (chlorine, boron, iron, manganese, copper, zinc, nickel, and molybdenum). The production of barley is often limited by the phytoavailability of the nutrients, with consequences in the quality of crop (White and Brown, 2010).
New technology provides new challenges in agriculture, food technology, molecular biology and other domains. Thus, the molecular biology work to the gene of cereals, and particularly to barley, modify the genetic characteristic to obtain genetic modify plants that are rich in some

nutrients or are more tolerant for different limiting growth factors (Fujii et al., 2012). One example of this molecular biology technics is genetic modify barley to be more tolerant for aluminum toxicity – this being a very important agriculture characteristic in areas where barley is cultivated on acidic soils, like Middle East.

Conclusion

Crop quality is very important for economic, nutritional, technological point of view. Barley is a grain used in agriculture for food and feed, being used as cereals or for food and beverage technology. The biominerals and heavy metals from barley are important to evaluate the quality and quantity crop, the possibility to use the cereals in human or animal nutrition. *Hordeum vulgare* (barley) is a good vegetal source for benefic minerals, and the barley seedling are taking over the nutrients from endosperm to grow. The distribution of minerals in various anatomical parts is different in grains. For all the samples the concentration of copper, manganese, iron and zinc was in normal limits compared to the literature data. Concentration of the tested biominerals was similar for both direct and dilluted using flame atomic absoption analysis, but for all the minerals from barley (copper, manganese, iron and zinc) th concentration determined after five times dillution was higher then the direct determination.

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