Analysis of NDMA (N-nitrosodimethyl-amine) in malt for beer and whisky production

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Figure 2: Traditional direct fired floor kiln (capacity ~ 20 t)

Figure 3: Modern indirect fired kiln (capacity ~ 200 t)

Barley for malting

NDMA sources

Exposure to N-nitrosodimethyl-amine (NDMA) can come from many directions – the environment, the workplace, the food and drink we consume. Some of the primary sources of exposure are tobacco (smoked and chewed), cured meats (particularly bacon), some cheeses, fish, toiletries and cosmetics (e.g. shampoos and cleansers) and combustion gases such as traffic fumes. Workplace exposure can occur in industries such as pesticides and rubber products manufacturing, fish processing and tanning. NDMA has been found in groundwater samples. It is naturally present in the stomach from digestion of some foods.

Effects of NDMA on human health

Laboratory studies on animals have demonstrated that NDMA is carcinogenic and it is possible that induction of tumours involves interaction with genetic material. As the metabolism of NDMA appears to be similar in humans to that in animals it is considered highly likely that NDMA is also carcinogenic to humans. In common with N-nitroso compounds in general, NDMA is known to be harmful to the livers of animals and humans.

NDMA in beer and whisky

Not too long ago beer and whisky could have been considered potential primary sources of NDMA but the risk is now minimal because of changes made in the production of one of the key ingredients viz: malt. Following a study in Germany in the 1970s [1] it was established that a significant source of NDMA in beer was from the malt used for brewing and the malting industry was summarily challenged to reduce levels to as low as practically possible in as short a time as possible.

Formation of NDMA

NDMA in malt is formed during the kilning process if oxides of nitrogen (NO_x), principally N_2O_3 and N_2O_4 from fuel combustion, come into contact with the malt in the early stages of drying. Although there are several possible routes to NDMA formation, it appears that nitrosation of hordenine is the principal one [2]. Hordenine, a protein breakdown product formed during the germination stage of malting, is nitrosated by N_2O_3 and N_2O_4 and, as kilning proceeds and the temperature rises, so the nitrosated hordenine breaks down to form dimethylamine (DMA) which is then further nitrosated to form NDMA. A simplified pathway is shown in Figure 1.

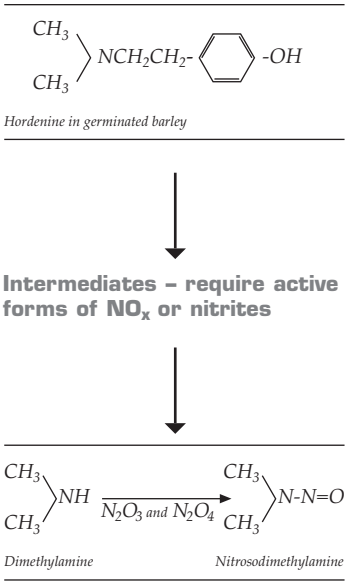

Figure 1

Concentrations of NDMA in malt and beer

Traditionally malt kilns (Figure 2) were direct fired i.e. the products of combustion from the fuel used to heat the air for drying passed directly through the grain bed. NDMA formation was therefore likely to have been a normal part of the process of malting, but its presence was probably not known about and so not a cause for concern. However, with increasing awareness of potentially harmful substances in the food chain and improvements in analytical equipment and techniques, NDMA in malt was identified as a problem. Although palliative treatments like reducing the pH at the surface of the grain during kilning by burning sulphur in the air stream offered a short term solution, indirect firing was seen as the ultimate answer. In indirect firing the hot air carrying the products of combustion from the heating fuel passes to exhaust through a heat exchanger which heats incoming, clean, ambient air to dry the malt. Major investment in indirect fired kilns (Figure 3) in malting companies around the world was set in train and now the ability to obtain NDMA levels in malt of around 1 µg/kg is commonplace; previously some levels had been recorded in the low hundreds. In the few remaining malting plants where direct fired kilns are still in operation the installation of low NO_x burners and/or palliative sulphur burning in the early stages of kilning provides almost equivalent control of NDMA formation, thus enabling maltsters to continue to meet the very tight specifications set by brewers and distillers.

Control of NDMA

Very low levels of NDMA in malt are now being consistently achieved and these levels are diluted a further 10-fold during the brewing of beer. Nevertheless, there remains a duty of care to all those who drink malt based beverages to ensure that the potentially harmful effects of NDMA are kept to an absolute minimum. To that end the monitoring of NDMA levels in malt continues to be necessary.

Analysis of NDMA at Crisp Malting Group

Previously a Thermal Energy Analyser was used to determine levels of NDMA in malt samples, but replacement with GCMS-QP2010 in early 2004 has proved very successful. Since that time hundreds of samples have been routinely analysed without problems and excellent correlation with laboratories using Thermal Energy Analysers has been achieved. Figure 4 shows the chromatogram of a malt sample with a concentration of 0.75 ppb (µg/kg). Details of the method are given below.

NDMA in malt: method details

Malted barley is blended with water in a homogeniser/blender and subsequently filtered through a Whatman No. 54 filter paper. NDPA internal standard and sodium chloride are added to the filtrate. After liquid/liquid extraction with DCM (dichloromethane) the DCM phase is dried with anhydrous sodium sulphate, filtered and evaporated in a water bath at 55 °C to about 1 mL. The cooled DCM phase is transferred to a GCMS vial and ready for injection.

GC-MS conditions:

Column: Stabilwax, 30 metres, 0.25 mm ID, 0.5 µm film thickness
Oven temperature: 50 °C for 1 min, then 20 °C/min to 175 °C holding at 175 °C for 1 min, then 40 °C/min to 250 °C holding at 250 °C for 10 min.

Injection port temperature:
240 °C

Interface temperature:
250 °C

Ion source temperature:
200 °C

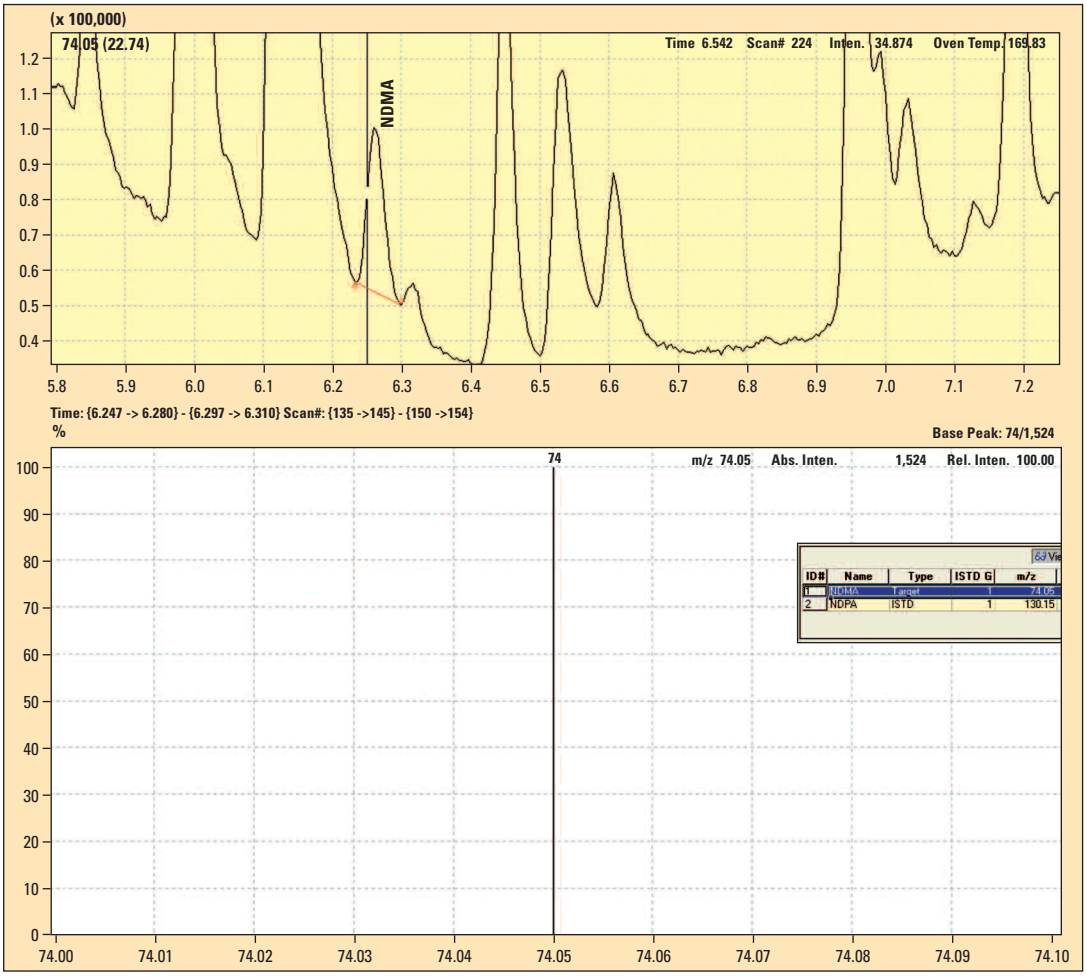

Figure 4: Chromatogram of NDMA

References:

[1] Nitrosamines in Malt and Beer; Wainwright, T., J. Inst. Brew., 1986, Vol 92, pp 73-80

[2] The Chemistry of Nitrosamine Formation: Relevance to Malting and Brewing; Wainwright, T., J. Inst. Brew., 1986, Vol. 92, pp 49-64