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ORIGINAL RESEARCH PAPER

THE USE OF FLUORIDE CONTAINING MINERAL WATER IN WORT PRODUCTION

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Abstract: The present work aims to study the quality of wort produced using fluoride containing mineral water. The results show that the mineral water has a negative impact on the enzymatic destruction of starch, proteins, color intensity and pH of the wort. The changes of pH during mashing process using tap and mineral water was studied. The lower acidity of wort obtained using mineral water didn't change during the brewing process. The fluoride content of beer is lower than 5 $mg.L^{-1}$ when wort is produced using mineral and tap water in 1:1 ratio and citric acid for pH correction. At the same time, the final degree of fermentation, α-amine nitrogen content and the intensity of color of produced wort are close to the control sample. The changes in fluoride ion concentration are monitored using ion-selective potentiometry. The fluoride content is decreased from 5.7 to 4.75 $mg.L^{-1}$, the most intense change is observed during the mashing process.

Keywords: *fluoride, mineral water, water hardness, wort*

INTRODUCTION

Water is a basic material for beer production being part of wort and of beer. In the most of cases, the quality of produced beer depends on the quality of water used in its production [1].
Humans obtain the fluoride mainly from their diet. All of the fluoride available in water reaches blood cycle. In contrast, between 50 and 80% of food fluoride is absorbed by human organism. About 50% of fluoride blood content takes part in bone and teeth formation. It is well known fact that 90% of body fluoride is found in the bones and the teeth [2].
Mineral waters contain more fluoride than surface or sea water. The fluoride content in tap water is less than 0.5 $mg.L^{-1}$; in the mineral water – it ranges from 5 to 25 $mg.L^{-1}$.
There are more than 225 mineral springs in Bulgaria. Most of hyperthermal water springs are situated along Struma and Mesta valleys and in the west part of the Rodopi Mountains. Usually the water is considered as mineral when its temperature in the spring is above 20 ºC and it contents various soluble substances at high concentrations. The chemical composition of mineral water determines its specific taste and therapeutic properties [3].
Fluorine is a halogen with a high chemical reactivity. The specific physicochemical properties of fluorine determine its biological activity. Its biological impact attracts more and more attention in the past years.
Acidity of fluoride containing mineral water usually is lower than the acidity of tap water most used in the beer production. The higher pH of mineral water causes some technological problems. It is well known fact that the water used in the brewing determines pH of mash, wort and beer [4 - 8].
The present work aims to study the effect of fluoride containing mineral water on the technological parameters and the quality of the wort produced in the brewing process.

MATERIALS AND METHODS

Fluoride containing mineral water from three springs in the Blagoevgrad region was analyzed. In the present work the springs are noted as springs 1 – 3.
The wort was produced from malt with 5.3% moisture; 78.7% of extract content; 12.6% proteins and 142 $mg.L^{-1}$ α-amine nitrogen. The saccharification time was 10-15 min, color was 3.5 EBC and viscosity 1.64 mPa.s.
Two sets of experiments were performed: 1) the control and the sample were produced using tap and mineral water, respectively; 2) the control is wort produced using tap water, but the samples (B_1 and B_2) were produced using citric acid as pH adjuster (pH = 5.4). The sample B_1 is produced using mineral water and sample B_2 - mixture of tap and mineral water in ratio 1:1. All mineral water used was from spring 2.
A single decoction method was used for mashing process (Figure 1). The water used during the sparing process was at the same composition as in the mashing.
The wort hopping was based on the α-bitter acids content of hop products (90 $mg.L^{-1}$). 70% of hop products were added 15 minutes and 30% - were added 45 minutes after the start of boiling process. The overall procedure continued 105 minutes.

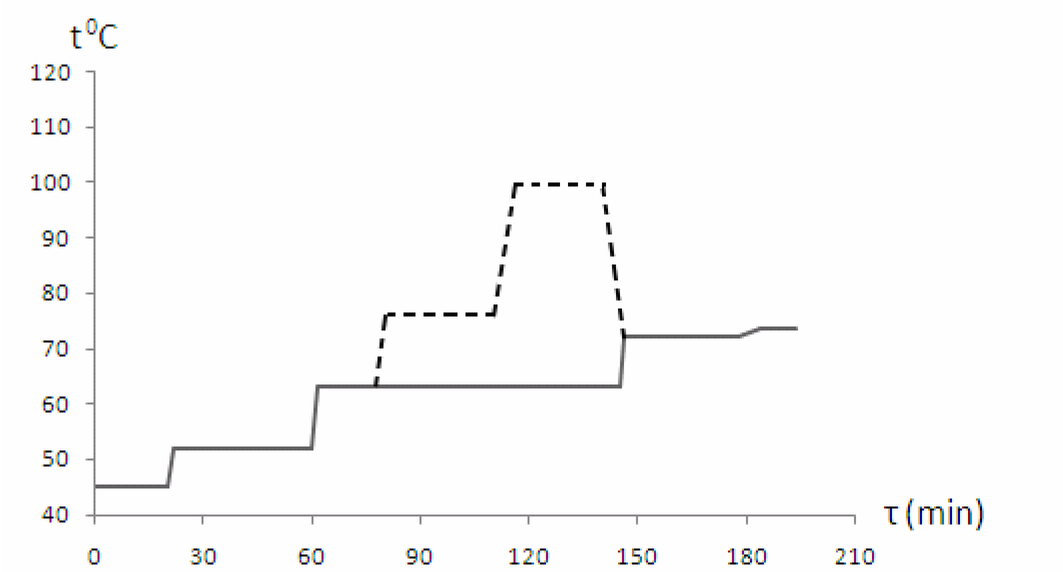

Figure 1. *Temperature change during single decoction mashing*

The standard analytical methods were used according to the European Brewing Convention and Bulgarian standards. The fluoride content was determined using ion-selective potentiometry based on standard addition method [9].

RESULTS AND DISCUSSION

The chemical composition of studied mineral waters is presented in Table 1. Total water hardness depends on the content of calcium and magnesium ions. The tap water from the region of Sofia and studied mineral water differed in a great extent in their calcium, magnesium and carbonate hardness. The carbonate hardness of tap water used as reference was much less than the hardness of studied mineral water (the mineral water from spring 2 had the most carbonate hardness). However, the magnesium and calcium hardness of mineral water was less than the hardness of tap water. Fluoride content in mineral water from Blagoevgrad region was between 9.0 and 11.5 mg L^{-1}, much higher than in tap water (0.3 mg L^{-1}).

If the acidity is concerned, the most suitable for brewing was tap water (pH about 7). The mineral water from the three studied springs was slightly alkaline (pH = 8.4 - 8.7). Hydrogen carbonates, calcium and magnesium had different effect on water acidity, respectively pH. The carbonate (especially hydrogen carbonates) slightly lowered the acidity, but the presence of calcium and magnesium ions had an opposite effect, twice more pronounced by calcium ion than by magnesium [5].

The residual alkali plays an important role in brewing. As results show the residual alkali in mineral water was higher than tap water. The residual alkali had a negative effect on wort and beer production influencing pH of mash and wort. The value of residual alkali is a criterion for rising pH-capacity of some ions on the water used. The lower was residual alkali of used water the lower was pH of the produced wort.

Table 1. *Chemical composition of used water*

Parameter	Tap water*	Mineral water		
		Spring 1	Spring 2**	Spring 3
pH	6.7	8.4	8.5	8.7
Calcium hardness, °H	1.0	1.0	0.1	0.1
Magnesium hardness, °H	1.4	0.2	0.2	0
Carbonate hardness, °H	2.6	7.0	13.0	4.5
Residual alkali	2.2	6.7	12.9	4.5
Ca^{2+}, $mg.L^{-1}$	14.4	12.8	2.0	1.6
Mg^{2+}, $mg.L^{-1}$	3.9	1.0	1.6	0
F^{-}, $mg\ L^{-1}$	0.3	11.1	11.5	9.0

* - control – Tap water
** - sample – mineral water from Spring 2

The mineral water chosen for this study had higher residual alkali and contented calcium and magnesium at lower concentrations, but fluoride ions at higher concentration.
The changes of pH during mashing process and their effect on physical-chemical characteristics of wort were studied. Figure 2 illustrates the changes of pH at different stages in wort production using tap and mineral water. As was mentioned above, the initial waters used in this study differed in their pH. Smaller difference in pH was observed after mixing the malt with water. The malt contained some salts of phosphoric acid, the most under the form of dihydrogen phosphates with acidic properties. Dihydrogen phosphates react with carbonates and hydrogen carbonates in water yielding hydrogen phosphate with slightly basic properties.
It is interesting fact that higher pH of mash obtained using mineral water didn't change during mashing process.

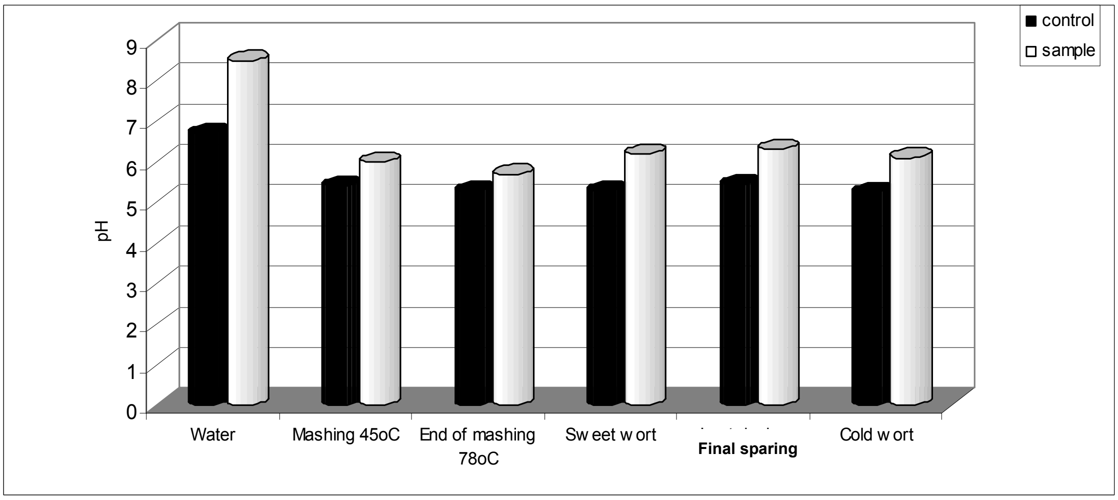

Figure 2. *pH variation during the mashing process*

It is well known that the brewing process is enhanced under slightly acidic conditions. The effect of pH on the mashing process and the wort composition is illustrated in Figure 3 and Table 2. The mash acidity is a crucial factor in biochemical mashing processes. The mashing is mainly based on biochemical degradation of starch by α- and β-amylase. The optimum pH range for α-amylase is 5.6 – 5.8 and for β- amylase is 5.4 – 5.6 [10, 11]. The higher value of pH during mashing process using mineral water hindered the activity of the enzymes and affected negatively the starch hydrolysis. The incomplete starch degradation lowered the final degree of fermentation. As the results show, the acidity of wort was a crucial factor for the activity of proteolytic enzymes. The proteolytic enzymes hydrolyze the malt proteins. The optimum enzymatic activity is at pH = 5.0 – 5.2 [10, 11].

Table 2. *Physical-chemical characteristics of the produced wort*

Parameter	Control	Sample
pH	5,20	6,10
Soluble nitrogen, $mg.L^{-1}$	88,1	79,6
Viscosity, mPa.s	1,72	1,71

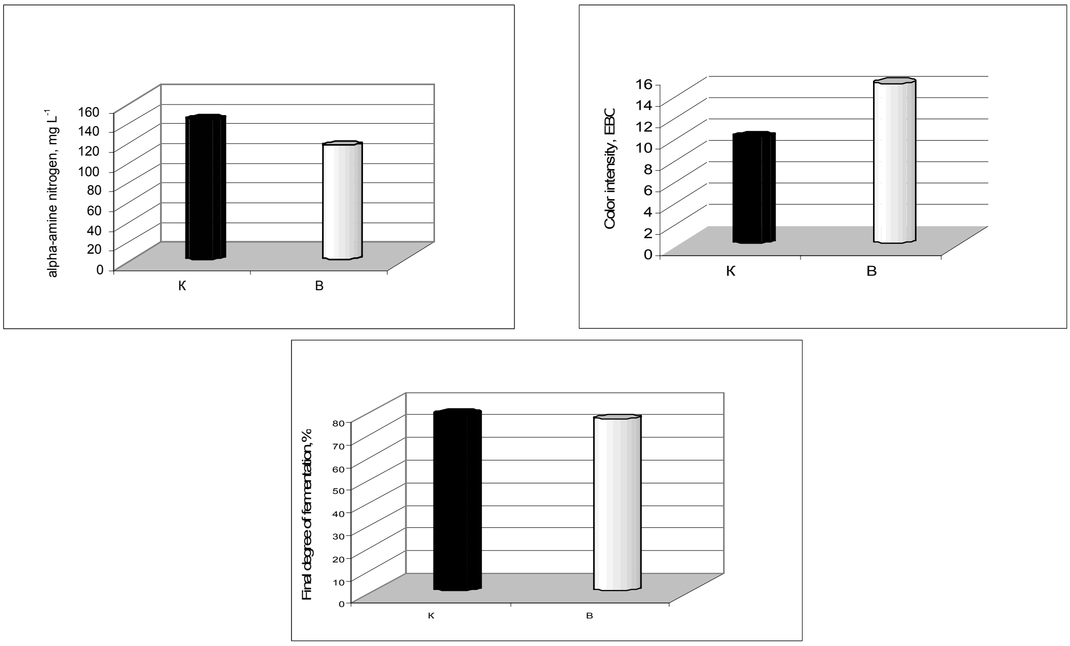

Figure 3. *Characteristics of the wort obtained using tap water (K) and mineral water (B)*

The higher pH of mineral water caused lowering of content of water soluble and α-amine nitrogen. The degree of protein degradation, described by ratio between different fractions of nitrogen-containing substances (low-, middle- and high-weight molecular), influenced important beer characteristics as taste, foam formation and stability, and colloidal stability. The low weight nitrogen-containing substances (amino-acids) are the main source of nitrogen for yeast influencing the fermentation processes and synthesis of the flavor active substances. This study shows that waters with high residual alkali hinder the proteolysis. The higher pH of the mash, sweet wort or sparing waters enhances the extraction of some undesirable substances such as polyphenols from malt flakes thus spoiling the color of wort and beer. The described process explains the higher color intensity of sample.

To summarize, the results show that the mineral water used during mashing process causes lowered quality of the wort. Some technological solutions for pH adjustment during brewing process have to be found.
Table 3 presents the results obtained after pH adjustment by adding citric acid to mineral water (experiment set 2). The “carbonate” water hardness is transformed into “citrate” hardness. The second type of water hardness is proved not to disturb the brewing process. The acidity of experimental worts was close to pH of the control. The pH of wort was adjusted as close as possible to the optimum acidity for amylolytic enzymes activity. As can be seen from Figure 4, the final degree of fermentation of sample B_2 is 1.8% higher than the control. The slightly increase of color intensity of samples B_1 and B_2 was observed (0.5 – 1 EBC) (Table 3).

Table 3. *Physical-chemical composition of the wort*

Parameters	Control	Samples	
		1	2
pH	5.25	5.30	5.14
Color intensity, EBC	8.0	9.0	8.5
Viscosity, mPa.s	1.72	1.71	1.71
Bitter compounds, BU.L^{-1}	24.6	26.5	25.8

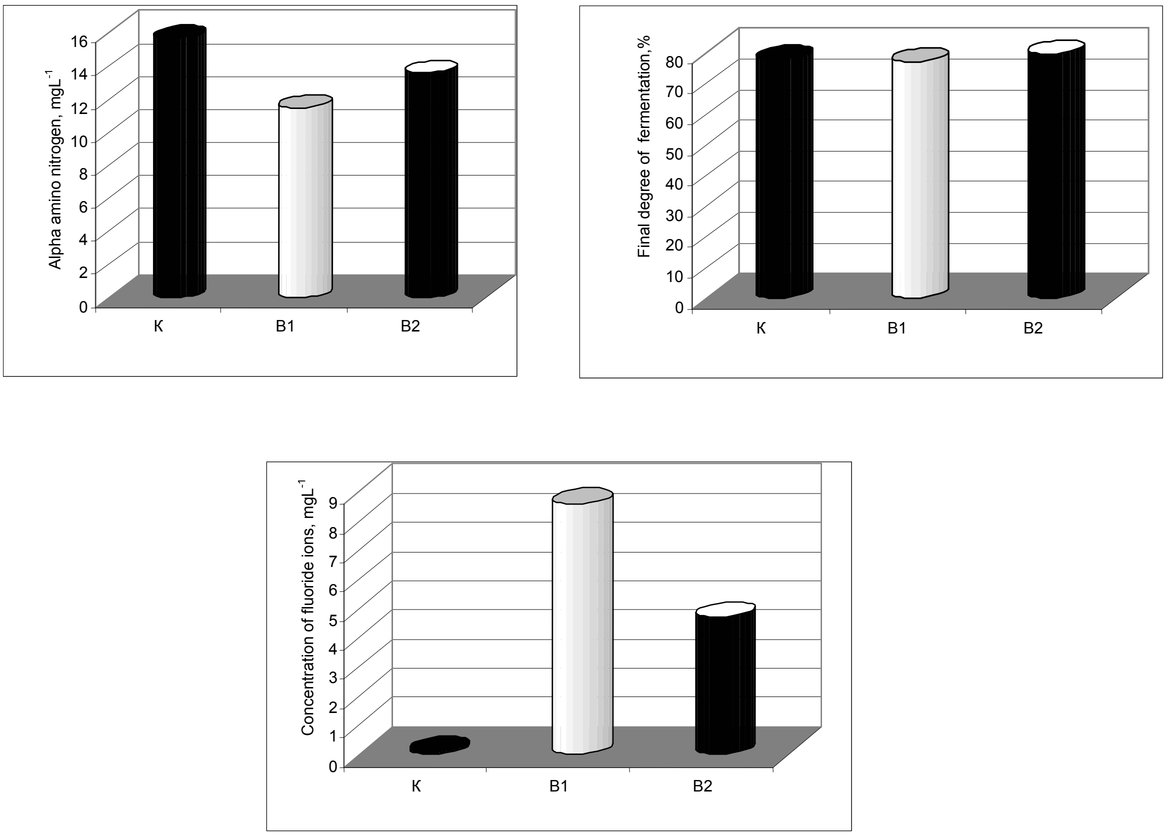

Figure 4. *Characteristics of the wort*
K – control (tap water); sample B_1 – 100% mineral water; sample B_2 – 50% mineral and 50% tap water; samples B_1 and B_2 – citric acid is used as pH adjuster

The α-amine nitrogen content in the sample wort was slightly lower than in the control (Figure 4). The solubility and isomerization of α-bitter acids were influenced mainly by two factors – pH and temperature. The isomerization of α-bitter acid depended crucially on the acidity of mineral water used. The pH adjustment using citric acid was applied. The pH of wort was 5.1 – 5.3. In such conditions the bitter acids are under colloidal form more than under molecular form.

The fluoride content was monitored during mashing, boiling and cooling of the wort. The fluoride concentration decreased by 22% in sample B_1 and by 12% in the sample B_2 (Figure 5). As results showed, the higher is the initial fluoride concentration in the water the more intense is fluoride decreasing during mashing process.

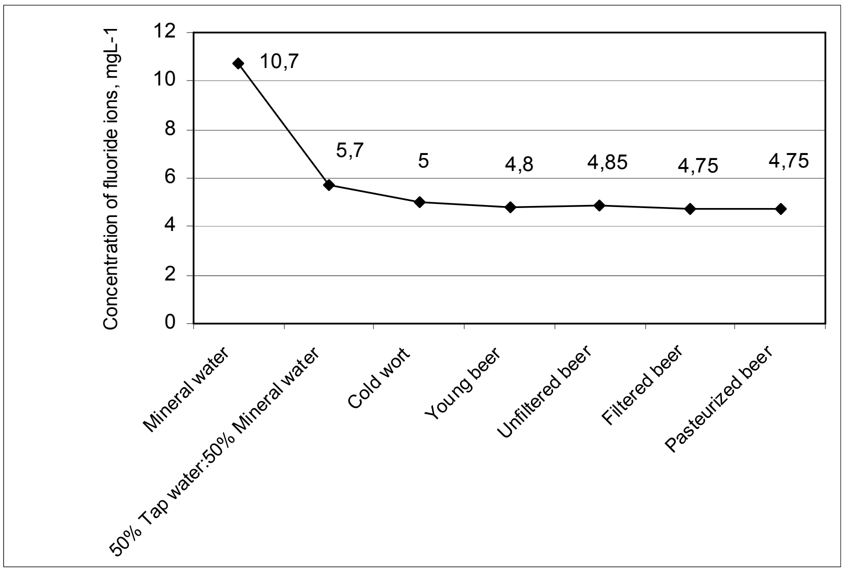

Figure 5. *Dynamics of changes of the concentration of fluoride ions during the brewing process*

CONCLUSIONS

The studied mineral waters from Blagoevgrad region contain carbonates and fluorides at higher concentrations than tap water. In contrast, the magnesium and calcium content is lower. Mineral water used during mashing process raised the alkality of the wort produced resulting in inefficiency of enzymatic degradation of starch and proteins. The technological solution proposed is pH adjustment of wort by citric acid. The results showed that the function of amylolytic and photolytic enzymes was enhanced. The best results were obtained using mixture of mineral and tap water in ratio 1:1. The fluoride concentration decreased from 5.7 to 4.75 $mg.L^{-1}$. The most intensively decrease was observed during mashing process. The final degree of fermentation, α-amine nitrogen and color intensity were close to the control.

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