Determination of Silicon in Czech Beer and its Balance During the Brewing Process

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ABSTRACT

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Inductively coupled plasma mass spectrometry was used for the determination of silicon in beer samples from the Czech market and in brewing raw materials and semiproducts. The content of silicon in barley malt depended on the barley variety and growing region. The goal was to establish silicon concentration in Czech beer and to find out which processes are the most significant in terms of silicon concentration in beer. The silicon concentration in Czech beer ranged from 16 mg/l to 113 mg/l depending especially on two factors. Firstly, the silicon content in beer increased as the original wort concentration and increased secondly, during decoction mashing, silicon from malt was leached to a much greater extent than in the case of infusion mashing.

Keywords: silicon; beer; wort; brewing; malt; hop; ICP-MS

Silicon is an important essential trace element in human nutrition. The recommended daily intake is about 10–25 mg (Nielsen 2000; Powell *et al*. 2005). Silicon deficiency is mostly associated with losses of connective tissue components, such as glycosaminoglycanes, collagen, and elastin. The most readily absorbable form of silicon is orthosilicic acid (H_4SiO_4) (Sripanyakorn *et al*. 2004, 2005).

Foods derived from plants rather than from animals provide the highest sources of dietary silicon, because certain plants, especially cereals, are silicon accumulators. (Pennington 1991; Powell *et al*. 2005). In particular, high levels of bioavailable silicon are found in beer, which is made from barley malt, from which orthosilicic acid is released into beer (Sripanyakorn *et al*. 2004). Barley grain and consequently barley malt are rich silicon sources, whereas the most of silicon (more than 80%) is located in the husks. Grain silicon content is in the range of 0 (under detection – by hull-less varieties) to 3800 mg/kg (Ma *et al*. 2003). For brewing purposes, silicon-richer hulled grains are used and barley malt is considered to be a major source of silicon in beer (Walker *et al*. 2008; Casey & Bamforth 2010).

Silicon concentration in beer has been measured by several authors (Mojsiewicz-Pieńkowska & Łukasiak 2003; Walker 2003; Sripanyakorn *et al*. 2004; Casey & Bamforth 2010). The measured concentrations were almost without any exception in the range of 20–50 mg/l.

This paper deals with the determination of silicon content in beers from the Czech market, whereas most of the surveyed brands were of Czech origin. Further, considerable attention is paid to how the

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brewing process itself influences the final silicon concentration in beer, and how the silicon concentration changes in the course of brewing. Also, infusion and decoction mashings are compared in terms of silicon concentration. All analyses were performed by inductively coupled plasma mass spectrometry (ICP-MS).

MATERIAL AND METHODS

Beer samples for analysis. Forty commercially available beer brands were purchased at local market and analysed for silicon contents. Three of them were imported beers. The individual beer types are specified in the subsection of Results and Discussion called Silicon content in Czech beer.

Preparation of sweet worts. Fourteen sweet worts were prepared under laboratory conditions (Basařová *et al.* 1992). Sweet worts were prepared using malts prepared from different barley varieties. Seven barley varieties from the region Kroměříž and the same seven varieties from the region Žabčice were available. All the malts were prepared in the same way according to the method described by Psota *et al.* (2011).

Wort boiling simulation. Hop pellets made from the cv. Magnum were used in the experiments. The method described by Basařová *et al.* (1993) was used only with the buffer being replaced by a pale or dark wort. One gram of pellets and 300 ml of wort were used. Both worts were prepared from corresponding hopped wort concentrates, produced by the Research Institute of Brewing and Malting, Public Limited Company, so that the original wort concentration was 11% (w/w). The wort for the concentrate was prepared by the classical two-mash method and then concentrated and dried.

Trial brewing. Two trial brews were prepared in a brewing pilot plant at the Department of Biotechnology, Institute of Chemical Technology Prague, Czech Republic.The first brew was prepared using an infusion mashing method, and the second was made by brewing with the use of a decoction mashing method (double mashing). In both cases, the same raw materials in identical quantities were used. Raw materials and their quantities used for brewing are summarised in Table 1. The infusion method was realised by mashing-in in 40 l of brewing water at 37°C for 10 min, after which the temperature was increased at a rate of 1°C/min to 50, 64, and 74°C, whereas the temperature was held for 10 min at each of these temperatures. Then, after reaching the final mash temperature (77°C), the mash was transported into the lauter tun. In the case of decoction, mashing-in was carried out in 38 l of brewing water at 37°C for 30 minutes. Then, 2 l of hot water were added and the temperature was raised to 50°C. After 15 min of mashing, before adding the hot water the first mash (19 l) was transferred to the mash cooker and heated up to 64 and 74°C (at a rate of 1°C/min). The temperature was held for 10 min at both temperatures. After this, the mash was brought to boiling (at a rate of 1.5°C/min), boiled for 20 min, and returned back into the mash tun where the temperature increased from 50°C to 64°C. Immediately, the second mash (19 l) was transferred and warmed (at a rate of 1°C/min) to 74°C, held 10 min at this temperature, then brought to boiling and boiled for 15 minutes. After returning it back to the mash tun, the final mash temperature (77°C) was set up and the mash was transported into the lauter tun.

Table 1. Raw materials for beer brewing

Malt	Hops – cv. Magnum (pellets)	
	type	amount (g)
Pilsner malt (5000 g)	1st hop addition (at the beginning of boiling)	15
	2nd hop addition (after 30 min of boiling)	15
	3rd hop addition (10 min before the end of boiling)	6

The next steps were identical for both brews. After 30 min of rest (mash settling), the lautering was started. The total volume of the sweet wort gained was 35 l. Subsequent wort boiling took 90 minutes. The hopped wort was then cooled down to the fermentation temperature and after the trub separation, 200 ml of yeast were added into the remaining 30 l of wort. The main fermentation was carried out in open glass vats at 8–10°C for 6 days. The maturation took place in closed PET bottles at 1–2°C for 14 days.

The original wort concentrations of the worts prepared using the infusion and decoction mashing were 10.2 and 10.6%, respectively. The following intermediates were sampled: brewing liquor (water), sweet wort, hopped wort, and beer.

Silicon determination. The determination of silicon was performed using the ICP-MS technique (spectrometer Elan DRC-e; Perkin-Elmer, Concord, Canada). The most abundant isotope ^{28}Si was used for the measurement while rhodium served as the internal standard. Before the measurement, the samples were diluted (0.5–1 ml of sample was pipetted into 50 ml plastic volumetric flask) with 0.28 mol/l HNO_3 solution (Suprapur®; Merck, Darmstad, Germany) and spiked with rhodium solution to obtain the final concentration of 500 µg/l Rh. Calibration solutions (0, 0.5, 1.0 and 2.0 mg/l Si respectively) were prepared by the dilution of the stock solution 1 000 mg/l (Analytika Prague, Ltd., Prague, Czech Republic) and were also spiked with the internal standard.

Note: The expanded combined uncertainty for all results was ± 7% of the measured value.

RESULTS AND DISCUSSION

Silicon concentration in Czech beer

The data are collated according to the type of beer. For each group the mean concentration, range of concentrations, and number of samples (*N*) are mentioned. For comparison, three imported beer brands were also analysed (Table 2).

Silicon concentration values are higher than those found in the previous literature (Mojsiewicz-Pieńkowska & Łukasiak 2003; Walker 2003; Sripanyakorn *et al.* 2004; Casey & Bamforth 2010). Silicon concentration was influenced by the raw materials used and their quantity. The beers brewed solely from barley malt without the addition of other malts or adjuncts were richer silicon sources than the other beers. Barley is a richer source of silicon than wheat (Casey & Bamforth 2010), which explains the lower (but still high) silicon concentration in the wheat-based beer. Of course, the original gravity must be taken into account. Higher original gravity means more raw materials used and thus a higher silicon content. Nevertheless, the silicon concentration in beer is generally influenced by the brewing technology. There were two top fermented beers among the analysed samples (one wheat-based beer and one ale). The former had a lower silicon content than the latter, however, their silicon contents were not significantly different from the lagers.

Table 3 compares the individual beer types using Student's t-test at a level of significance of $P = 0.05$. Non-alcoholic beers had significantly lower silicon concentrations than other beers due to their low original gravities. Similarly, silicon concentrations in special beers and imported lager beers, but not in lager beers, were significantly higher than those in light lager beers. However, the differences between silicon concentrations in lager beers, special beers, and imported lager beers were insignificant.

Table 2. Silicon concentration in commercial beers

Beer category	Si mean (mg/l)	Range (mg/l)	*N*
Non-alcoholic	19.5	16.3–21.5	3
Light lager	43.5	27.5–66.3	14
Lager	50.4	41.5–69.2	13
Special	63.0	40.8–113.0	5
Ale	55.2	–	1
Wheat	44.0	–	1
Imported lager	63.1	53.8–70.1	3

N – number of samples

Silicon concentration in sweet wort

Barley malt is a major silicon source in beer (Walker *et al.* 2008; Casey & Bamforth 2010). The aim of this part was to find out how the silicon concentrations in sweet wort and in beer depend on various barley cultivars used for their preparation. The Figure 1 shows the impact of the individual barley cultivars from two regions (Kroměříž and Žabčice). Barley cultivar plays a significant role in the silicon concentration of sweet wort (Figure 1). It is evident that the cultivars from the region Žabčice were slightly richer silicon sources than those from the Kroměříž region. This can be explained by divergent environmental conditions (mainly by

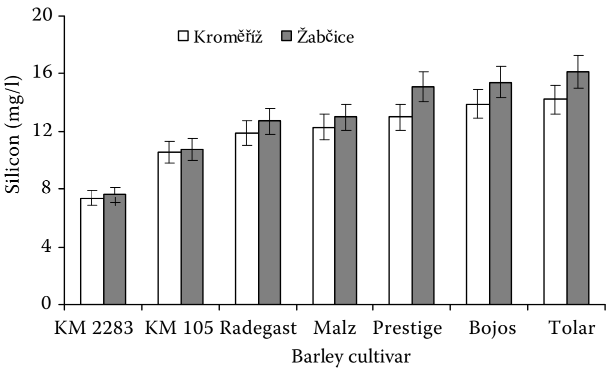

Figure 1. Silicon concentration in sweet worts made from malts of various barley varieties from two growing regions

Table 3. Comparison of individual beer types on the basis of Student's *t*-test

Beer category	Beers				
	non-alcoholic	light lager	lager	special	imported lager
Non-alcoholic	+				
Light lager	–	+			
Lager	–	+	+		
Special	–	–	+	+	
Imported lager	–	–	+	+	+

+ $P \geq 0.05$; – $P < 0.05$

different soil types). However, the varietal variation was more crucial than the environmental factors. The lowest silicon concentrations were found in sweet worts made from hull-less cultivars (KM 2283 and KM 1057), because the hull is the part of grain where silicon is accumulated (Ma *et al.* 2003; Sripanyakorn *et al.* 2004).

Effect of wort boiling on silicon concentration in wort

Hops contain high levels of silicon (about four times more than malt). However, hops are used in much smaller quantities than malts. Highly hopped beers, however, are expected to contain higher silicon levels. On the other hand, a higher amount of silicon is removed with the precipitate (trub) formed during wort boiling than is that which enters with the hops (Casey & Bamforth 2010). To determine how the wort boiling influences the wort silicon content, its concentrations before and after boiling were measured (Figure 2). During the boiling of both solutions, a vapor condenser was used, so that the silicon concentration could not be affected by vaporisation.

In both cases, a slight decrease of silicon content occurred. The silicon loss is probably caused by the already mentioned binding of silicon compounds to the precipitate particles which are subsequently separated from the wort. The loss of silicon was 11% in the pale wort and 6% in the dark wort.

Impact of mashing type on the silicon concentration in beer

In this part, the impacts of infusion and decoction mashings were compared. The progression of silicon content during the whole brewing process can be tracked (Figure 3).

From Figure 3 it is obvious that barley malt was a main silicon source in beer, regardless of the mashing method used, but it is also evident that the overall silicon concentration in beer highly depends on the respective mashing method. Higher beer silicon contents can be attarently achieved only by the application of decoction mashing, which is

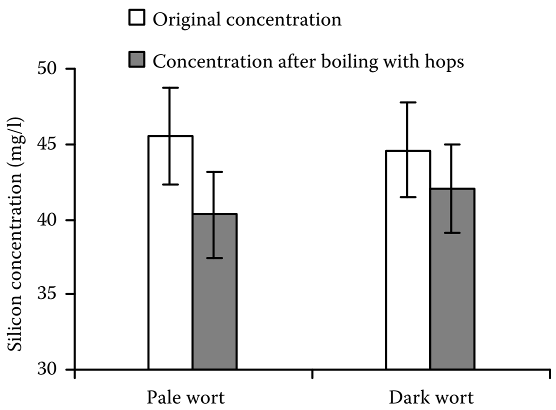

Figure 2. Effect of boiling with hops on wort silicon concentration

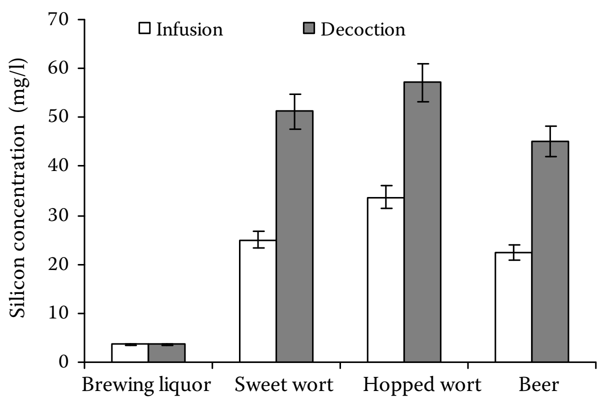

Figure 3. Changes of silicon concentration during the brewing process

a more intensive way of mashing in comparison with infusion mashing. In the case of decoction, where the silicon content in wort was almost twofold, not only does the mashing last longer but the mashes are also boiled during the process. These facts contribute to the intensification of the mass transfer. Therefore, it can be concluded that the traditional decoction mashing method is also favourable in the view of the silicon concentration in beer.

Next findings were common for both brewing procedures. The brewing liquor as a silicon source was insignificant. Of course, there are some water supplies with a high silicon content (Giammarioli *et al.* 2005), but these are not usually used for brewing purposes. It was also examined, how silicon from the barley malt passes into the forming sweet wort. It was realised that the highest amounts of silicon were leached during the mashing process and the initial phase of sparging. Silicon leaching rapidly falls away as sparging continues as the washed husks become depleted of dissolvable silicon (Walker *et al.* 2008).

Wort silicon contents were in both cases higher than the respective sweet wort silicon contents. That is seemingly in contrast with the previous statement, that the stage of wort boiling inflicts the solution silicon loss. However, the increase in silicon concentration was caused by solution thickening as water evaporated in the course of wort boiling. To establish how the hops influence silicon concentration, wort samples were analysed after 15 min of boiling. There is no significant vaporisation yet and, in addition, coagulation and thus binding of silicon to the forming trub is unlikely in this early phase, so these factors can not affect the silicon concentration. The silicon concentrations in these samples almost did not differ from those in the original sweet worts. Therefore, it was concluded that hops are not of particular significance when discussing the origin of silicon in beer.

Silicon concentrations in beer were lower than those in the cold wort. The loss of the dissolved silicon was ascribed to its sorption on yeast and other solid particles which are then removed during the filtration process. There is a mild disagreement with former literature. Either fermentation did not influence the concentration (Walker *et al.* 2008) or only a slight decrease showed up (Casey & Bamforth 2010). However, it is important to note that the brewing procedures used by these authors, especially the courses of fermentation, were significantly dissimilar from the typical Czech production. In the first event, the sweet wort was fermented at 18°C for 6 days and in the second case, a wort with 15 bitterness units was prepared and fermented at 20°C for 12 days. Thus, the fermentation conditions could play a considerable role in the binding of silicon compounds to solid particles of the fermented wort.

CONCLUSIONS

The silicon concentrations in Czech and foreign beers were comparable and depended on the raw materials used, their quantities, and brewing technology. The silicon content in beer increased as the original wort concentration increased. However, the silicon contents can differ strongly between the individual barley varieties. Very important was the mashing type used. It was realised that during the decoction mashing silicon was leached to a greater extent than in the case of the infusion mashing. After wort boiling, silicon concentration was even higher due to water evaporation. Within the further processing steps, especially during the fermentation, the silicon content decreased (because of the sorption of silicon on yeast and other solid particles) and the silicon concentration in beer is, consequently, about halved in comparison with that in the wort.

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