



Furan in Thermally Processed Foods - A Review

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Furan (C₄H₄O) is a volatile compound formed mostly during the thermal processing of foods. The toxicity of furan has been well documented previously, and it was classified as “possible human carcinogen (Group 2B)” by the International Agency for Research on Cancer. Various pathways have been reported for the formation of furan, that is, thermal degradation and/or thermal rearrangement of carbohydrates in the presence of amino acids, thermal degradation of certain amino acids, including aspartic acid, threonine, α -alanine, serine, and cysteine, oxidation of ascorbic acid at higher temperatures, and oxidation of polyunsaturated fatty acids and carotenoids. Owing to the complexity of the formation mechanism, a vast number of studies have been published on monitoring furan in commercial food products and on the potential strategies for reducing furan. Thus, we present a comprehensive review on the current status of commercial food monitoring databases and the possible furan reduction methods. Additionally, we review analytical methods for furan detection and the toxicity of furan.

Key words: Furan, Monitoring, Reduction, Thermally processed foods

INTRODUCTION

Furan (C₄H₄O) is a colorless, heterocyclic compound with high volatility (boiling point: 31°C), consisting of a five-membered aromatic ring with four carbon atoms and one oxygen atom. It has been reported that thermal processing is a main cause of furan formation. Thermal processing such as cooking, roasting, baking, pasteurization, and sterilization (1,2) is involved in many food preparing processes, from the home kitchen to industrial food processing facilities, and it ensures the microbiological safety of the food for preservation and maintains particular sensory features (3). One of the known reactions during thermal processing is the Maillard reaction. This is a non-enzymatic browning

reaction, which involves the reaction of amino acids, peptides, and proteins with reducing sugars and vitamin C (4). Some studies have reported that furan formation occurs to a large extent during the Maillard reaction. This review presents the current status of commercial food monitoring databases and possible methods applied by various agencies for reducing furan formation in food.

Various pathways involved in furan formation. There are multiple pathways underlying furan formation, such as (i) thermal degradation or rearrangement of carbohydrates alone or in the presence of amino acids, (ii) thermal degradation of certain amino acids, (iii) oxidation of ascorbic acid under high temperatures, and (iv) oxidation of polyunsaturated fatty acids and carotenoids. The potential pathways of furan formation have been illustrated in a previously published paper (5).

Thermal degradation or rearrangement of carbohydrates: Thermal degradation and rearrangement of carbohydrates is observed in the Maillard reaction or non-enzymatic browning reactions during food processing and cooking. Even in simple component mixtures, large numbers of furan compounds are formed. Carbohydrate degra-

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dation can be divided into four pathways that lead to the formation of aldotetrose derivatives. After the final cyclization of aldotetrose, toxic furan can be generated. Reducing hexoses typically go through the Maillard reaction in the presence of amino acids and produce reactive intermediates such as 1-deoxy- and 3-deoxyosones, aldotetrose, and 2-deoxy-3-keto-aldotetrose, as was demonstrated previously (4). 1-Deoxyosone undergoes α -dicarbonyl cleavage to form aldotetrose. Aldotetrose is a compound derived from retro-aldol cleavage in the absence of amino acids, and it is known to form a limited quantity of furan. After a dehydration reaction, the formation of 2-deoxy-3-keto-aldotetrose follows retro-aldol cleavage. Consequently, 3-deoxyosone undergoes α -dicarbonyl cleavage, followed by oxidation and decarboxylation to form 2-deoxyaldotetrose. All the aldotetrose derivatives can easily be converted into furan (4). Another study reported the precursors of furan, such as aldotetrose and 2-deoxy-aldotetrose (6). A further study, using labeling, described that furan formation originates from the aldotetrose intermediate (7). Pentose sugars (e.g., ribose) are known to form furan intermediates in the presence of amino acids, as these are converted into their 3-deoxyosone derivatives. Each derivative completes a reaction with amino acids or undergoes dehydration at the C-3 hydroxyl group. The resulting intermediate can undergo α -dicarbonyl cleavage to produce 2-deoxyaldotetrose, which is a direct precursor of furan (2). Locas reported that pentose acts in a manner similar to hexose and is converted into its 3-deoxyosone derivative after an amino acid reaction or elimination of the C-3 hydroxyl group (4). The intermediate formed in this manner can undergo R-dicarbonyl cleavage to form 2-deoxyaldotetrose, from which furan can be produced directly (4). The formation of furan from the thermal degradation of carbohydrates is very complex, and the pathway involves mainly the Maillard reaction.

Thermal degradation of amino acids: The mechanism underlying furan formation from amino acids has been reported in a carbon-13 labeling study, which stated that amino acids that can form acetaldehyde and glycolaldehyde are able to produce furan by aldol condensation and cyclization (4). Formation of furan from thermal degradation of amino acids depends greatly on the type of amino acids involved in the process. Some amino acids such as serine and cysteine can be shunted into two pathways to produce glycolaldehyde through the Strecker reaction or to produce acetaldehyde through decarboxylation, with the loss of one ammonia molecule (8). Therefore, the amino acids stated above do not require sugar or other sources of glycolaldehyde to form furan. Both of these amino acids can be metabolized to acetaldehyde and glycolaldehyde by aldol condensation to produce aldotetrose derivatives, which are then cyclized to form furan. Several amino acids require sugar to produce furan; these include aspartic acid, threonine, and α -alanine. These amino acids can produce only

acetaldehyde (Strecker aldehyde), which implies that they require the presence of reducing sugars, serine, or cysteine to produce the glycolaldehyde that is formed during Strecker degradation (9).

Oxidation of ascorbic acid: According to recent studies, ascorbic acid is a precursor of furan (4). Ascorbic acid is known to behave in the same manner as reducing sugars, and is decomposed by two parallel mechanisms (10). Ascorbic acid is quickly oxidized into dehydro-ascorbic acid under acidic and aerobic conditions. Then, it is hydrolyzed to 2,3-diketogulonic acid (DKG) by ring cleavage with the addition of water. This DKG can be decarboxylated to form xylosone (4) and 2-deoxyaldotetrose, which is used in furan formation. On the other hand, dehydro-ascorbic acid cannot be formed under anaerobic conditions (4). Under non-oxidative pyrolytic conditions, ascorbic acid cannot be oxidized to form DKG. Hence, it can be hydrolyzed and undergoes β -elimination, followed by decarboxylation to form 3-deoxypentosulose (DP), which can then be processed in the ribose pathway to produce furan. Under heating and in the absence of water, furan formation is avoided because dehydro-ascorbic acid can be cyclized and exists mainly in its hemiketal form (4). Ascorbic acid forms furan substitutes on heating at 300°C in the absence of water. The compounds that are primarily produced under these conditions are furfural and furoic acid (9). Under acidic aerobic conditions, ascorbic acid can be oxidized to dehydro-ascorbic acid and is then hydrolyzed to DKG by ring cleavage with the addition of water. Decarboxylated DKG then forms xylosone, which is ultimately dehydrated to 3-hydroxy-2-pyrone and 2-furoic acid or 3-deoxypentosulose, and ultimately forms furfural. Ascorbic acid can form 2-deoxyaldotetrose, from which furan is finally generated (4). Ascorbic acid is one of the compounds that affects the browning reaction of orange juice, along with 3-hydroxy-2-pyrone, 5-hydroxymethylfurfural (HMF), furfural, 5-hydroxymaltol, and 2-furoic acid (11). A study of orange juice and a juice model system confirmed that ascorbic acid produces furan precursors such as furfural and 2-furoic acid, which react with sugars or chelating agents (9).

Under anaerobic conditions, however, the formation of dehydro-ascorbic acid is less likely to occur, because ascorbic acid undergoes hydrolysis under anaerobic conditions, followed by β -elimination and decarboxylation, which leads to the formation of 3-deoxypentosulose, the intermediate of 2-deoxyaldotetrose. Furfural can also be produced from ascorbic acid under both aerobic and anaerobic conditions (4).

Oxidation of polyunsaturated fatty acids and carotenoids: In general, oxidative degradation of polyunsaturated fatty acids (PUFAs) and the ensuing formation of lipid peroxides are undesirable reactions in food processing because lipid peroxides can cause a disagreeable, rancid, off flavor in food, and some lipid peroxides are known to be

carcinogenic to humans (4). In a combinatory reaction with oxygen species and/or an enzymatic reaction by lipoxygenases, lipid hydroperoxides can be produced from PUFAs. At the intermediate stage of these reactions, 2-alkenals, 4-oxo-2-alkenals, and 4-hydroxy-2-alkenals can be produced. Among these intermediates, 4-hydroxy-2-alkenals can act as precursors for furan as demonstrated previously (4). Similarly, 5-pentylfuran could be produced from 4-hydroxy-2-butenal through cyclization. Ironically, this process alters the 4-hydroxy-2-alkenals into less toxic furan derivatives with high volatility. Xu reported that transition of metal ions catalyzes homolytic cleavage of PUFA hydroperoxides to form 2-alkenals, 4-oxo-2-alkenals, and 4-hydroxy-2-alkenals (12). Sayre reported that 5-pentylfuran was related to formation of 4-hydroxy-2-nonenal (4-HNE) when the furan is formed from ethanolic 4-HNE solutions under acidic conditions (8). Vichi reported the proportional relation between 5-pentylfuran concentrations and the level of olive oil oxidation (13).

Some model systems showed that monounsaturated acid (oleic acid) did not form furan. Linoleic acid heated for 30 min at 118°C in water formed 125 ng/g furan and linolenic acid formed 625 ng/g furan (14). It has previously been reported that furan is produced from linolenic acid at lower temperatures (110–220°C) than that reported for furan formation from ascorbic acid or the Maillard reaction (13).

Analytical methods for furan detection. The FDA reported the first method for furan detection and quantification in foods (15). This method involves the preparation of samples under cold conditions and headspace sampling incubation at 80°C. Porous layer open tubular (PLOT) columns are used for chromatographic separation with mass spectrometric detection in selected ion monitoring (SIM) mode. The column, with bonded polystyrene-divinylbenzene, can separate small volatile molecules well. Quantification was based on a standard addition method and used a deuterated furan internal standard (d_4 -furan).

Headspace analysis: Separation of furan from the food sample into the headspace vial varies depending on time, temperature, and the liquidity of the sample. Effective separation is only possible with the appropriate equilibration time, and/or efficient agitation by the addition of magnetic bars to the headspace vial (16). An appropriate amount of water must be present or added to ensure that the sample is entirely fluid before analysis. Typical headspace procedures involve heating the sample to ensure volatilization of the analyte into the headspace. However, furan does not require excessive heating; in fact, this is inadvisable and unnecessary because of its highly volatile nature (17). Some papers have reported increases in the headspace incubation temperature from 30°C to 50°C. This led to an increase of only 50% in the furan peak area. Addition of salt is much more effective in increasing the sensitivity of detection of

the furan signal (18). Based on many studies, a consensus has been reached that an incubation temperature of 50°C or below is appropriate, as this provides the proper sensitivity for detection (10,18). It is necessary to confirm that furan is formed at the selected incubation temperature in each study prior to sample analysis (17).

Headspace sampling by solid phase microextraction (SPME): It is now advised that SPME be implemented for effective furan analysis (19). The SPME method focuses on an SPME needle that is coated with a polymeric material. The SPME needle is first exposed to the headspace of the vial that contains the analytes to absorb volatile compounds for 10–60 min, and these are then desorbed thermally for 15 min at 90–300°C in the injection port of the GC to send the volatiles into the GC column. On the other hand, in direct headspace analysis, the headspace gas is taken from the vial and injected directly into a gas chromatography-mass spectrometry (GC-MS) system. SPME allows sample concentration and is more sensitive. The limits of detection for furan are low (16).

Several parameters, including the fiber type, extraction (exposure) time/temperature, and the saturation of the aqueous phase in the headspace vial, affect optimal SPME conditions. Some studies focused on the selection of optimal fibers for the analysis of furan. They report that the best option for the analysis of furan is a carboxen/polydimethylsiloxane (CAR/PDMS) fiber, as it shows marked advantages such as selectivity; the next best options were the divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polyacrylate, and carbowax/divinylbenzene (CW/DVB) fibers (3). The fiber should be baked at 300°C for an hour before the analysis of furan. Several studies have also reported on optimization of the fiber exposure temperature and time for furan analysis (16,17,20). These studies showed that the exposure temperature should be 50°C or below, to discourage the formation of additional furan, which can increase the sensitivity of the system. Exposure time did not have a marked effect on the formation of additional furan, and 20 min of exposure was typically chosen (17). The optimal SPME conditions for furan analysis thus involve equilibration for 20 min at 50°C. Different SPME fibers have been compared, and the CAR/PDMS was selected for furan analysis because of its high sensitivity.

A previous study also investigated the SPME conditions for furan analysis (17), and reported on optimal sample preparation and equilibration temperature and time. Three approaches to sample preparation, depending on sample states, were reported. The amounts of furan for analysis were 1 g for solid samples and 5 g for liquid and paste samples, as the latter samples contained low levels of furan. The optimal SPME fiber exposure temperature among the various temperatures tested, viz., 30°C, 40°C, 50°C, 60°C, 70°C, and 80°C, was 50°C. Furan production increased with

higher temperatures because furan was being formed during the equilibration step, in addition to the furan already present in samples (10). An exposure time of 20 min was selected, as exposure time did not markedly affect furan formation, thus confirming the findings of the previous study (21).

Identification and quantification of furan using GC-MS: There are several ways to identify furan using GC-MS, such as evaluating the GC retention time (e.g., $\pm 2\%$ of the standards), or the ratio of the quantification ion of furan at m/z 68 compared to the qualification ion at m/z 39 and again compared to the ratio with standards (e.g., agreement to $\pm 25\%$). Quantification methods use various standards, such as external calibration graphs, or internal calibration graphs using d_4 -furan as a deuterium-labeled internal standard. High amounts of internal standard must be avoided to prevent an allocation to the m/z 68, which is the signal for quantification of the furan ion from the fragment ion of $[M-d_2]^+$. HP-PLOT Q columns showed relatively high sensitivity and worked well with the selected CAR/PDMS fiber (10).

Toxicology of furan. The presence of furan in commercial food products is of great concern to many public health agencies such as the US Food and Drug Administration (FDA) and European Food Safety Authority (EFSA) and has prompted research into and identification of risks conferred by furan by many international organizations, including the National Toxicology Program (NTP) and International Agency for Research on Cancer (IARC). The toxicity of furan is well documented from animal studies, and a summary of the classified furan risks can be found in Table 1.

Oral toxicity and carcinogenicity: In rats, furan is bioactivated to its reactive intermediate due to the high activity of CYP2E1, and reaches the liver, which is the main target organ of furan toxicity (22,23). Male F344 rats given a single dose of 30 mg/kg body weight of furan by oral gavage developed hepatocellular necrosis, inflammation, and elevated liver enzyme activities in the serum within 24 hr of furan administration, followed by regenerative cell proliferation for 48 hr, and demonstrated residual inflammation after 8 days. Approximating a single dose, exposure of Sprague-Dawley rats to furan at 40 mg/kg body weight for up to 14 days resulted in a significant decrease in body weight, with increased relative liver weights, and significant increases in serum transaminases, alkaline phosphatase, cholesterol, triglycerides, and total bilirubin (22). To

determine furan toxicity in the low-dose range, which more closely approximates potential human exposures, several researchers have recently investigated macroscopic and histological changes in livers of male and female F344 rats after 90 days of oral treatment with various furan doses, i.e., 0.0, 0.03, 0.12, 0.5, 2.0, and 8.0 mg/kg body weight (22). Gross morphological alterations, characterized by nodular structures, were seen in the livers of all animals in the high-dose group, with the caudate and left lateral lobe being affected most markedly (23). Given the results of this study, 0.03 mg/kg body weight was announced as a NOAEL for furan hepatotoxicity in rats.

Genotoxicity: Genotoxicity of furan has also been reported in many studies. Furan appears to be mutagenic to mouse lymphoma cells, independent of S9 activation. High doses of furan caused structural chromosome abnormalities, but did not affect chromatid exchange in mouse bone marrow cells. With a single oral dose of 200 or 100 mg/kg body weight, furan did not cause uncontrolled DNA synthesis in mouse or rat hepatocytes *in vivo* (5). Mutagens such as *cis*-2-butene-1,4-dial are similar to unsaturated compounds that react with DNA. This was directly mutagenic at non-toxic concentrations in a *Salmonella enterica* Typhimurium strain (TA104) that was sensitive to aldehydes, but not to some other strains (4). It is possible that furan or *cis*-2-butene-1,4-dial reacts with DNA in target cells and can play a major role in furan-induced tumors. After bioactivation into its metabolites, furan induces loss of ATP, which causes an inevitable uncoupling of hepatic mitochondrial oxidative phosphorylation. This would activate cytotoxic enzymes, including endonucleases that produce DNA double-strand cleavage, leading to cell death (4). Based on these findings of previous studies, furan is considered a genotoxic compound.

Furan monitoring databases. In 2004, the U.S. FDA analyzed the level of furan in commercial canned and jarred foods, the production of which typically involves harsh thermal processing followed by sealing and packaging. Since then, the techniques for analyzing furan in food products have improved greatly, allowing better detection of furan. Greater public concern about the risks of furan in common food products has led to the investigation of the raw materials used for the production of all commercial food products. Hence, many international agencies such as the EFSA, FDA, and Food Standards Agency (FSA), and countries such as Korea, Taiwan, China, and Chile have

Table 1. The classification of furan risks

Organization	Class	
IARC	2B	Possibly carcinogenic to humans
NTP	R	Reasonably anticipated to be human carcinogen
EU	C2	Substances which should be regarded carcinogenic to humans

Table 2. The detected levels of furan as analyzed by EFSA in 2004 (24)

Product category	Number of samples	Furan (ng/g)
Coffee instant	109	394
Coffee, roasted bean	30	3660
Coffee, roasted ground	110	1936
Coffee, not specified	596	2016
Coffee brew	89	42-45
Baby food	1617	31-32
Infant formula	11	0.2-3.2
Baked beans	57	22-24
Beer	102	3.3-5.2
Cereal product	190	15-18
Fish	47	17
Fruit juice	250	2.2-4.6
Fruits	142	2-6.4
Meat products	174	13-17
Milk products	64	5-5.6
Sauces	271	8.3-11
Soups	270	23-24
Soy sauce	94	27
Vegetable juice	80	2.9-9
Vegetables	192	6.9-9.6
Cocoa	14	9-10
Snacks and crisps	133	9.6-10
Soft drinks	18	0.8-1.2
Soya products	15	6.7
Sweets	61	5-6
Tea	22	1-1.7
Vegetable fats	13	1.5-1.7
Wine and liquors	20	1.3

been monitoring furan in food products and have constructed databases for estimation of exposure.

In Europe, the EFSA collects data on furan concentrations in heat-treated commercial food products to better estimate dietary exposure since 2004 and present exposure estimates for different populations annually. Their database contains 5,050 analytical results for furan levels in food from 20 countries in Europe. As shown in Table 2, the highest furan levels were detected in coffee, with mean values between 42 and 3,660 ng/g for brewed coffee and roasted coffee beans. Furan was detected at levels between 0.2 and 3.2 ng/g in infant formula, and ranged from 22 to 24 ng/g in baked beans, from 13 to 17 ng/g in meat products, and from 23 to 24 ng/g in soups. In soy sauce, furan was detected at 27 ng/g, which forms during thermal processing. In vegetable and vegetable juice, furan levels ranged between 6.9 and 9.6 ng/g, and 2.9 and 9 ng/g, respectively. Mean furan exposure was estimated to range between 0.03 and 0.59 ng/g body weight per day for adults and between 0.09 and 0.22 ng/g body weight per day for infants (24). A major contributor to furan exposure for adults was brewed coffee, accounting on average for 85% of total furan exposure. Major contributors to furan exposure in toddlers and other children were fruit juice, dairy products, and cereal-based products, while jarred baby food was another major contributor to furan exposure in toddlers.

In the US, the FDA also collected data on the monitoring of furan in various commercial food products publically available since 2004. Subsequently, the FDA also issued an

Table 3. Furan contents as analyzed by the FDA in 2008 (15)

Product category	Product	Furan (ng/g)
Baked Goods	Archway Ginger Snaps	5.6
	“JIFFY” Corn Muffin Mix	ND
	Bagel Nation Plain Bagels (toasted)	ND
	Biscuit Shack Restaurant Biscuits	ND
	Bodacious Bagels Plain Bagels (Toasted)	ND
	Bodacious Bagels Whole Wheat Bagels (Toasted)	ND
	Dunkin’ Donuts French Cruller Doughnuts	3.6
	Nabisco Fig Newtons	1.7
	Nabisco Lorna Doone Shortbread Cookies	3.6
	Newman’s Own Organics Fig Newmans	12.5
	TOPS Ginger Snaps	30.1
	Whole Foods Blueberry Muffins	ND
	Whole Foods Morning Glory Muffins	ND
	Beverages	Celestial Seasonings 100% Green Tea Bags
Dominick’s 100% Orange Juice (Canned)		1.4
Gold Peak Tea Lemon Iced Tea		0.8
Lipton Summer Peach Ice Tea Mix		ND
Lipton Unsweetened PureLeaf Iced Tea		0.4
Mountain Dew Live Wire		1
Nestea Unsweetened Ice Tea Mix		ND
Safeway Green Tea 100% Natural Tea		0.5
Sunkist Orange Soda		0.4

Table 3. Continued

Product category	Product	Furan (ng/g)
Breakfast Cereals	B&G Cream of Wheat Enriched Farina	ND
	Food Lion Raisin Bran	13.8
	Great Value Oven-Toasted Old Fashioned Oats	ND
	Harris Teeter Bran Flakes	16.1
	Harris Teeter Frosted FruitO's	6.1
	Heartland Granola Cereal	ND
	Kellogg's All-Bran Complete Wheat Flakes	25.4
	Kellogg's Fruit Loops	15
	Nabisco Cream of Wheat	ND
	Post Grape-Nuts	11.6
	Post Raisin Bran	15
Post Shredded Wheat	2.3	
Infant Foods	Beech-Nut Mixed Cereal For Baby	3.9
	Earth's Best Organic Whole Grain Rice Cereal	ND
	Gerber Graduates Biter Biscuits	6.4
	Gerber Prunes With Apples	10.1
	Gerber Single Grain Barley Cereal For Baby	ND
	Gerber Single Grain Rice Cereal For Baby	ND
	O Organics For Baby Organic Prunes	11.6
Meats	IHOP Sausage Links	ND
	Waffle House Sausage Patties	ND
Mixtures	Flavorite Worcestershire Sauce	14.1
	French's Worcestershire Sauce	14.9
	Hunt's Bold Barbecue Sauce	15.5
	Kraft Honey Hickory Smoke Barbecue Sauce	13.5
	Open Pit Original Barbecue Sauce	28
Snacks	Alpine Valley Butter Flavor Popcorn	28.5
	Anderson's Frozen Custard Curly Que Fries	ND
	Arby's Curly Fries	ND
	Bachman Thin'n Right Baked Pretzels	62.8
	Cape Cod Old Fashioned Kettle Cooked Potato Chips	3.5
	Doritos Nacho Cheese Flavored Tortilla Chips	12
	McDonald's French Fries	ND
	Rold Gold Classic Style Sticks Pretzels	40.1
	Ruffles Original Baked! Potato Crisps	21.7
	TOPS Festingos Round Bite Size 100 % White Corn Tortilla Chips	5.8
	TOPS Pretzelwerks Snaps Pretzels	37.9
	Tostitos 100 % White Corn Crispy Rounds	6.2
	Troyer Farms Potato Chips	7.3
Troyer Farms Premium Popcorn with White Cheddar Cheese	30	

action plan for furan monitoring in 2005, which involved expanding the furan databases to about 600 food samples, cooperating with the Alcohol and Tobacco Tax and Trade Bureau to accumulate data on furan levels in alcoholic beverages, and conducting exposure assessments on furan. Since then, the studies have been processed and posted for public awareness. Table 3 shows the results of furan detected in commercial food commodities in 2008. In the category of baked goods, furan was not detected in most of the samples tested, except for ginger snaps (5.6 ng/g), doughnuts (3.6 ng/g), and cookies (3.6 ng/g). In the beverage category, several products contained a low level of furan, but all were

below 1.4 ng/g. Among the category of breakfast cereals, furan was detected at its highest in all-bran wheat flakes, at a level of 25.4 ng/g. Infant foods contained furan at levels ranging from not-detectable to 11.6 ng/g. Furan was not detected in all meat/processed meat products tested. Among the sauce categories, the levels of furan ranged from 13.5 ng/g to 28 ng/g. The highest furan level in this report was in the snacks category, with 62.8 ng/g furan being present in pretzel snacks (15).

The FSA also monitored a range of retail foodstuffs from England, from 2011 to 2013, as shown in Table 4. The significance of the data monitoring system in England is that it

Table 4. Furan contents as analyzed by the FSA in 2014 (25)

Sampling date	Product	Number of samples	Furan (ng/g)
2012	Breakfast Cereals	22	51
2013		22	41
2012	Biscuits & crackers	20	45
2013		20	39
2012	Coffee / coffee substitutes	20	1533
	Coffee / coffee substitutes, as consumed	20	47
	Roast	8	3412
	Roast, as consumed	8	116
	Instant	6	457
	Instant, as consumed	6	2
	Other	6	103
	Other, as consumed	6	0.07
2013	Coffee / coffee substitutes	20	1554
	Coffee / coffee substitutes, as consumed	20	43
	Roast	8	3368
	Roast, as consumed	8	104
	Instant	6	589
	Instant, as consumed	6	4
	Other	6	100
	Other, as consumed	6	1
2012	Baby Food excluding processed cereal	20	48
2013		20	39
2012	Vegetable crisps	4	17
2013		4	15
2012	Popcorn	2	78
2013		2	91
2012	Tortilla / corn snacks	2	15
2013		2	17
2012	Cereal bars / granola	4	7
2013		4	4
2012	Prefab snacks	4	24
2013		4	23
2012	Novelty gingerbread	4	0.07
2013		4	5
2012	Cocoa / Choc powder	3	20
2013		3	12
2012	Prunes (canned)	2	39
2013		2	30
2012	Olives (canned)	2	8
2013		2	8
2012	Jams / preserves	4	2
2013		4	3

allows the direct comparison of detected furan levels in the same sample category in each year. In the UK, furan was detected at 1533 to 1554 ng/g in coffee, and at 39 to 48 ng/g in baby foods. Over the course of a year, the detected levels of furan in many food commodities, including breakfast cereal and crackers decreased, except for the furan levels in

popcorn which increased (from 78 in 2012 to 91 ng/g in 2013). The furan levels in breakfast cereal decreased from 51 to 41 ng/g; in biscuits and crackers, it decreased from 45 to 39 ng/g; in baby food, excluding processed cereal, it decreased from 48 to 39 ng/g; in vegetable crisps, it decreased from 17 to 15 ng/g; in cocoa, it decreased from 20 to 12 ng/

g; and in prunes (canned), it decreased from 39 to 30 ng/g (25).

In Korea, levels of furan in commercial heat-processed

foods have been monitored by use of optimized furan analysis conditions, using SPME-GC/MS, since 2010 (17). The results obtained on the analysis of various commercial

Table 5. Furan levels as analyzed in Korea (17)

Product category	Package type	Product	Furan (ng/g)	Range (ng/g)	Number of samples
Vegetables	Canned	Sweet corn	9.44	5.05-17.45	4
		Kidney bean	45.60	43.60-47.45	1
		Bamboo shoot	3.29	3.08-3.58	1
		Mushroom	29.04	25.56-30.92	1
		Sesame leaf	53.64	47.36-58.30	2
		Baby corn	5.66	5.57-5.76	1
	Jarred	Olive	3.29	1.33-6.26	6
		Cucumber pickle	3.99	2.29-5.80	2
		Caper	2.94	2.55-3.93	2
Meats	Canned	Pork luncheon meat	7.42	2.84-15.39	6
		Korean seasoned pork or beef	85.72	14.21-193.95	3
		Chicken	19.94	18.54-21.96	1
Juice	Canned	Grape	4.96	2.62-9.19	3
		Orange	4.59	3.33-7.59	4
		Pomegranate	2.68	2.65-2.74	1
		Mango	3.78	3.67-3.84	1
		Apple	5.24	5.06-5.40	1
		Grape	3.18	2.62-4.12	3
		Orange	3.45	3.24-3.60	2
Baby foods	Jarred	Strawberry	2.74	2.20-3.53	4
		Grape	2.42	1.92-3.02	3
		Blueberry	2.32	2.30-2.35	1
		Apple	4.75	4.49-4.97	1
		Mixed fruits	3.10	2.55-3.39	1
		Apple	6.19	6.15-6.24	1
		Pear	11.63	10.86-12.93	1
		Mixed fruits	9.45	9.02-9.75	1
		Chicken, rice	61.94	58.68-65.10	1
		Broccoli, carrot, cheese	33.91	32.65-35.60	1
Nutritional/diet drinks	Jarred	Apple, blueberry	3.43	3.39-3.50	1
		Apple, pear, oat, meal	7.69	7.59-7.75	1
		Butternut squash	47.41	46.15-48.96	1
		Peach, banana, muesli	20.43	18.54-21.59	1
Soup	Canned	Sweet potato, apple	97.21	92.64-102.48	1
		Vitamin	7.43	4.85-10.08	4
		Red ginseng	7.12	0.77-19.57	3
		Dietary fibre	7.84	2.39-13.68	2
		Royal jelly, honey	6.02	3.49-7.40	1
Sauce	Jarred	Mushroom	16.93	15.48-18.41	1
		Potato	32.48	27.22-36.20	1
		Chicken, noodle	10.19	8.99-11.15	1
		Clam chowder	14.23	12.40-15.51	1
		Bean, bacon	18.86	15.72-20.68	1
		Chili sauce	6.71	6.10-7.03	1
		Pork rib sauce	12.04	10.26-13.68	1
		Pepper sauce	12.67	9.54-17.82	1
		Oyster sauce	38.11	35.19-43.82	1
		Spaghetti sauce	40.57	37.68-45.87	1

canned and jarred food products consumed in Korea are summarized in Table 5. In aseptically processed and packaged food products, such as canned and jarred products, furan levels have to be estimated, as furan may be lost by

evaporation. In this study, furan was detected in all food samples, and ranged from 0.77 ng/g to 193.95 ng/g, with red ginseng drinks containing the lowest levels and Korean seasoned beef containing the highest levels of furan. Food

Table 6. Furan levels as analyzed in Taiwan (26)

Product category	Product	Furan (ng/g)
Baby foods	G apple prune food	9.9
	G apple jam baby food	14.1
	G mixed vegetable baby food	58.5
	G vegetable chicken baby food	124.1
Baby formulas	W gold baby formula	6.3
	N baby formula	26.1
	K milk powder	6.5
	W fruits milk powder	13.9
	F high quality milk powder	2.7
	N baby cereal powder apple-pear flavored	28.7
Beers	G beer	11.3
	B beer	20.0
	H beer	3.0
Coffee	G cafe	150.0
	B coffee	85.2
	N coffee 3 in 1	58.4
	M reduced sugar low fat coffee 3 in 1	56.5
	M freeze dried coffee mix	55.7
	U special blended instant coffee	58.0
Juices	C 100% tomato juice	7.0
	C asparagus drink	4.0
	P mixed fruit and vegetables juice drink	33.8
	W's grape juice	46.7
Miscellaneous	K soybean sauce	71.2
	B H barbecue sauce	21.7
	K salad dressing	65.3
	C tomato ketchup	44.2
	M chili sauce	12.2
	B H clear chicken broth	26.1
	H clear chicken broth	37.1
	S clear chicken broth	50.2
	C vegetarian vegetable	114.2
	W barbecue sauce	123.0
	W L fried bean sauce	113.2
Jams	L strawberry jam	15.2
	L grape jam	9.2
	G peanut jam	13.2
	F L fructose	9.2
Fish	F tuna slice packed in water	4.2
	O roasted fish	75.2
	R mackerel in tomato sauce	35.6
Canned foods	I oriental pickling melon in sauce	30.5
	W fried gluten with peanuts in soy sauce	99.5
	H pork taste flavored	76.2
Cereals	N nutritious cereal drink	24.1
	N koko crunch	30.1
	N honey star	16.8

samples that are cooked with soy sauce, including canned sesame leaf and Korean seasoned beef, showed higher levels of furan than did other food samples. Some studies have reported that the furan levels in soy sauce ranged from 29 to 91 ng/g (10). Acidic, neutral, and basic volatile fragments originating from hydrolyzed soy protein can form a certain amount of furan. In addition to the acid hydrolyzed soy sauce per se, the thermal processing involved in the canning process increases the furan levels significantly to 370 ng/g after thermal processing of soy (27). The levels of furan in the fruit juice category ranged between 1.65 and 9.19 ng/g. A high level of vitamin C or ascorbic acid in fruit juice may have contributed to the formation of furan, as vitamin C and thermal processing are major contributors to furan formation. All jarred baby foods analyzed in this study contained furan, with levels ranging from 3.39 to 102.48 ng/g. Baby foods are generally heated at high temperatures to protect against microbiological contamination, which may enhance furan formation.

Researchers in Taiwan published the furan levels of 10 categories of commercial food products, including baby foods, baby formulas, beers, coffee, juices, miscellaneous, jams, fish, canned foods, and cereals, using an advanced HS-SPME-GC-MS method, in 2010 (Table 6). The groups of food products containing high levels of furan included baby foods, coffees, sauces, and soups. The levels ranged between 0.4 ng/g (in beverages) and 150 ng/g (in coffee) (26). For baby foods, the detected furan levels ranged from 4.25 ng/g to 124.24 ng/g, depending on the composition of the baby foods. Furan was also detected in infant formulas, with levels ranging from 2.4 ng/g to 28.7 ng/g. The detected furan levels were higher in fruit-based food samples than in milk-based foods. Among the food groups, coffee contained the highest furan levels. It is assumed that excessively high temperature during roasting may be the major reason for the high levels of furan in coffee. A group of miscellaneous foods, including sauces, broths, and soups, was also analyzed in this study. The furan concentrations detected in these food commodities ranged from 1.5 ng/g to 123.0 ng/g. The highest level of furan in this group was detected in barbecue sauce. The major component of barbecue sauce is soy sauce, which contains a relatively high level of furan.

Another study analyzed furan levels in foodstuffs in China. Frequently consumed foods in China were divided to 11 categories, including infant formula (11 samples), bread (10 samples), coffee (nine samples), fruit juice (19 samples), dairy product (15 samples), nutritional drinks (12 samples), canned jam (seven samples), flavorings (five samples), vinegars (18 samples), beers (13 samples) and soy sauce (14 samples) and analyzed. Furan was detected in all analyzed food samples at levels ranging between not-detectable in infant formula and 210.7 ng/g in soy sauce (Table 7). In coffee, furan was present at high levels, rang-

Table 7. Furan levels as analyzed in China (28)

Product category	Furan (ng/g)	Range (ng/g)	Number of samples
Infant formulas	15.0	0.0–43.8	11
Bread	4.0	0.0–10.4	10
Coffee	60.6	13.5–150.7	9
Juice	5.3	0.0–14.3	19
Milk product	1.5	0.0–3.3	15
Nutritional drinks	16.2	0.0–44.4	12
Jams	30.4	2.1–79.4	7
Flavors	9.3	1.9–16.8	5
Vinegars	38.3	2.9–145.8	18
Beers	4.9	0.0–15.2	13
Soy sauce	128.8	51.0–224.7	14

ing between 13.5 and 150.7 ng/g, with an average of 60.6 ng/g. These high levels were in agreement with previous studies (9,20,27). However, the detected levels of furan in soy sauce was slightly higher than those reported in previous studies, with levels in China ranging from 59.5 to 210.7 ng/g, with an average of 128.8 ng/g (28). This study suggests that soybean is one of the raw materials that more easily forms furan during thermal processing, as soybean includes high levels of fat and proteins.

In a study conducted in Chile, the furan levels were monitored in 14 groups of Chilean commercial food products (5). These results are summarized in Table 8. Furan was present in most of the samples analyzed in this study. Furan levels varied considerably, depending on the food samples, and ranged from not-detectable in fried meat to high levels in crisps (259 ng/g) and coffee (936 ng/g). In the case of wheat crackers, Chilean products had a darker color than those from European countries. This color difference would explain the higher levels of furan in the Chilean product. A darker color implies that the food was exposed to thermal

Table 8. Furan levels as analyzed in Chile (5)

Product category	Number of tested samples		Furan (ng/g)
	Total	Positive	
Tomato sauce	8	6	4.0
Orange juice	4	4	6.5
Canned peaches	2	2	6.9
Jarred fruit baby food	3	3	8.5
Peas	3	3	3.5
Peach marmalade	5	5	3.0
Brewed coffee	4	4	6.5
Automatic machine coffee	6	5	936.0
Crisps	7	6	259.0
“Soda”-type crackers	6	6	91.0
Toasted bread	6	3	3.9
Whole breakfast cereal	4	4	20.0
Breakfast cereal	6	2	22.2
Fried meat	5	0	0

processing for a long time; therefore, more furan would be formed (5).

Considering all the data described above, the highest furan levels were detected in roasted coffee beans (average: 3660 ng/g), followed by not-specified coffee (average: 2016 ng/g) and roasted ground coffee (average: 1936 ng/g). The three highest levels were all reported by the EFSA (24). The lowest furan levels in coffee were found in brewed coffee, at 6.5 ng/g as analyzed in Chile (5). In baby foods, such as infant formula categories, furan was detected at 124.1 ng/g in vegetable/chicken baby food consumed in Taiwan (26). According to an FDA report, furan levels in all the samples ranged from not-detectable to 11.6 ng/g (15). There were remarkable differences in the results of baby food analyses across countries. It is assumed that the differences in components in baby food samples underlie these discrepancies. In Korean seasoned pork or beef, furan was detected at 85.72 ng/g, which is high compared to furan levels in other meat products (17). The EFSA reported furan levels in meat products ranging from 13 to 17 ng/g, whereas it was not-detectable according to the FDA report and the monitoring data analyzed in Chile.

Strategies for reducing furan levels in food products.

The common strategy to reduce the toxin levels in foods includes changing the heating conditions or reducing the precursor levels (29). Reducing furan levels is challenging, as compared to reducing the levels of other contaminants. First, changing the thermal processing parameters, such as temperature and time, cannot be modified substantially, as it is required for ensuring the microbiological safety of foods. Second, furan is produced from a variety of precursors such as carbohydrates, polyunsaturated fatty acids, and ascorbic acid. Ascorbic acid is the most frequently found latent precursor of furan, followed by unsaturated fatty acids and sugars (30). With multiple pathways involved in the formation of furan, controlling this process becomes more challenging. Lastly, the high volatility of furan makes the development of a strategy for reducing furan more challenging.

Most of the furan reduction strategies to date have focused on addition of food additives and/or controlling the precursors of furan formation. To date, many previous studies had been conducted on the use of food additives. The effect of food additives on the Maillard reaction has recently been reported by using a food model system (30,31). Using model systems including glucose, alanine, and serine, the reaction of furan with 0.1 M of various metal ions, such as iron sulfate, magnesium sulfate, calcium sulfate, and zinc sulfate, and with antioxidants, such as butyl hydroxytoluene (BHT) and butyl hydroxyanisole (BHA) and sodium sulfite, were analyzed (32). The furan levels in the glucose/alanine model system increased with all additives, by 36~419%, except with addition of sodium sulfite. A significant

decrease in furan formation was shown in the glucose/alanine model when sodium sulfite was added, while it increased by 419% in a sample to which zinc sulfate was added. In most cases, furan levels were decreased, except for samples with added zinc sulfate, in the model system containing alanine and serine, or magnesium and BHT in the model system containing serine. Reduction in furan formation occurred in the following order: sodium sulfite > BHA > iron sulfate > BHT > calcium sulfate (32). The reduction efficiency of the different food additives in a soy sauce model system has also been reported (29). Addition of calcium, magnesium sulfate, BHT, BHA, and sodium sulfite decreased the formation of furan significantly in the following order: calcium sulfate > magnesium sulfate > BHT > BHA > sodium sulfite. In comparison with these additives, other additives such as manganese sulfate, zinc sulfate, iron sulfate, and ascorbic acid, resulted in levels analogous to those in the control (no added food additives) or significantly increased the amount of furan (29).

Adding antioxidants can be an efficient way to reduce furan levels. Antioxidants potentially inhibit furan formation from thermal oxidation of PUFAs and carotenoids because they are scavengers of free radicals formed by PUFA oxidation. One study published in 2011 reported that antioxidants such as tocopherol acetate and BHA reduced furan formation from a PUFA by up to 70% (14). On the other hand, another study reported increased furan formation from a linoleic acid model system, despite the addition of BHT (31). Furthermore, the presence of metal ions in the Maillard reaction affects the rate of formation of Maillard reaction products; however, the mechanism underlying this phenomenon is not clearly established (29).

Use of precursor control has also been reported as a reduction strategy. In a model system using orange juice, development of furfural from ascorbic acid was hindered by the presence of mannitol and ethanol as free radical scavengers (9). Mitigation of atmospheric oxygen reduces furan development from some precursors, particularly ascorbic acid, as do the addition of sulfite and the autoxidation of unsaturated fatty acids (14).

CONCLUSIONS

Furan is a naturally occurring compound present in many types of foods. There are multiple pathways by which furan is formed, such as thermal degradation or rearrangement of carbohydrates alone or in the presence of amino acids, thermal degradation of some amino acids, oxidation of ascorbic acid at high temperatures, and oxidation of PUFAs and carotenoids. Owing to its high volatility, furan has been analyzed using a headspace or SPME coupled with GC-MS. Furan detectability is much more sensitive now than it was in previous years, and detection of low levels is possible because of improved techniques for furan analysis. For

these reasons, the interest in furan risks has increased markedly worldwide. Monitoring and estimation of dietary exposure to furan has been conducted by various national agencies such as the EFSA, FDA, FSA, and by countries such as Korea, Taiwan, China, and Chile. The highest furan levels were detected in coffee categories such as roasted coffee beans, not-specified coffee, and roasted ground coffee, based on the information obtained from the monitoring databases reviewed above. Furan is inevitably absorbed by the intestine and lungs. It can pass through biological membranes and finally reaches various organs. Studies have shown that furan is carcinogenic to rats and mice, and it has been classified as being possibly carcinogenic to humans. Reduction of furan levels in foodstuffs is more challenging than reducing those of other contaminants because thermal processing such as sterilization and pasteurization, which can lead to furan formation from various precursors, is necessary to ensure the microbiological safety of foods. Moreover, given the high volatility of furan, would limit applicability evaluation. Food additives such as calcium sulfate, magnesium sulfate, BHT, BHA, and sodium sulfite have been shown to reduce furan levels in a soy sauce model system.

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