



## **Managing neoformed contaminants in the bakery sector**

Acrylamide, Furans and 3-MCPD and glycidyl Esters

### **ABSTRACT**

**Keeping baked goods safe: neoformed contaminants.**

**We can all enjoy foods without needing to know the science, but it is reassuring to appreciate that the knowledge of bakers' and their industry partners has led to the reduction of contaminants formed in the cooking process, here are three types of these "neoformed contaminants".**

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## Managing neoformed contaminants in the bakery sector

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As a generalization, bakery dough consists of several dispersed phases, such as gas cells, lipid particles and starch granules, within a continuous matrix of gluten and water. Its final properties are determined by the complex interactions of the raw materials, the quantities and qualities used and the dough processing method. During baking, heat treatment promotes chemical reactions, particularly the Maillard reaction, resulting in the desired sensory attributes of the food product and reduction in the number of pathogenic microorganisms present.



Figure 1. Prehistoric fireplaces used by Natufian hunter-gatherers 14,400 years ago where bread-like remains were discovered at the site of Shubayqa 1 in Northeast Jordan

While baking may have prehistoric origins (Figure 1) [1], the realisation that undesirable chemicals may also be generated during this process is a more recent phenomenon. For example, chemicals that might affect human health and bring about nutritive losses of food products can be formed at elevated temperatures by reaction pathways such as caramelisation, the Maillard reaction, lipid oxidation and other reaction pathways. Acrylamide [2], furan [3, 4] / alkyl furans, monochloropropanediol esters (MCPDEs) and the related glycidyl esters (GEs) are recent examples

of such processing or neoformed contaminants (NFC). Consequently, the control of food product quality (sensory and nutrition) and mitigation of undesirable NFCs is challenging. The EC has initiated numerous activities to harmonise analytical methods, monitor, identify health effects and mitigate NFCs [5] in foods. From an industry perspective, the main mitigation strategies for these NFCs are captured in so-called “Toolboxes” that catalogue the measures to help food manufacturers implement the “tools” applicable to their processes. This article summarises the key NFCs under study by food manufacturers, including the legal frameworks and specific challenges in managing these heat-induced contaminants.

### Acrylamide

Acrylamide: at a glance	
Historical	Industrial chemical with widespread use (agriculture, construction, cosmetics, flocculants, oil drilling, paper and pulp, plastics, textiles). Reported for the first time in 2002 to be present in a wide range of thermally treated foods (baked, fried, grilled) but not in boiled foods.
Analysis	Harmonised methods based on GC/MS and LC/MS established for many matrices which are robust at the µg/kg level [6-8].
Health risks	IARC probable human carcinogen (group 2A). Glycidamide, the main metabolite, is believed to be responsible for the genotoxicity of acrylamide.
Occurrence	A wide range of heat-treated foods (e.g. bread, coffee, fine bakery wares, speciality malts, potato products (crisps, French fries), some types of thermally processed olives, prunes and canned fruit (autoclaved).
Formation	Maillard reaction pathway in which the essential amino acid asparagine provides the acrylamide backbone. Risk factors (biscuits): ammonium based raising agents; high fructose; added ginger; added fruit.
Mitigation	FoodDrinkEurope publishes a catalogue of measures for each sector which is continuously updated with the latest developments [9]. Recipe: Asparaginase; multivalent metal ions (e.g. Ca <sup>2+</sup> , Mg <sup>2+</sup> ); yeast. Agricultural / environmental: reducing plant stress due to pests and inadequate nutrition; control of N and S fertilization; selective breeding / gene-editing to produce wheat with reduced asparagine.
Regulatory	No maximum limits (yet) but Regulators have established mitigation measures, Benchmark Levels and analytical performance criteria [10] to control acrylamide.
Knowledge gaps	Occurrence in cakes (long bake, high sugar)

Since the accidental release and exposure of railway tunnel workers to acrylamide monomer [11] led its coincidental discovery in foods [2], acrylamide has been studied extensively and monitored in a wide range of retail products. Figure 2 shows recent UK acrylamide monitoring data for retail samples of soft bread (wheat based) and biscuits (including crackers, crispbreads and wafers) [12] obtained in accordance with EU recommendations [13].

Acrylamide is predominantly formed in the low moisture and high temperature regions of cereal products [14] and this is reflected in the large differences in mean acrylamide levels for bread and biscuits (Figure 2). Although acrylamide is readily formed in the drying outer crust regions of bread,

the overall value for the loaf is diluted by the relatively large volume of crumb in which no formation occurs.

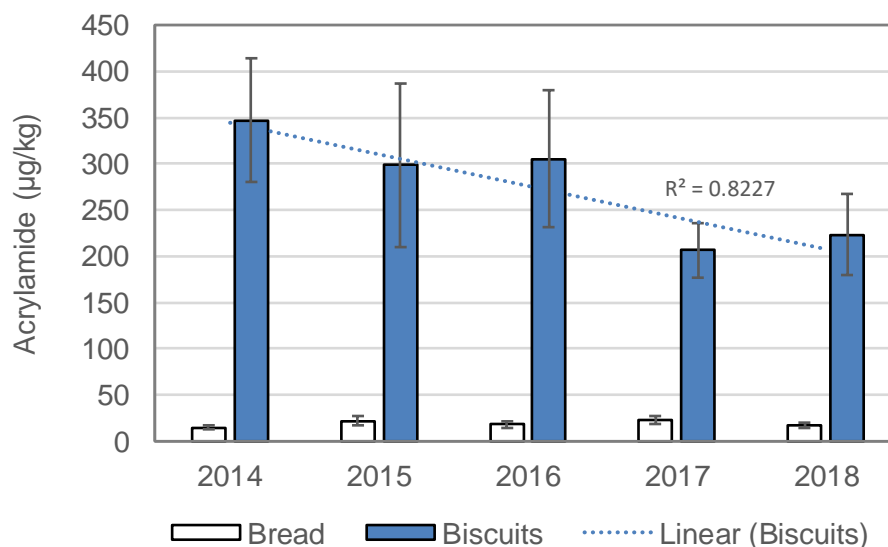


Figure 2. Trends in mean acrylamide levels for UK retail samples of soft bread and “biscuits” (includes crackers, crispbread, wafers; UK FSA data)

However, the reduced formation of acrylamide in bread compared with biscuits is not solely due to moisture effects. Compared with EU data [15] (mean 51 µg/kg; 2007-2010;), mean acrylamide levels in UK plant bread were significantly lower ( $p < 0.05$ ) over the same period (mean 19 µg/kg; 2007-2010) [12]. Most plant bread in the UK is produced from wheat by the Chorleywood bread process (CBP). While the range of processes and raw materials used to produce bread in the EU differ from the UK, studies have shown that yeast plays a significant role in mitigating acrylamide in CBP bread [16-19]. In the presence of other free amino acids during the proving of CBP dough, yeast preferentially consumed the acrylamide precursor asparagine (Asn); yeast can utilise Asn as a nitrogen source [20].

The data shown in Figure 2 also reflects the substantial work carried out by the baking sector to reduce acrylamide in established biscuit products; the year-on-year reduction of acrylamide in biscuits, crackers and crispbreads was ~9% for the period 2014-2018 [12]. The reduction of acrylamide in products not utilising yeast processes is challenging. This is because key process ingredients that may promote acrylamide formation, such as ammonium based raising agents and high fructose syrups, cannot be replaced without compromising the unique flavour characteristics of some established products [14, 16-19, 21]. Furthermore, biscuit dough is typically of lower moisture compared with bread dough and mitigation agents such as asparaginase may be less effective (“mobile”) under these conditions. Table 1 shows the progression of the EU regulatory system for controlling acrylamide in selected foods.

Table 1. Progression of the EU regulatory system for controlling acrylamide in selected foods

Food	Indicative value (2011-2017)	Benchmark Level (2017- )	Reduction (%)
French fries (ready-to-eat)	600	500	17
Potato crisps from fresh potatoes and from potato dough	1000	750	25
Soft bread	80-150	50-100	33-67
Breakfast cereals (excl. porridge)	200-400	150-300	25-63
Biscuits, crackers, wafers, crisp bread, and similar (excl. ginger bread)	450-500	300-400	20-40
Roast coffee	450	400	11
Instant (soluble) coffee	900		
Baby foods, other than processed cereal based food	80	40	50
Biscuits and rusks for infants and young children	250	150	40
Processed cereal-based foods for infants and young children (excl. biscuits and rusks)	100	40	60

Analytical methods for acrylamide have favoured LC/MS/MS detection in the last decade, mainly due to developments in clean-up procedures for small molecules and the advantages of direct detection (without derivatisation). Interestingly, as the regulatory framework pushes for lower limits of detection, there has been renewed interest in GC/MS methods, particularly GC/MS/MS [22]. Although these methods require the preparation of a higher molecular weight derivative of acrylamide for optimum GC performance, they are capable of lower limits of detection and higher selectivity in a wide range of complex matrices. In this respect, cereals and coffee remain a challenge for LC/MS/MS methods. The capital investment associated with GC/MS/MS instrumentation is also significantly less than that for LC/MS/MS, mainly due to the costs associated with the liquid chromatography equipment and ancillary nitrogen generation.

Furan / alkyl furans

Furans: at a glance	
Historical	Furan is a known flavour volatile, particularly in coffee.
Analysis	Headspace analysis combined with GC/MS; official standard methods (e.g., CEN, ISO) are not available for the combined analysis of furan and alkyl furans in foods.
Health risks	Furan is an IARC possible human carcinogen (group 2B); metabolically activated to a ring-open intermediate (cis-but-2-ene-1,4-dialdehyde) although evidence of adducts with DNA supporting a genotoxic mechanism of action is lacking; based on structural similarities, 2-, and 3-methyl furan, 2,5-dimethyl furan, and 2-pentylfuran may be metabolised in the same way.
Occurrence	Widespread, e.g. canned / jarred foods, bread and rolls, coffee (especially roasted), raw pasta, breakfast cereals, fine bakery wares, popcorn.
Formation	Can be formed under certain oxidative / thermal conditions from polyunsaturated fatty acids, carbohydrates, amino acids, ascorbic acid, and carotenoids.
Mitigation	No specific measures identified so far that can be applied at the industrial scale; in the domestic environment, reheating in open containers may result in some reduction of furan by volatile losses.
Regulatory	No authorities have set specific limits to date, but the possibility of risk management measures can not be excluded, particularly for infants and small children.
Knowledge gaps	Insufficient occurrence data for alkyl furans; occurrence in cakes

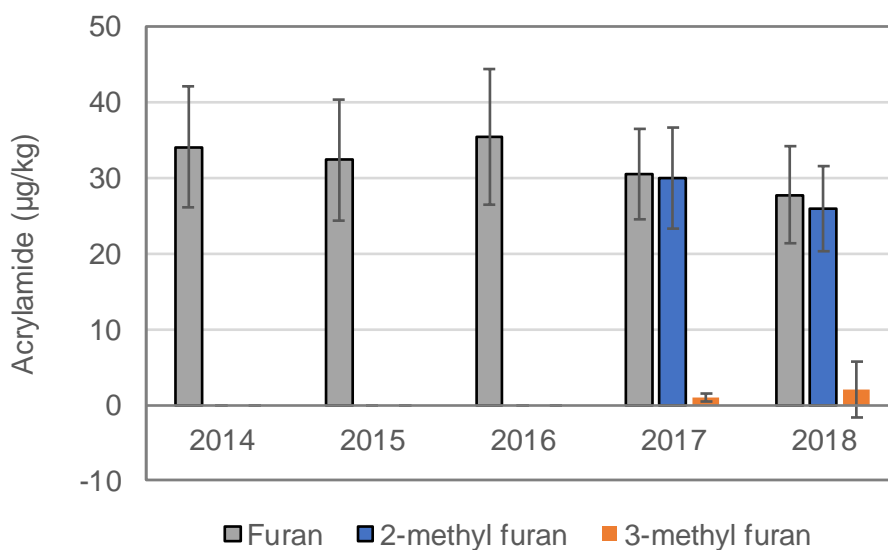


Figure 3. Furans in UK retail samples of “biscuits” (includes crackers, crispbreads, wafers; error bars are standard error of the mean; 2- and 3-methyl furan not monitored before 2017; FSA data)

Compared with acrylamide, several chemicals and chemical classes can lead to the formation of furan under certain oxidative / thermal conditions, e.g., polyunsaturated fatty acids, carbohydrates, amino acids, ascorbic acid, and carotenoids. Consequently, almost any food that is heated will generate low amounts of furan, but ultimately exposure will be dependent on the degree of retention in the food due to its high volatility. Alkyl furans have been studied far less and there is a paucity of data concerning their occurrence in foods. They are believed to be formed from the same precursors as

furan. Compared with coffee, which can attain relatively high amounts of furan (mg/kg), levels in biscuits, crackers, crispbreads and wafers appear to be significantly lower (Figure 3). Interestingly, the formation of furan, pentyl furan and the key sensory marker furfural has been demonstrated in model cake systems (e.g., sponge cake) [23, 24]. However, to date, data on the occurrence of furans in cake is not available.

Although analytical methods based on headspace analysis appear to be robust and sensitive, there are no official standard (e.g., CEN, ISO) methods for the combined analysis of furan and alkyl furans in foods.

2- and 3-MCPDEs and GEs

2- and 3-MCPDEs and GEs: at a glance	
Historical	MCPDEs originally discovered in acid-hydrolysed vegetable proteins and the first occurrence in foods was reported for milk from goats [25] and humans [26]; the discovery of MCPDE and GE in wider foods was subsequently linked to formation in refined edible oils.
Analysis	Harmonised methods available for the analysis of fats and oils based on the measurement of total ester bound MCPDs and glycidol [27-29]; robust methods for composite foods are not widely available.
Health risks	Risk assessments have assumed 100% release of these contaminants from their esters in vivo. JECFA has confirmed that glycidol is both genotoxic and carcinogenic and a BMDL <sub>10</sub> of 2.4 mg/kg bw per day was established. 3-MCPD was not genotoxic in rodent models and based on the BMDL <sub>10</sub> , a group tolerable daily intake (TDI) of 4 µg/kg bw for 3-MCPD and its esters (singly or in combination) was set by JECFA.
Occurrence	Predominantly refined edible oils; some evidence for in situ generation in cereal products.
Formation	MCPDEs are mainly formed from the reactions of chlorinated precursors (assimilated by the oil fruit during growth) with triacylglycerols during the deodorisation stage of edible oil refining; the precursors of GEs are believed to be diacylglycerols.
Mitigation	Various measures encompassing cultivation / harvesting of oil fruit and key stages of refining [30].
Regulatory	Maximum levels established for 3-MCPDEs and GEs in edible oils, infant formulae and foods for special medical purposes [31].
Knowledge gaps	In situ formation and the role of metal ions.

Contamination of bakery products by MCPDEs and GEs occurs mainly via ingredient fats / oils. Some studies have reported the in situ generation of 2- and 3-MCPDEs during the toasting of bread [32] and cereal model systems [33] although amounts formed may be relatively small and further studies are required.

Reliable standard (AOAC) methods for the determination of total MCPD and glycidol released from their esters are available for refined fats / oils and developments in GC/MS/MS and rapid GC now permit instrumental run times of < 5 min. Some methods for composite foods are available; a procedure based on pressurised liquid extraction for cereal (and potato) products has recently been evaluated by collaborate trial [34, 35].

*Knowledge gaps and outlook*

In practice, it will be impossible to completely avoid the generation of NFCs in bakery products and maintain important quality and safety requirements. However, significant progress has been achieved by the food industry and academia to identify viable measures to mitigate these contaminants to “as low as reasonably achievable.” Despite these efforts, many challenges remain, particularly for NFCs that have multiple formation routes (e.g., furan and alkyl furans), or where intervention requires control measures at the cultivation / harvesting stages.



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