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MULTIELEMENT ANALYSIS AS A BASIS FOR THE SELECTION OF RAW MATERIALS ON THE BARLEY MARKET

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Abstract: Barley is one of the most used grains in the alcoholic beverage industry. Inductively coupled plasma optical emission spectrometry (ICP-OES) were evaluated for metal contents of ten barley samples which are acquired from different markets in Serbia. The low detection limit and wide working range for many elements make the ICP-OES method ideal for the analysis of samples of plant origin. Barley samples were prepared by dry mineralization process. The elements determined are divided into two groups. All barley samples contained the major elements belonging to the first group and. The major metals of barley are K (3572–4692 µg/g), Mg (758.3–1032 µg/g) and Ca (349.8–441 µg/g). Concentration of Na was ranged from 47.7 to 83.5 µg/g. The second groups of elements are minor and trace metals. Barley samples are a good source of Fe (18.88–24.87 µg/g), Se (0.022–0.1938 µg/g) and Zn (16.44–24.00 µg/g). The content of heavy metals in all samples is within acceptable limit. Heavy metals can be present in foods from nature or as a result of human activities such as exhaust gases, industrial emissions and contamination during industrial processes. The presence of heavy metals in food and beverages indicates the degree of environmental pollution. The aim of this work was to point out the high nutritional benefits of whole grain consumption and its increased inclusion in a healthy diet, which would support the growth of the barley market through multielement analysis of barley samples. Malt is a scarce product on the world market, so the increased use of barley for the production of alcoholic and non-alcoholic beverages is of great economic importance for Serbia and countries in the region.

Keywords: barley, ICP-OES method, quality, market.

Field: Economy

1. INTRODUCTION

Barley (Hordeum Vulgare L.) is mainly used for the production of beer and for use as animal feed. Recently, the use of barley in the food industry has increased (Oscarsson, Andersson, Salomonsson, & Aman, 1996). Due to its complex genetic structure, barley is an adaptable cereal. Barley breeders can produce different varieties to obtain end products (Jayarathna et al, 2023). Macro and micro elements, depending on their concentration, can have positive and negative effects on human health. Metals like iron, copper and zinc are included in the composition of many enzumes that are important for the development of biological processes (Aberie, Sallilh, & Medfu Tarekegn, 2021). Cadmium, lead, mercury and nickel can be toxic even in low concentrations, depending on the time of accumulation in the plants (Onianwa, Adetols, Iwegbue, Ojo, & Tela, 1999).

Population growth and urbanization have led to an increase in industrial and agricultural production and the production of wastewater containing large amounts of toxic compounds such as heavy metals. Improper management of wastewater streams containing heavy metals has led to risks for the environment, thereby endangering the health of animals and humans (Marwan, Doa, & Munqez, 2023). Irrigation water containing heavy metals significantly affects the yield, growth and quality of barley (Mohammed, Morrison, & Baldwi, 2021).

Determining the content of macro and microelements in samples is preceded by mineralization of the sample. The two techniques that have been in use and are still most commonly applied are based on dry combustion at a defined temperature and wet digestion with oxidants in open and closed systems (Gamela, Costa, & Pereira-Filho, 2020). Dry mineralization is applied to samples that contain a large amount of organic matter and are analyzed for non-volatile elements. Most often, these are food samples (nutritional elements in food), plant materials, biological materials, etc. (Manousi, Isaakidou, & Zachariadis, 2022).

In this study, the ICP-OES method was employed to determine 24 elements (Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sn, Sr, V and Zn) in samples of barley obtained from markets in Serbia.

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2. MATERIALS AND METHODS

Samples

All barley samples are from different producers and commercially available. Then, samples were ground, stored in a refrigerator at 4°C and analyzed.

Instruments:

-ICP-OES ICAP 6000 (Thermo Scientific, Cambridge, UK)
-Scale – Metteler Toledo, AB204-S/A
-Device for deionized water - TKA MicroMed (TKA Wasseraufbereitungs systeme GmbH, Niederelbert, Germany)
-Automatic variable pipettes
-pH meter (Hanna instruments, GmbH)
-Dryer
-Piconometer

Chemicals:

-HNO3 p.a., Merck® (KGaA, Darmstadt, Germany)
-Multi standard, Ultra scientific (North Kingstown, RI, USA) (30 elements, 20.00±0.10 ppm, except P, K and Si 100.0±0.5 ppm and Ag 5.00±0.03 ppm, matrix is 2% HNO3 and traces of tartaric acid)
-Argon 5.0 (purity 99.999%)
-Deionized water (χ = 0.05 μS/cm)
-Buffer solutions for calibration, pH 4.00 and pH 7.00 (Hanna instruments)

Metal content

The content of 20 g of barley is homogenized and sample of 2 g was ashing at 450ºC. The final residue was dissolved in 5% nitric acid solution and made up to 50 ml. Working standard solutions were prepared by diluting the stock solution with 5 % nitric acid for checking the linearity.

3. RESULTS

Barley samples were recorded at the selected wavelength, and each measurement was repeated three times. A manual correction was made in order to obtain the highest possible signal/background ratio. The results obtained are given as the mean value of three replicates (csr ± SD, n = 3, mg/kg).

The results for the total metals content of 10 samples of barley are summarized in Tables 1 and 2.

Two groups of elements were established for obtained data.

The first group contained the major elements and they are present in all barley samples, e.g. K, Ca, Mg and Na (Table 1).

Table 1. Major metals content (μg/g) in samples of barley.

Sample	Ca	K	Mg	Na
B1	441±1	4692±5	1032±1	64.8±0.1
B2	394.3±0.3	3975.0±0.4	846±1	74.7±0.1
B3	366.8±0.1	3847±3	836.3±0.4	79.85±0.04
B4	349.8±0.1	3620±1	778±1	47.7±0.1
B5	357.5±0.2	3722±1	776.3±0.3	54.28±0.04
B6	355.5±0.1	3572±2	775.3±0.3	60.85±0.04
B7	367.8±0.1	3812±2	789.0±0.3	68.03±0.03
B8	376.8±0.2	3775±3	783.8±0.2	69.68±0.04
B9	384.5±0.1	3640±2	774±1	83.5±0.1
B10	350.0±0.1	3700±2	758.3±0.2	60.08±0.04

The second group contained tne minor and trace metals (Table 2). Some of them such as Zn, Fe, Mn, Cu, Sr, Se, Ba and B are known to be essential for life. Ni, Cr, Cd, Cd, Pb and Al reflect the exogenous influence that may be related to environmental pollution and they are known as non-essential elements.

Table 2. Minor and trace metals content (µg/g) in samples of barley.

Sample	**Al**	**As**	**B**	**Ba**	**Cd**
B1	3.54±0.01	0.1075±0.0002	1.84±0.01	1.255±0.001	0.0475±0.0001
B2	3.22±0.02	0.0625±0.0004	0.63±0.03	0.832±0.001	0.0525±0.0002
B3	3.20±0.01	0.098±0.002	0.308±0.001	0.7400±0.0001	0.0600±0.0001
B4	3.07±0.01	0.0650±0.0004	0.260±0.001	0.958±0.001	0.0350±0.0001
B5	3.22±0.01	0.0850±0.0004	0.1363±0.0001	0.8450±0.0004	0.0425±0.0001
B6	3.29±0.01	0.072±0.002	0.0925±0.0003	0.915±0.001	0.0400±0.0001
B7	2.154±0.003	0.0700±0.0004	0.1438±0.0002	0.9700±0.0004	0.0350±0.0001
B8	2.35±0.01	0.058±0.001	0.1300±0.0001	1.0000±0.0003	0.0313±0.0001
B9	2.00±0.01	0.100±0.001	0.2250±0.0001	1.065±0.001	0.0015±0.0001
B10	2.41±0.01	0.040±0.001	0.260±0.001	0.8675±0.0003	0.0019±0.0001
Sample	**Mo**	**Ni**	**Pb**	**Sb**	**Se**
B1	0.622±0.002	0.1900±0.0001	0.1063±0.0002	0.130±0.001	0.1938±0.0002
B2	0.450±0.001	0.0375±0.0001	0.0750±0.0003	0.1100±0.0001	0.096±0.001
B3	0.520±0.001	0.0638±0.0002	0.062±0.001	0.1025±0.0003	0.098±0.001
B4	0.3675±0.0004	0.0238±0.0001	0.344±0.001	0.199±0.001	0.149±0.001
B5	0.3850±0.0002	0.0213±0.0001	0.0763±0.0004	0.1413±0.0002	0.022±0.001
B6	0.3875±0.0004	0.0113±0.0002	n.d.	0.1913±0.0004	0.0388±0.0001
B7	0.5200±0.0004	0.0063±0.0001	0.0425±0.0004	0.1175±0.0001	0.1750±0.0003
B8	0.548±0.001	n.d.*	0.0550±0.0004	0.1625±0.0001	0.1850±0.0003
B9	0.5725±0.0001	0.0450±0.0001	0.075±0.001	0.226±0.001	0.1100±0.0003
B10	0.590±0.001	0.0275±0.0001	0.0350±0.0003	0.175±0.001	0.161±0.002
Sample	**Cr**	**Cu**	**Fe**	**Li**	**Mn**
B1	0.320±0.001	4.460±0.004	23.72±0.03	4.443±0.005	13.50±0.01
B2	0.358±0.001	4.36±0.02	21.49±0.02	0.600±0.001	11.95±0.01
B3	0.370±0.003	4.963±0.002	24.87±0.01	0.358±0.001	12.68±0.03
B4	0.385±0.001	3.043±0.002	18.88±0.01	2.103±0.002	10.36±0.01
B5	0.413±0.003	3.928±0.002	19.40±0.01	2.193±0.001	11.11±0.01
B6	0.383±0.001	3.585±0.003	19.18±0.01	7.115±0.005	10.60±0.04
B7	0.383±0.001	3.790±0.001	20.70±0.01	5.738±0.003	12.00±0.1
B8	0.428±0.002	3.508±0.004	19.24±0.01	6.540±0.003	11.94±0.02
B9	0.355±0.001	3.563±0.004	19.13±0.02	6.04±0.01	11.32±0.01
B10	0.410±0.001	3.053±0.001	19.5±1.1	3.043±0.002	11.60±0.03
Sample	**Si**	**Sn**	**Sr**	**V**	**Zn**
B1	11.46±0.01	0.209±0.001	1.050±0.001	10.393±0.002	22.35±0.02
B2	9.56±0.01	0.1188±0.0001	1.368±0.001	9.748±0.004	19.08±0.02
B3	7.853±0.005	0.1163±0.0004	1.185±0.002	9.693±0.001	24.00±0.01
B4	6.263±0.004	0.1425±0.0003	1.158±0.001	9.413±0.002	15.76±0.01
B5	5.868±0.002	0.1225±0.0003	1.265±0.001	9.525±0.002	16.44±0.01
B6	7.058±0.003	0.1275±0.0004	1.200±0.001	9.415±0.001	17.00±0.02
B7	8.488±0.003	0.108±0.001	1.375±0.001	9.745±0.002	19.77±0.03
B8	9.20±0.01	0.1613±0.0004	1.475±0.003	9.863±0.001	18.56±0.01
B9	9.933±0.005	0.1163±0.0002	1.773±0.002	9.728±0.002	19.12±0.02
B10	10.980±0.004	0.0788±0.0004	1.305±0.001	9.703±0.001	18.71±0.03

*not detected

4. DISCUSSIONS

The major metals of tested barley samples are K (3572-4692 µg/g), Mg (758.3-1032 µg/g) and Ca (349.8-441 µg/g). Concentration of Na was ranged from 47.7 (sample B4) to 83.5 µg/g (sample B9). Tested barley samples from Pakistan showed higher content of major metals (Shar et al, 2007). Cheng et al. reported similar results of Mg content and higher results of Ca content (Cheng, Yao-bin, & Xue-lian, 2012). Nikkhah reported similar or higher results of major metals in barley (Nikkhah, 2012). The content of K was 5700 µg/g, Ca 500 µg/g and the content of Mg was 1200 µg/g. Barley from China showed lower content of major metals (Liu, & Zhang, 2010).

As Table 2 shows, the lowest content of Al was in sample B9 (2.00 µg/g) and the highest content was in sample B1 (3.54 µg/g). The results from this study for Al are lower than results from Pakistan (Shar et al, 2007, 2013). The content of As was ranged from 0.040 to 0.1075 µg/g in samples B10 and

B1, respectively. Sample B6 had the lowest content of B (0.0925 µg/g) and sample B1 the highest content of B (1.84 µg/g). The content of Ba was ranged from 0.7400 to 1.255 µg/g in samples B3 and B1, respectively. The other authors showed higher values of As, B and Ba (Shar et al, 2007, 2013). Cadmium is a highly toxic element and a serious contaminant. The content of Cd is too low and was ranged from 0.0015 µg/g in sample B9 to 0.0600 µg/g in sample B3. Shar et al. reported Cd content varying from 0.23 to 0.45 mg/kg (Shar et al, 2013). Barley from China showed similar content of Cd (0.033 mg/kg) (Cheng et al, 2012). Chromium exists in different oxidation states and the biological effects of those species are considerably different. The highest content of Cr was in sample B8 (0.428 µg/g) and the lowest in sample B1 (0.320 µg/g). Our results of Cr content are lower than results for barley from Pakistan (Shar et al, 2007, 2013). The content of Cu was ranged from 3.043 to 4.963 µg/g in samples B4 and B3, respectively. The content of Cu is lower than results from others (Shar et al, 2007, 2013; Liu, & Zhang, 2010). Cheng et al. reported the same results of Cu content (4.19 mg/kg) (Cheng et al, 2012). Iron is the most abundant of all the metals examined. All samples had a high content of Fe (18.88 – 24.87 µg/g in samples B4 and B3, respectively). Other authors reported higher content of Fe (Shar et al, 2007, 2013; Cheng et al, 2012; Liu, & Zhang, 2010). Sample B3 had the lowest content of Li (0.358 µg/g) and the highest content of Li was in sample B6 (7.115 µg/g). Sample B4 had the lowest content of Mn and Mo (10.36 and 0.3675 µg/g, respectively) and the highest content of Mn and Mo was in sample B1 (13.50 and 0.622 µg/g, respectively). Shar reported similar or higher results of Mn content (Shar et al, 2007). Also, higher results of Mn content are reported by Cheng et al. (Cheng et al, 2012). Sample B7 had too low content of Ni (0.0063 µg/g) and the highest content was in sample B1 (0.1900 µg/g). Ni was not detected in sample B8. Lower or higher results of Ni content had reported from other authors (Shar et al, 2007; Liu, & Zhang, 2010). Sample B10 had the lowest concentration of Pb (0.0350 µg/g) and the highest concentration was in sample B1 (0.1063 µg/g). Sample B6 did not show the content of Pb. Similar content of Pb was in barley from China (Cheng et al, 2012). The level of Sb was ranged between 0.1025 and 0.226 µg/g in samples B3 and B9, respectively. The concentration range of Se found to be between 0.022 and 0.1938 µg/g for samples B5 and B1 respectively. Selenium is known for its protective action against oxidative stress and is discussed in the prevention of cancer. The concentration range of Sn for the tested samples was found to be from 0.0788 to 0.209 µg/g in samples B10 and B1, respectively. The highest content of Si was in sample B1 (11.46 µg/g) and the lowest in sample B5 (5.868 µg/g). Sr content in the samples ranged from 1.050 (sample B1) to 1.773 µg/g (sample B9). V content was the lowest in sample B4 (9.413 µg/g) and the highest content was in sample B1 (10.393 µg/g). Among all metals, Zn is the least toxic and an essential element in the human diet as it is required to maintain the proper functions of the immune system. Sample B5 had the lowest content of Zn (16.44 µg/g) and sample B3 had the highest content of Zn (24.00 µg/g) (Table 3). Cheng et al. reported the same results of Zn content (23.31 mg/kg) (Cheng et al, 2012). The results of barley from Pakistan are higher (Shar et al, 2007, 2013). Our results are higher than results from barley from China (6-12 mg/kg) (Liu, & Zhang, 2010). Metals such as Fe, Cu, Zn and Mn are essential metals since they play an important role in biological system whereas non-essential metals, such as Cr, Ni and Cd are toxic even in trace amounts.

5. CONCLUSIONS

The presence of metals in barley samples is of great importance for brewers and consumers. The obtained results in this research are of great importance for the food industry in choosing the quality of barley varieties which affects the formation of prices on the market. ICP-OES is a kind of sensitive, simple, rapid and accurate method which has been applied to simultaneous determination of multielements in samples with satisfactory results. The advantages of dry mineralization are the possibility of burning a large amount of samples, the low need for reagents and the suitability of the technique for the preparation of a large number of samples. Disadvantages include losses due to lagging on vessel walls, contamination from the incinerator and annealing furnace, loss of low-density ash due to air flow (open annealing furnace door), and difficulty in dissolving certain metal oxides.

The main major metal in barley samples was K. The most common minor metals were Fe and Zn. The experiment data could provide an accurate and credible evidence for further exploitation of barley.

For a reliable assessment of the quality of barley as a raw material for the production of malt, it is not enough to analyze only the grain of barley, but it is necessary to produce malt and, based on that, to determine the technological properties of brewing barley. Malt extract is one of the most important economic indicators, and includes the sum of soluble components of malt and components that become soluble during mashing.

The use of barley in the diet is increasing due to its great benefits for human and animal health, is an ongoing trend boosting market growth. However, the barley market in the Republic of Serbia is not sufficiently developed and is still narrowly specialized. Infectious plant diseases, bad climatic conditions, poor soil quality and various pests contribute to these negative connotations.

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