Is barley malt safe as a food ingredient?

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Introduction

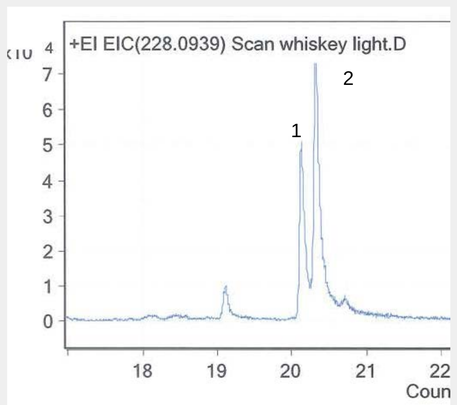
Todays increased focus on sustainability require increased focus on the safety of the products in use. Barley malt is used for beer and whisky production and the spent grain by-products from brewing makes up to 85 % of brewers total by-products. Spent grain has previously been used mainly for animal feed and recently the high nutritive value has made it feasible as bread flour supplement [1] and therefore human food.

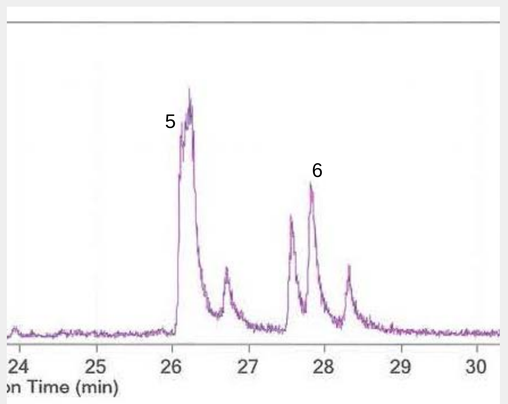
Process contamination such as the genotoxic acrylamide formed due to Maillard reactions between reducing sugars and amino acids at raised temperature could appear during drying of the malt. Previously, acrylamide has been detected among others in potato products, coffee and bread [2].

The use of smoked barley malt for enhanced flavours for certain beer and whisky types may increase the content of carcinogenic process contaminants in the by-products. Carcinogenic polycyclic aromatic hydrocarbons (PAH) are such process contaminants previously identified in e.g. smoked fish [3]. Germinated barley is smoke treated and for many whisky malt dried over peat-fuelled furnace for flavour addition probably with increased health risks for spent grain consumers as a result. To evaluate our concern we studied different barley malt types.

Table 1. Analysed malt types divided into processing techniques with obtained values for content of fat (%) dry matter (%), sum of PAH 4 (µg/kg) and Acrylamide (µg/kg). N.d. not detected, - not relevant.

Process	Malt	Fat (%)	Dry matter (%)	PAH 4 (µg/kg)	Acrylamide (µg/kg)
	Raw barley malt	1.5	90.7	n.d.	n.d.
Dried	Barley malt 1	2.4	95.9	n.d.	< 5.0
	Barley malt 2	2.0	93.5	n.d.	< 5.0
	Wey	2.3	96.1	n.d.	16
	Caramunch	2.8	94.1	n.d.	126
	Carafa O	3.4	96.4	n.d.	86
	Munch black	4.5	94.9	n.d.	33
Smoked	Barley malt 2 (Smouldering beech)	2.3	93.3	0.12	10
	Wey (Smouldering beech)	2.4	95.7	0.12	6.2
	Peated (Peat smoked)	1.8	94.8	15.0	25
	Whisky light (Peat smoked)	1.6	94.7	24.2	29
	Whisky (Peat smoked)	2.2	96.2	68.8	63
Recovery	Added standards	-	-	81.6 %	100.1 %





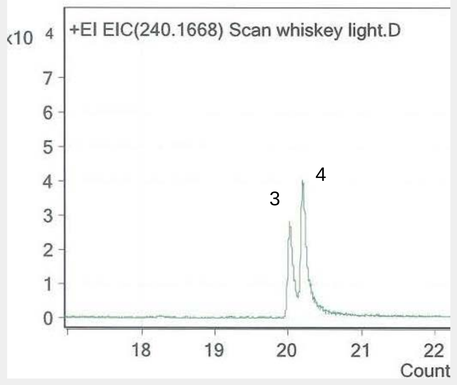


Figure 2 Whisky light chromatogram of at the top m/z = 228, namely benz[*a*]anthracene (1) and chrysene (2) and m/z =240, namely benz[*a*]anthracene D12 (3) and chrysene D12 (4) at the bottom

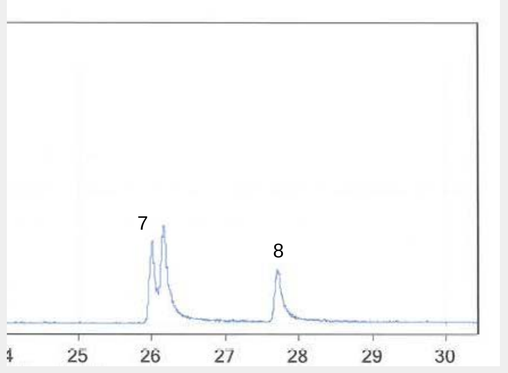


Figure 3. Whisky light chromatogram of m/z = 252 at the top, namely benzo[*b*]fluoranthene (5) and benzo[*a*]pyrene (6) and m/z = 264 with benzo[*b*]fluoranthene D12 (7) and benzo[*a*]pyrene D12 (8) at the lower part

Results and Discussion

Figure 1. Samples of malt : Munch black (1), Caramunch (2), Wey (3), Whisky (4) and Raw Barley (5).

For PAH we focused on four marker PAH (PAH 4), namely the sum of benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene and benzo[*a*]pyrene proposed by the Scientific Contamination panel at EU in 2008 [4]. Dried malt did not contain detectable levels of PAH 4, whereas smoked malt levels were found to depend on the smoke source used (table 1). Highest PAH 4 levels were found in peat smoked malts. For European citizens the daily intake of PAH 4 is approx. 1200 ng/day for all foods [4] corresponding to the dietary intake of 20 g peat smoked whisky malt per day.

Highest acrylamide levels was as expected found in a medium roasted malt (Caramunch) with second highest levels in chocolate based malt (table 1). Average acrylamide levels were 40 µg/kg, slightly lower than the Swedish reported levels for bread [2]. Full substitution of flour with spent grain is therefore expected to increase the total dietary intake of acrylamide with approx. 10 %.

Use of spent grains for beer snacks, is due to heat addition expected to increase the acrylamide level, whereas the PAH 4 level is expected to be unchanged. Analysis of the actual by-products is relevant for further risk assessment of the products.

Materials and methods

For PAH 4 analysis 5 g homogenised malt sample (grinded samles of malt from figure 1) were mixed with 10 g polyacrylic acid and 10 g Ottawa sand (dried at 450 °C) and added to a 66ml stainless steel cell together with isotopic internal standards [3]. Samples were extracted by PLE using acetone:hexane (1:1, v:v) with 2 cycles at 100°C [3]. Clean-up by first GPC (Bio-beads S-X3) followed by Silica based SPE (500mg) [3] was followed by GC separation by 2 times 15m DB-5MS with Q-TOF MS detection. Chromatograms are found in figure 2 and 3.

For acrylamide, 3 g homogenised samples were extracted with Milli-Q water on ultra thurrax followed by SPE (multimode) clean-up. Acrylamide were separated by LC on a Hypercarb column with tandem mass spectrometric detection (MRM mode) [5].

Gravimetric fat determination of PLE extracted malts dried at 70°C and gravimetric dry matter determination of malt samples at 102°C were done.

Conclusions

- Peat smoked malt should have limited use in human food products due to their content of PAH 4
- Acrylamide dietary intake levels will increase due to use of malt in bread flour
- For further risk evaluation controlled smoke experiments and analysis of the actual spent grain by-product should be performed

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