

## INFLUENCE OF DIFFERENT SELENIUM CONCENTRATIONS ON THE PROTEIN AND STARCH CONTENT IN RYE MALT

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### Abstract

The research object was rye malt. Experiments were carried out at the Faculty of Food Technology of the Latvia University of Agriculture. The main aim of this study was to investigate the influence of different selenium concentrations on the content of protein and starch in rye malt. The protein, starch, also hectolitre mass were tested by Grains Analyzer Infratec 1241 (Sweden), the Falling number was analysed using Hagberg-Perten method, according to the ISO 3093:2009. Rye grain of 95% viability were soaked and germinated at temperature  $+6\pm 2$  °C for 3 days, using sodium selenate  $\text{Na}_2\text{SeO}_4$  solutions (Se concentration in solution 3 mg L<sup>-1</sup>, 5 mg L<sup>-1</sup>, 10 mg L<sup>-1</sup>), dried in the drier for 24 hours at temperature from 70 to 112 °C. The germination of grain with deionised water served as a control. The obtained results showed that the increase of selenium concentration in solution significantly decreases hectolitre mass (from 60.6 to 59.3 kg hL<sup>-1</sup>), the protein (from 10.28 to 10.02 mg 100 g<sup>-1</sup>dm), starch (from 68.7 to 66.9 mg 100 g<sup>-1</sup>dm) content and falling number (from 90.5 to 81.0 s) in rye malt comparing with control sample.

**Keywords:** rye malt, selenium, protein, starch.

### Introduction

During recent years significant progress has been made in the understanding of the processes of uptake and pathways of various chemical elements in plants (Shtangeeva et al., 2011; Kranner, Colville 2011).

Selenium (Se) is not an essential element for plants; it is an essential micronutrient for both humans and animals. More than 20 different selenoproteins have been characterized, including glutathione peroxidases and thioredoxinreductase, which are involved in controlling tissue concentrations of highly reactive oxygen-containing metabolites. The consumption of food provides the principal route of Se intake for the general population. The Food and Agriculture Organization of the United Nations (FAO, 2001) recommends a daily Se-allowance for humans of between 6 and 42 µg day<sup>-1</sup> depending on age and gender (Bitterli et al., 2010). Average Se concentration in cereals amounts 0.024 mg kg<sup>-1</sup> of grain dry matter, ranging from 0.006 to 0.122 mg kg<sup>-1</sup>, for barley 0.06 mg kg<sup>-1</sup>, for wheat 0.011 mg kg<sup>-1</sup> on the average (Dūma, 2006). Plant Se accumulation can vary more than two orders of magnitudes at a given soil Se concentration for a specific form of soil Se (i.e. "native" soil Se, Se added as selenate, or as selenite) among different plant taxa. Differences observed in the transfer of Se from soil into plants appear to result primarily from differences in the solubility of Se species in soil and only to a minor degree from differences in plant uptake efficiency among these species (Shtangeeva et al., 2011; Bitterli et al., 2010).

Plant roots can take up Se in form of selenate, selenite and also organo-Se compounds, e.g., selenocysteine and selenomethionine. Selenium is not available for plant uptake in the form of colloidal elemental Se or metal selenides (Kranner, Colville 2011; Bitterli et al., 2010).

It is important to remember that under ordinary conditions, each plant part may have its own characteristic concentrations of elements; therefore, comparisons of element concentrations in plants may not be referred to the plant as a whole but should refer to the same plant parts (e.g. roots, or leaves, or seeds). Lastly, may assume that not only concentration of one or another element in a particular plant part of any two plant species growing in the same environment may differ significantly but relations between elements in the plants may also be different (Shtangeevaa et al., 2011).

Rye (*Secale cereale* L.) is an important source of whole grain foods in Eastern and Northern European diets (Katina et al., 2007). Rye malt is a natural food product produced by germinating rye grains (Luoto et al., 2012; Siwela et al., 2010).

Germinated cereals / pseudocereal or sprouts are believed to have a greater nutritive and physiological value than cereal and pseudocereal grains and their products (Donkor et al., 2012). During germination (i.e. hydrothermal treatment in ambient conditions) the biosynthetic potential of grains is exploited and a number of hydrolytic enzymes are synthesised. The reactions in germinating grain lead to structural modification and the synthesis of new compounds, some of which have high bioactivity and can increase the nutritional value and stability of the grains (Kaukovirta-Norja et al., 2004; Gomand et al., 2011). Plant derived foods provide an important source of proteins and dietary minerals. This is especially true in developing countries where plant foods are a predominant portion of the diet. The concentrations of some minerals, especially iron, zinc, iodine, and selenium, are inherently low in plants as opposed to animal derived foods. As a result, more than 3 billion people worldwide suffer from micronutrient malnutrition (Waters, Sankaran, 2011).

Protein content shows grain suitability for processing. The temperatures and water stress occurring during grain filling period affects changes in rye protein aggregation. Usually in whole grain rye flour contains 8–13% proteins. The starch composition of cereal grains plays a major part in the digestibility and bread-making quality of flour. Generally in whole grain rye flour contains 56–70% starch.

Hectolitre mass (HM) is often used as an index of milling potential. The HM can be used as a silo management tool to optimize the storage space in the silo. The moisture content, weathering, kernel size, density, and packing factors affect hectolitre mass. (Zarina, 2012). The minimum hectolitre mass requirement for intervention of rye in the European Union (EU) is 68.0 kg hL<sup>-1</sup>.

Hagberg falling number (hereinafter falling number) is one of the most important grain quality indices of rye. The Hagberg falling number is an indicator of  $\alpha$ -amylase activity and a measurement of how far the break-down of starch has progressed in the kernel through enzymatic activities. It is expressed in seconds (s) and generally provides a measure of  $\alpha$ -amylase enzyme activity in the grain. A high falling number indicates minimal activity, whereas a low falling number indicates more substantial enzyme activity (Buchanon, Nicholas 1980). Alpha-amylase activity depends on weather conditions, especially precipitation. Under rainy conditions, the grains of wheat germinate in the ear either before or at harvest-ripeness, known as sprouting in the ear (Kunkulberga et al., 2007).

There is much investigation about selenium uptake, accumulation, biofortification, translocation, enrichment, toxicity, and tolerance in higher-plants (Shtangeeva et al., 2011; Kranner, Colville 2011; Bitterli, 2010; Waters, Sankaran, 2011), but information about selenium influence on the content of starch, protein, hectolitre mass and falling number in rye malt is scarce. The aim of this research was to investigate the influence of different selenium concentrations on the protein and starch content, grains hectolitre mass and falling number in rye malt.

## Materials and Methods

### Plant material

The object of the research was rye grain (variety 'Kaupo') from Ltd. Naukšēni (Latvia) harvested in 2011. Rye grain were soaked and germinated at temperature  $+6\pm 2$  °C for 3 days, using sodium selenate Na<sub>2</sub>SeO<sub>4</sub> solutions (Se concentration in solution was 3 mg L<sup>-1</sup>, 5 mg L<sup>-1</sup> and 10 mg L<sup>-1</sup>). The germination of grain with deionised water served as a control. After germination, all sprouts were dried for 24 h at a temperature from 70 to 112 °C; then they were grounded.

### Determination of protein content, starch and hectolitre mass

The content of protein, starch and hectolitre mass of rye malt grains were determined by a near-infrared

spectroscopy Grain Analyzer Infratec 1241. The contents of protein and starch were calculated based on grain dry matter (dm).

### Determination of Falling number

The Hagberg falling number –  $\alpha$ -amylase activity – was measured by the Hagberg-Perten method using a Perten Instruments (Sweden) „Falling number 1500” assessed to ISO 3093:2009. The Falling Number laboratory measurements with some modifications are conducted according to a standardized method aimed at measuring the viscosity of a mixture of 6g milled wheat with 1 g milled rye malt and 25 mL water placed in a bath at 100 °C (Gaaloul et al., 2011).

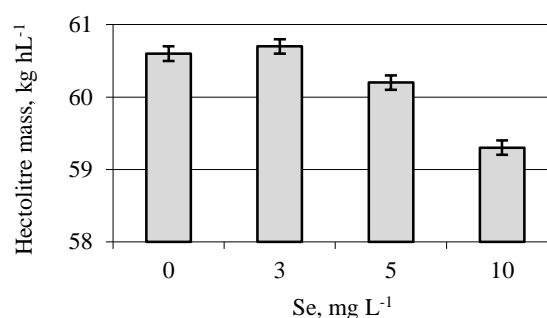
### Mathematical data processing

The results were processed by mathematical and statistical methods. The statistical analyses of data were carried out using Microsoft Excel for Windows 7.0 (Microsoft Corporation, Redmond, WA). Mean value, standard deviations and significant value were calculated. p-values < 0.05 were regarded as significant.

## Results and Discussion

### Hectolitre mass

The influences of different selenium concentrations on the hectolitre mass of rye malt are present in Figure 1.



**Figure 1. The influence of different selenium concentrations on hectolitre mass of rye malt**

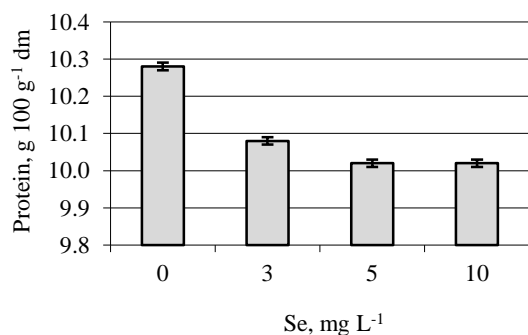
Analyzing obtained results we can see that significantly changes of rye malt hectolitre mass depends on selenium concentration in solution ( $p < 0.05$ ). The relative decreases for 2.2% of hectolitre mass in rye can be observed at selenium concentration in solution 10 mg L<sup>-1</sup> ( $p = 0.00$ ).

### Protein content

The obtained results have shown that content of protein in rye malt changes significantly ( $p < 0.05$ ) using for germination solutions with different selenium concentrations. These results are shown in Figure 2.

The content of protein in rye malt significantly decreases for 2.5% comparing with control sample using solution where selenium concentration was 5 and 10 mg L<sup>-1</sup> ( $p = 0.00$ ). Accordingly, if the concentration of selenium in solution was 3 mg L<sup>-1</sup> the decrease was 2% ( $p = 0.001$ ). The decrease of protein and starch content could be reason for the changes of hectolitre

mass and it shows the increase of proteolytic enzymes activity in rye malt.

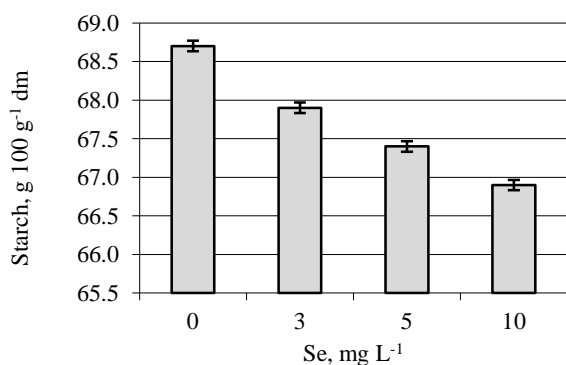


**Figure 2. The influence of different selenium concentrations on the content of protein in rye malt**

The results of research relate to Rakcejeva (2007) statement that the proteins were split by proteolytic enzymes, as a result of which the total protein content decreased.

#### Starch content

Starch is the major carbohydrate of ryes. The starch content is limited mainly to the endosperm, and contents between 57.1 and 65.6 g 100 g<sup>-1</sup> of dry matter (dm) are reported in rye grains (Hansen et al., 2004). Starch consists of a mixture of amylose (AM) and amylopectin (AP). Typical levels of AM and AP in cereal starches are 22–28% and 72–78% (Gomand et al., 2011). The changes of starch content in rye malt using solutions with different selenium concentrations are shown in Figure 3.



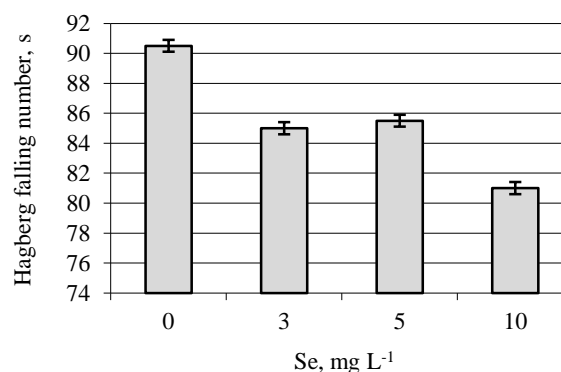
**Figure 3. The influence of different selenium concentrations on the content of starch in rye malt**

Significant differences in starch content were found in two analyzed samples ( $p < 0.05$ ) (Fig. 3). The obtained results showed that content of starch in rye malt depend on the selenium concentration. It decreases with increasing selenium concentration in solution. At selenium concentration 5 and 10 mg L<sup>-1</sup> the content of starch in rye malt relative decreases for 1.9% and 2.6% compared with control sample, but at selenium concentration in solution 3 mg L<sup>-1</sup> these changes were not so significant ( $p = 0.240$ ). These changes can be explained that the different selenium concentration

affect the activity of amylolytic enzymes as a result of which the total starch content decreased in analyzed samples.

#### Hagberg Falling number

The potential activity of  $\alpha$ -amylase in rye flour characterized Hagberg Falling Number (FN). The Hagberg Falling Number is an internationally recognized measure that allows the indirect determination of  $\alpha$ -amylase activity. FN is the major quality attribute of rye grain. FN low values reflect high  $\alpha$ -amylase levels causing the loaves of bread to be discoloured, sticky and of poor resilience and texture (Gaaloul et al., 2011). If the rye grain is harvested during the optimum time and not sprout-damaged normally has a FN in the range of 150 s, when weather conditions was dry and sunny the FN are 300 s and higher. The minimum FN requirement for intervention of rye in the EU was 100 s (Hansen et al., 2004).



**Figure 4. The influence of different selenium concentrations on the falling number of rye malt**

The influence of different selenium concentrations on the falling number of rye malt is shown in Figure 4. The obtained results have shown that all analyzed Se concentrations significantly promoted the decrease of rye malt falling number and the highest decreases was observed when selenium concentration was 10 mg L<sup>-1</sup> ( $p < 0.05$ ). In this case the falling number of rye malt decreases for 10.5% comparing with control sample. Results of present research show the different selenium concentration positive affects the activity of amylolytic enzymes and relative decreases the falling number.

#### Conclusions

The different selenium concentration in solutions affects the composition and of rye malt. The most significant change in rye malt was observed at selenium concentration in solution 10 mg L<sup>-1</sup>. The relative content of protein and starch decreases for 2.5% and 2.6% compared with control sample it gives evidence about that degradation. The degradation of protein and starch affects the hectolitre mass, the relative decreases of hectolitre mass was 2.2% at selenium concentration in solution 10 mg L<sup>-1</sup>. The Hagberg Falling Number decreases for 10.5% (selenium contraction in solution 10 mg L<sup>-1</sup>) that characterized the increase of amylase activity.

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### References

1. Bitterli C., Bañuelos G.S., Schulin R. (2010) Use of transfer factors to characterize uptake of selenium by plants. *Journal of Geochemical Exploration*, Vol. 107, p. 206–216.
2. Buchanon A.M., Nicholas E.M. (1980) Sprouting, alpha amylase and bread making quality. *Cereal Research Communication*, Vol. 8, p. 23–28.
3. Donkor O.N., Stojanovska L., Ginn P., Ashton J., Vasiljevic T. (2012) Germinated grains – Sources of bioactive compounds. *Food Chemistry*, Vol. 135, p. 950–959.
4. Dūma, M., Kārkliņa, D. (2006) Fortified wheat grains with microelement selenium. *In: International Scientific Conference Proceedings „Research for Rural Development 2006”, 17–20 May, Jelgava, Latvia*, p. 210–213
5. FAO, WHO (2001) Human vitamin and mineral requirements. *Report of a Joint FAO/WHO Expert Consultation*, Bangkok, Thailand, Food and Nutrition Division, FAO, Rome.
6. Gaaloul I., Riabi S., Ghorbel R. E. (2011) Implementation of ISO 22000 in cereal food industry “SMID” in Tunisia. *Food Control*, Vol. 22, p. 59–66.
7. Gomand S.V., Verwimp T., Goesart H., Delcour J.A. (2011) Structural and physicochemical characterisation of rye starch. *Carbohydrate Research*, Vol. 346, p. 2727–2735.
8. Hansen H. B., Møller B., Andersen S. B., Jørgensen J. R., Hansen A. (2004) Grain characteristics, chemical composition, and functional properties of rye (*Secale cereale* L.) as influenced by genotype and harvest year. *Agricultural and Food Chemistry*, Vol. 52, p. 2282–2291.
9. Katina K., Liukkonen K. H., Kaukovirta-Norja A., Adlercreutz H., Heinonen S.M., Lampi A. M., Pihlava J. M., Poutanen K. (2007) Fermentation-induced changes in the nutritional value of native or germinated rye. *Journal of Cereal Science*, Vol. 46, p. 348–355.
10. Kaukovirta-Norja A., Wilhelmson A., Poutanen K. (2004) Germination: a means to improve the functionality of oat. *Journal of Agricultural and Food Science*, Vol. 13, p. 100–112.
11. Kranter I., Colville L. (2011) Metals and seeds: Biochemical and molecular implications and their significance for seed germination. *Environmental and Experimental Botany*, Vol. 72, p. 93–105.
12. Kunkulberga D., Ruza A., Linina A., Galoburda R. (2007) Evaluation of wholegrain flour baking properties depending on variety. *Food Chemistry and Tehnology*, Vol. 41 (2), p. 24–29.
13. Luoto S., Jiang Z., Brinck O., Sontag-Strohma T., Kanerva P., Bruins M., Edens L., Salovaara H., Loponen J. (2012) Malt hydrolysates for gluten-free applications: Autolytic and praline endopeptidase assisted removal of prolamins from wheat, barley and rye. *Journal of Cereal Science*, Vol. 56, p. 504–509.
14. Rakcejeva T, Skudra L (2007) Biological value changes in grain during biological activation time. *LLU raksti, nr. 18 (313)*, p. 25–33.
15. Shtangeeva I., Steinnes E., Lierhagen S. (2011) Macronutrients and trace elements in rye and wheat: Similarities and differences in uptake and relationships between element. *Environmental and Experimental Botany*, Vol. 70, p. 259–265.
16. Siwela M., Taylor R.N., J. de Milliano A.W., Duodu K. G. (2010) Influence of phenolics in finger millet on grain and malt fungal load, and malt quality. *Food Chemistry*, Vol. 121, p. 443–449.
17. Waters B.M., Sankaran R.P. (2011) Moving micronutrients from the soil to the seeds: Genes and physiological processes from a biofortification perspective. *Plant Science*, Vol. 180, p. 562–574.
18. Zariņa L. (2012) Test weight of rye depending of crop rotation. [accessed on 01.02.2014.]. Available at : [http://stendeselekcija.lv/konference/jaunumi/data/augsuplades/files/2.%20Zarina\\_Test%20weight.pdf](http://stendeselekcija.lv/konference/jaunumi/data/augsuplades/files/2.%20Zarina_Test%20weight.pdf)