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Published in: Czech Journal of Food Sciences

Link to article, DOI: 10.17221/341/2013-CJFS

Publication date: 2014

Document Version Publisher's PDF, also known as Version of record

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Furan and Alkylated Furans in Heat Processed Food, Including Home Cooked Products

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Abstract


The occurrence of furan in home cooked food was studied. Cooking was found to reduce the level of furan in ready-to-eat foods, however on average around 50% of furan remain in the foods. The analysis of furan occurrence revealed that it is most commonly formed in foods with high levels of carbohydrates. Interestingly, breakfast cereals, dry bread products, and dried fruit products including raisins, plums and bananas contained furan at levels up to 387 µg/kg. Furan was also found in the dry ingredients of cookies and bread, and in snacks such as crisps and popcorn. The 2-alkylfurans, 2-methylfuran, 2,5-dimethylfuran, 2-ethylfuran, and 2-pentylfuran were present at levels in the same range as furan (885 µg/kg) and the level of 2-methylfuran (1328 µg/kg) exceeded this level in coffee.

Keywords: breakfast cereals; coffee; crisps; 2,5-dimethylfuran; ready-to-eat products; dried fruit

Furan has been identified in a number of food products (Maga 1979), especially in jarred and canned food items that undergo heat treatment within a sealed container. Furthermore, furan has been detected in food items such as meats, beer and nuts (FDA 2004). Since in their report on furan in food the European Food Safety Authority (EFSA) suggested that the carcinogenicity of furan is probably attributable to a genotoxic mechanism (EFSA 2005, 2011a), much research has focused on the formation of furan in foods. In addition, the EFSA has reported concern over the genotoxicity of 2-alkylfurans (EFSA 2011b). The diversity of foods which contain furan suggests that multiple pathways are likely to be involved in the formation of furan in foods (Morehouse et al. 2007; Owczarek-Fendor et al. 2011; Van Lancker 2011). Studies performed in model systems have shown that furan and methylfuran can be generated from heating ascorbic acid, polyunsaturated fatty acids, unsaturated aldehydes, sugars, and amino acids (Perez & Yalayan 2004; Becalski & Slaman 2005; Crews et al. 2007; Limacher et al. 2007; Limacher 2008; Roberts et al. 2008; Vranová & Ciesarová 2009; Owczarek-Fendor et al. 2010a,b, 2012; Adams et al. 2011; Duan & Barringer 2012; Anese & Suman 2013).

In addition to heat processing during manufacturing, it has been shown that home cooking by the consumer also affects the amount of furan in food products (Roberts et al. 2008). As expected from its low boiling point, furan concentration significantly decreases when food products are heated (EFSA 2005). Furan volatilisation during heating strongly depends on the food matrix. In particular, lipophilic compounds, such as oils, cause significant retention of furan. This issue may explain the occurrence of furan not only in sealed container products but also in low moisture starchy products (Van Lancker et al. 2009). This suggests that furan will be generated by several mechanisms in foods processed at high temperatures, and its formation is influenced by the effect of several extrinsic factors. The present study determines the influence of different food preparation and reheating procedures on the occurrence of furan in a range of home cooked foods. Furthermore, the levels of 2-alkylfurans, compounds which may
be formed during the preparation process or added to the food as flavouring substances, is investigated in canned food and coffee.

**MATERIAL AND METHODS**

**Chemicals.** Furan, 2-methylfuran, 2-ethylfuran, and 2,5-dimethylfuran (> 99%) were purchased from Sigma-Aldrich (Steinheim, Germany); 2-pentylfuran from Alfa Aesar (Karlsruhe, Germany); $d_4$-furan (98 atom% D) from Isotec (Ohio, USA); methanol from Rathburn (Walkerburn, Scotland), and NaCl from Merck (Darmstadt, Germany).

**Selection of ready-to-eat products and recipes of the home cooked meals.** Recipes which contain ingredients with the potential to form furan by heat treatment (Zoller & Reindard 2007) and which are typical European meals (Fagt et al. 2008) were chosen for the study. Recipes and ingredients can be found in Fromberg et al. (2009). The ready-to-eat products included cooked products which are reheated before consumption.

**Food preparation.** Both ready-to-eat food products, raw food ingredients and the home cooked meals were sampled. Ready-to-eat food was prepared either directly in the tin, in a pot, in an oven or in a microwave oven. Jarred infant foods containing fruit or vegetables were analysed directly.

For canned products in water the product and the water from the can were analysed separately. For the homemade crisps, slices (diameter 40 mm, width 2.0 mm) of potato cv. Verdi were used (72% moisture content). The crisps were prepared by frying in palm oil (Fritex, Aarhus olie, Denmark) at 160°C for 6 min, 175°C for 4 min. and 190°C for 3 minutes. Crisps were fried at 150, 170, and 190°C for 7, 5, and 3.5 min, respectively, until a final moisture content of about 2% weight basis was present. Browning of meat and fish: meatballs were prepared to different levels of browning using vegetable oil or butter for frying. Slices from the same industrially made bread containing ascorbic acid were toasted to different levels of browning. Coffee was prepared from ground coffee beans, all medium roasted or from instant coffee. 40 g of coffee were used per litre of water. 1.5 g of instant coffee was used per 150 ml of water.

**Instrumentation and chromatographic conditions.** For the determination gas chromatography-mass spectrometry (Agilent, Santa Clara, USA) with a CombiPAL (CTC Analytics AG, Zwingen, Switzerland) static headspace autosampler was used. The syringe temperature was 70°C and 1 ml from a 10 ml vial was injected splitless at 200°C. The column was a 15 m x 0.32 mm x 20 µm HP-Plot Q and a helium flow of 1.7 ml/min was used. The oven temperature program was: 50°C (1 min), 10°C/min to 130°C, 3°C/min to 157°C, and 20°C/min to 260°C for 2.5 minutes. Furan was determined using $m/z$ 68 and 39; 2-methylfuran $m/z$ 82 and 53; 2-ethylfuran $m/z$ 96 and 53; 2,5-dimethylfuran $m/z$ 96 and 95; 2-pentylfuran $m/z$ 138 and 81, and the internal standard (IS) $d_4$-furan $m/z$ 72 and 42.

**Analytical method.** 5 g of liquid samples were homogenised and transferred to a headspace vial and spiked with $d_4$-furan (Crews et al. 2007). 0.75 g of homogenised French fries, 0.5 g of samples with low moisture/high fat content and 2.5 g of other homogenised samples were used. All samples were added 5M NaCl-solution to 5 ml and equilibrated at 60°C for 30 min (Wenzl et al. 2007). Quantification of furan was carried out using the standard addition method. The limit of quantification (LOQ) for furan was 2.4 µg/kg for all samples, except crisps, where it was 2.9 µg/kg.

**RESULTS AND DISCUSSION**

**Thermally processed and prepared potato and bread products.** Industrially precooked French fries were prepared by deep-frying at different temperatures (Figure 1). There was no significant difference in furan content between those fried at 160°C and those at 175°C, however a higher level of furan (18.3 µg/kg) was found in French fries fried at 190°C, when at this temperature the French fries also took on a browner appearance. The furan formation may depend on the level of sugars in the raw potatoes, as shown for the formation of acrylamide (Olsson et al. 2004). In addition, the formation of furan may depend on...
the level of ascorbic acid in the raw potatoes, and on the ability of frying oil to contribute not only to the furan formation but also to its retention on the potato surface (Mariotti et al. 2012).

Crisps revealed a linear correlation between the frying temperature and the furan content. Since the home-cooked crisps had a final thickness of about 1 mm, the entire crisp was expected to reach the frying temperature during cooking, and the water content is low in the crisps. In contrast, only the surface of the French fries was expected to reach the temperature of the frying oil, whereas the temperature of the core remains at around 100°C, since French fries contain high amounts of water. The combination of higher temperatures and lower water content leads to a higher furan content; the furan levels increased from 13 µg/kg to 42 µg/kg when the temperature was increased from 150°C to 190°C.

As furan seems likely to form in browned products, especially if the water activity is low, the furan occurrence in toasted, industrially made bread was studied. The bread contained ascorbic acid, an antioxidant which may be added to the flour in order to achieve a satisfactory structure for the bread. After toasting, the bread toasted to a brown to very dark colour had high levels of furan. The furan level increased with the browning level (2.5, 17.3, 83, and 179 µg/kg, respectively).

Homemade dishes. Homemade oatmeal porridge, bread, omelettes, pancakes, orange cream, fruit compote, syrup cake, and cookies were not found to contain furan, however, apple pie and apple cake were found to have contents of 4.4 and 23.4 µg/kg, respectively, resulting from the furan content of homemade bread crumbs (133 µg/kg). Furan has been shown to occur in industrially made soups (LOQ 6.9 µg/kg), such as beans, water from canned beans and peas (but not in the peas themselves) and in canned tomatoes, and therefore furan may be present in the prepared soups, however at levels below LOQ.

To assess the level of furan formed during the browning of meat and fish, meatballs were prepared to different levels of browning. The ingredients used for the meatballs did not contain furan, however, the olive oil used for the frying contained furan at a level of 5.1 µg/kg oil. Only a low level of furan (up to 3.1 µg/kg) was found in the heavily-fried fish meatballs using butter as the frying agent. In the medium-fried fish meatballs, using vegetable oil as the frying agent, low levels of furan were found. To further investigate homemade meat dishes, a traditional meat sauce was prepared based on minced beef without furan content and canned tomatoes with a content of 6.0 µg/kg furan, however the final dish did not contain a detectable level of furan.

Furan has been previously reported in dishes containing soy sauce and oyster sauce (Crews & Castle 2007). In the present study, these dishes did not contain any measurable levels of furan, even though the soy sauce and oyster sauce used contained 32 and 39 µg/kg, respectively, and a lower level was found in the sambal oelek used (2.7 µg/kg).

Ready-to-eat foods. Ready-to-eat food was prepared either directly in the tin, in a pot, in an oven or in a microwave oven. The furan loss did not appear to depend on the heating method. On average, heating reduced the furan content in the sample to roughly a half of the initial level, however, a negative correlation was observed between the maximum heating temperature and the percentage of furan remaining after heating (Figure 2).

Beverages. The beverages (n = 32) investigated include fruit and vegetable juice, milk, cream, tea, soft drinks, syrup and cocoa. Previous studies have found low levels of furan in juices and beers (Crews & Castle 2007; Morehouse et al. 2007; Zoller et al. 2007). In the present study, varying levels of furan were found in beer and coffee with the lowest levels observed in ready-to-drink beer (LOQ 2.9 µg/kg) and instant coffee (LOQ to 6.6 µg/kg). The highest levels of furan were found in coffee prepared from ground beans (31–76 µg/kg). Levels of furan in the ground coffee beans were be-
between 1222 µg/kg and 1966 µg/kg and in the instant coffee powder between 39 µg/kg and 1330 µg/kg. A mean of 72% of the furan from the coffee beans was transferred into the brewed coffee, which is in agreement with previous studies (Kim et al. 2009; Guenther et al. 2010; Mariotti et al. 2013a).

Up to 11.0 µg/kg of furan was found in chocolate and cookies and up to 10.8 µg/kg in canned fruit products, however these levels are low compared to the up to 83 µg/kg found in raw raisins (Table 1). Dried fruits and vegetables are product groups not previously reported to contain furan; however in the present study furan was found in raisins, sundried dates, dried plums, dried pineapple, dried banana, and sundried tomatoes. The reason for the presence of furan in dried fruit and vegetables has not been elucidated, however, it is assumed that furan is formed in Maillard reactions that take place during the drying process.

**Products containing cereals.** Popcorn and crisps contained high levels of furan (91 µg/kg and up to 52 µg/kg, respectively). These findings are consistent with those reported by Zoller et al. (2007). A mean concentration of 57.4 µg/kg furan was found in breakfast cereals \((n=11)\), with particularly high levels found in honey coated products. On the contrary, Mariotti et al. (2013b) found furan levels in breakfast cereals to be below the detection limit and up to 23 µg/kg. As these foods contain high levels of carbohydrates, it is likely that the furan formation is related to the level of carbohydrate precursors. Relatively large amounts of furan were found in dry bakery products, including toasted bread, crust and particularly crispbread and rice cakes, however it is noticeable that all the samples of dry bakery products contained furan. The furan level here might be associated with the use of ascorbic acid in the flour used in the production, combined with a baking process which leaves low levels of water in the final products. In samples of infant foods containing fruit no furan was found, however in two samples containing vegetables, furan levels of about 45 µg/kg were observed, which is in agreement with results reported by Zoller et al. (2007); Jestoi et al. (2009) and Mesiás et al. (2012).

**CONCLUSIONS**

In most homemade dishes furan was not detected, however, foods rich in carbohydrates were found to be likely to form furan upon heat treatment, probably due to a Maillard browning reaction of the food.

### Table 1. Levels of furan in ready-to-eat products (µg/kg)

<table>
<thead>
<tr>
<th>Product</th>
<th>n</th>
<th>Mean (µg/kg)</th>
<th>Range (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chocolate and cookies</td>
<td>9</td>
<td>3.9</td>
<td>&lt; 2.4–11.0</td>
</tr>
<tr>
<td>Dried fruit</td>
<td>18</td>
<td>6.5</td>
<td>&lt; 2.4–83</td>
</tr>
<tr>
<td>Canned vegetables</td>
<td>18</td>
<td>3.8</td>
<td>&lt; 2.4–12.0</td>
</tr>
<tr>
<td>Crisps</td>
<td>9</td>
<td>24.3</td>
<td>&lt; 2.4–91</td>
</tr>
<tr>
<td>Dry bakery products</td>
<td>5</td>
<td>35.8</td>
<td>4.9–74</td>
</tr>
<tr>
<td>Breakfast cereals</td>
<td>11</td>
<td>57.4</td>
<td>&lt; 2.4–387</td>
</tr>
<tr>
<td>Infants food</td>
<td>5</td>
<td>17.8</td>
<td>&lt; 2.4–45</td>
</tr>
</tbody>
</table>

### Table 2. Levels of furan, 2-methylfuran, 2-ethylfuran, 2-pentyl, and 2,5-dimethylfuran in canned foods and coffee

<table>
<thead>
<tr>
<th>Product</th>
<th>Compound</th>
<th>n</th>
<th>Mean (µg/kg)</th>
<th>Range (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canned food</td>
<td>furan</td>
<td>12</td>
<td>20.5</td>
<td>&lt; LOD – 47</td>
</tr>
<tr>
<td></td>
<td>2-methylfuran</td>
<td>12</td>
<td>4.7</td>
<td>&lt; LOD – 8.0</td>
</tr>
<tr>
<td></td>
<td>2-ethylfuran</td>
<td>12</td>
<td>8.5</td>
<td>&lt; LOD – 17.7</td>
</tr>
<tr>
<td></td>
<td>2-pentylfuran</td>
<td>12</td>
<td>2.7</td>
<td>&lt; LOD – 3.2</td>
</tr>
<tr>
<td></td>
<td>2,5-dimethylfuran</td>
<td>12</td>
<td>67</td>
<td>&lt; LOD – 105</td>
</tr>
<tr>
<td>Coffee</td>
<td>furan</td>
<td>15</td>
<td>885</td>
<td>47–2821</td>
</tr>
<tr>
<td></td>
<td>2-methylfuran</td>
<td>15</td>
<td>1328</td>
<td>117–5982</td>
</tr>
<tr>
<td></td>
<td>2-ethylfuran</td>
<td>15</td>
<td>76</td>
<td>&lt; LOD – 98</td>
</tr>
<tr>
<td></td>
<td>2-pentylfuran</td>
<td>15</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td></td>
<td>2,5-dimethylfuran</td>
<td>15</td>
<td>217</td>
<td>32–466</td>
</tr>
</tbody>
</table>
For example, levels of furan in toasted bread were correlated to the browning of the bread. For food with an initial level of furan, cooking reduced the level to some extent, but nevertheless furan remained in the hot food. Furan was detected in several dried fruits but with large variations in concentration between individual samples. Furthermore, high levels of furan were observed in samples of breakfast cereals. Finally, the putative genotoxic 2-alkylfurans were found in canned food and coffee at similar or even higher levels than furan in the product.

Acknowledgements. Supported by EFSA, however, this task has been carried out exclusively by the authors and may not be considered as an output adopted by EFSA (Fromberg et al. 2009). We would like to thank Vibeke Balsweld and Vera Lykkerask for their technical work and Karin Hess Ygil for advice on the recipes.

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Received for publication July 21, 2013
Accepted after corrections January 27, 2014

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