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ESTIMATION OF FURAN LEVELS IN SOME CANNED FOODS IN EGYPT AND HOW TO REDUCE IT

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Abstract
Furan is naturally occurring compound found at low levels in many foods. Furan has been formed in a wide range of thermally treated foods especially heated foods sealed in cans and jars. The primary source of furan in food is thermal degradation and rearrangement of organic compounds. Furan is a five-membered ring which can induce tumors and liver toxicity in experimental animals and is classified as 'possibly carcinogenic to humans' by the International Agency for Research on Cancer. In this study furan levels in several kinds of canned and jarred foods from Egyptian markets have been estimated. Also, several heat treatments have been applied for some food samples aiming to reduce furan content in these samples. Noticed levels of furan have been shown in tested samples. Coffee samples had higher content of furan in comparison to other products. After thermal treatments the obtained results show that, furan content reduced to about 38-50% of the original content for 50 ^{o} C at 5 min and the loss percent raised to about 55-71% at 20 min. At 60 ^{o} C, furan content reduced to about 47-56% of the original content at 5 min and the loss percent raised to about 62-78% at 20 min. And at 70^{o} C, furan content reduced to about 53-59% at 5 min and the loss percent raised to about 70-89% at 20 min.
Key words: Furan, canned foods, thermal treated, Egypt

Introduction

Furan is a heterocyclic, lipophilic compound which can induce tumors and liver toxicity in experimental animals. Furan is clearly carcinogenic to rats and mice, showing a dose-dependent increase in hepatocellular adenomas and carcinomas in both sexes. Furan is rapidly and extensively absorbed from the intestine and the lung. It can pass through biological membranes and enter various organs and is classified as "reasonably anticipated to be a human carcinogen" by the U.S. Department of Health and Human Services and as "possibly carcinogenic to humans" by the International Agency for Research on Cancer (IARC) of the WHO (IARC 1995).

Maga, 1979 reviewed early work of the formation of furan in thermally treated food, identifying the primary source of furans in food as thermal degradation and rearrangement of organic compounds, particularly carbohydrates such as glucose, lactose, and fructose. Maga identified a number of experimental systems known to produce furan in food, including heating of sugars, heating of sugars in the presence of amino acids or protein, and thermal degradation of vitamins including ascorbic acid. Based on studies in model systems of thermally induced furan formation, Perez and Yaylayan 2004 proposed a series of formation pathways for furan in food from sugars, amino acids, ascorbic acid and its derivatives. Ascorbic acid had the highest furan formation potential of the precursors examined in simple model systems. Mark et al. 2006 and Limacher et al. 2007 elaborated further on probable reaction pathways from ascorbic acid to furan.

The US Food and Drug Administration (US FDA) published a report on the occurrence of furan in a number of foods that undergo thermal treatment, especially canned and jarred foods with levels ranging from non detectable to 174 µg/kg. Very similar results were published by the researchers from the Swiss Federal Office of Public Health. Parent furan was identified in a small number of heat-treated foods, such as coffee, canned meat and cooked chicken. Other investigations focused on heated foods sealed in cans and jars, such as baby foods, infant formulas, canned vegetables, baked beans, soups, sauces, stews, and canned meats and fishes. When consumed

in high concentrations (2 mg/kg body weight and day) furan proved to be carcinogenic and mutagenic in animal testing. The International Agency for Research on Cancer (IARC) has therefore classified furan as carcinogenic in animal testing and presumably carcinogenic for humans. According to a preliminary recommendation of the National Toxicology Program (NTP), the acceptable daily intake (ADI) of 1 µg/kg body weight should not be exceeded **(**US FDA 2004**)**. The toxicity of orally administered furan has been extensively studied in mice and rats over a wide dose range. The primary site of toxicity of furan is the liver, although the kidneys and lungs are also affected at high doses (>30 mg/kg-bw per day). In addition, changes in some haematological and hormonal parameters occur at doses as low as 0.12 mg/kg-bw per day administered 5 days/week. In the latest risk assessment on furan carried out by the joint Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Expert Committee on Food Additives (JECFA) it was concluded that the margin of exposure for furan indicates a human health concern for a carcinogenic compound that might act via a DNA-reactive genotoxic metabolite. Mean exposures for adults ranged between 0.25 and 1.17 µg/kg-bw/d and upper percentile exposures ranged from 0.60 and 2.22 µg/kg-bw/d. JECFA chose an exposure of 1 µg/kg-bw/d for the average consumer and 2 µg/kg-bw/d for the high consumer as the basis of its MOE calculation (JECFA, 2010).

A great concern is given to the analysis of this substance naturally occurring in food. This study aims first, to estimate furan levels in several kinds of canned and jarred food. Second, study reducing furan concentration in some food samples using different treatments. Fortunately, furan is a volatile substance, so several heat treatments may affect furan content in test samples.

Materials and methods

Samples of canned and jarred foods which undergo thermal treatment while manufacturing were collected from the local market. The samples included: bean, sweet corn, white beans, sauces, beef, sausages, infant formula, baby food, snacks and coffee. Four cans or jars of each kind of food products have been collected. Samples were prepared and analyzed using FDA/CFSAN, 2004 method as describe below.

Gas chromatography-mass spectrometry (GC/MS) with headspace sampling was used to detect furan in selected-ion monitoring mode (SIM) using ions: m/z 39 and 68 for furan.

Reagents:

1- Furan standard minimum purity 99% (Fluka), store in -20°C freezer.

2- Water, purified by water purification system (Milli-Q)

3- Methanol, HPLC grade

Apparatus:

1. Refrigerator at 4°C.

2. Freezer at -20°C.

3. Analytical balance capable of weighing to nearest 0.1 mg.

4. GC/MS/MS (Agilent 7890N GC with Agilent 7000 MSD with Dynamic headspace auto-sampler).

5. GC column: HP-5, 15 m, 0.32 mm I.D., 20 µm film.

Preparation of standards:

10 µL of the stock solution was diluted to 10 mL in methanol to give a standard solution of 1 µg/mL. From this stock solution 10, 50 and 100 ppb furan concentrations were prepared as working standard solutions and sealed in headspace vials. The stock solution should be stored in a 4°C refrigerator to minimize loss of furan by evaporation.

Samples preparation:

Test portions of 5 g were used, each diluted with 5 g of water. For foods that are not homogeneous, samples were homogenized as follows: the unopened container was chilled at 4 °C in a refrigerator for approx. 4 h. The sample was transferred to a beaker immersed in an ice bath, and the sample was homogenized with a hand blender. Portions of 5 g of the homogenates were used diluted with 5 g of water. All samples were capped immediately with Teflon-lined crimp seals.

Operating Conditions:

Headspace operating conditions: equilibration temperature 60°C, equilibration time 15 min, volume of headspace gas sampled 500 µl.

GC-MS operating conditions: carrier gas helium, constant flow 1.0 ml min-1, oven temperature profile: initial 50 °C (1 min), rate 10 °C min-1 to 230 °C; 150 °C injector; injection mode splitless, purge 0.25 min; MS

ionization mode 75 eV EI+; source temperature 230 °C; scan mode: selected ion monitoring (SIM); ions (m/z): 39, 68 (furan); dwell time 100 ms each ion.

Identification and quantification:
Identification of furan was based on the relative retention time (RRT) and the presence of diagnostic ions. For MS confirmatory purposes, the response ratio for the test portions should agree with the average of the response ratios for the calibration standards by ± 10 percent, and the retention time (RT) for the test portions should agree with the average RTs for the calibration standards by ± 2 percent, considering m/z 39/68 according to the acceptance criteria as stipulated in European Commission Decision, 2002. The quantification of furan in samples proceeded by extrapolation from a linear analytical curve.

All samples have been analyzed twice and the means were calculated.

Samples treatments:
For studying the effect of different heat treatments on furan content in samples, some samples were heated to three degrees (50º, 60º & 70º C) with stirring and for four different periods (5, 10, 15 & 20 min). The treated samples were also analyzed as described above.

Results and discussion
The obtained chromatograms for furan standards are shown in Fig. (1). Whereas, Fig. (2) shows the obtained MS chromatogram of furan compound. By integrating the peak areas of the standards chromatograms, furan standard curve was estimated. The standard curve is viewed in Fig. (3) with its linear equation and correlation coefficient.

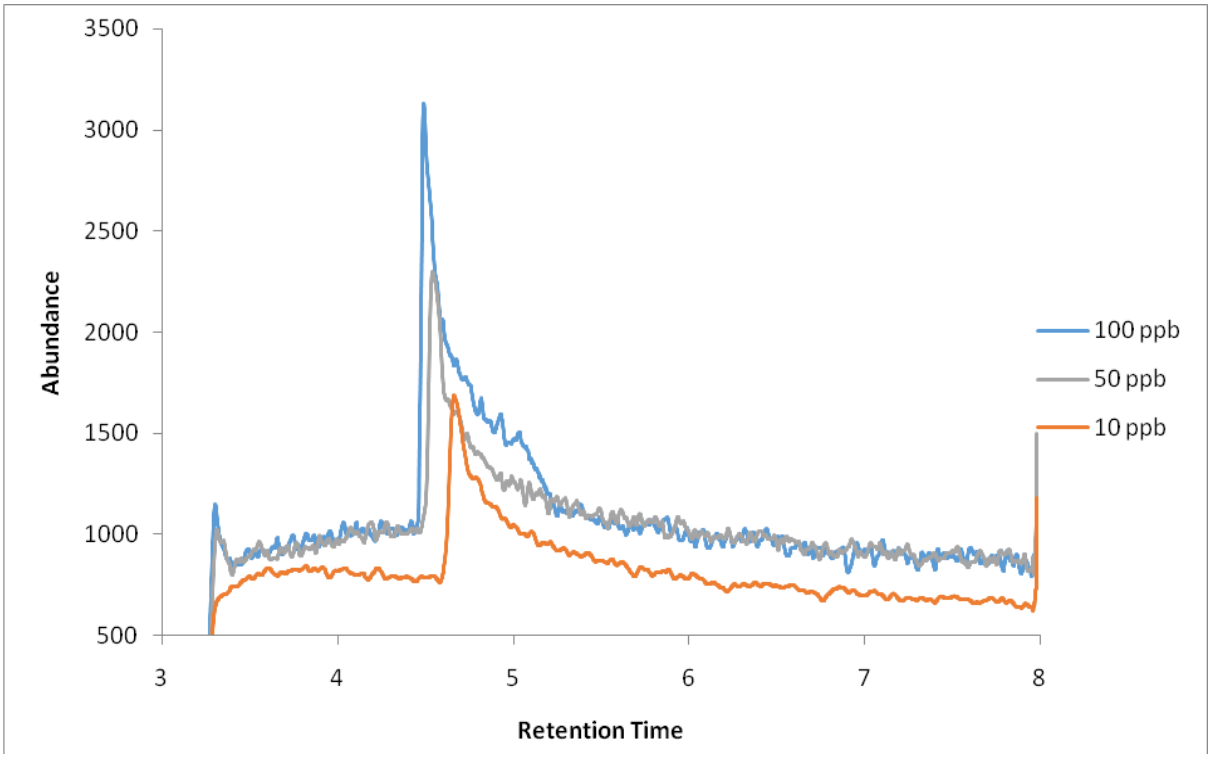

Fig. (1): GC/MC chromatograms for furan standards

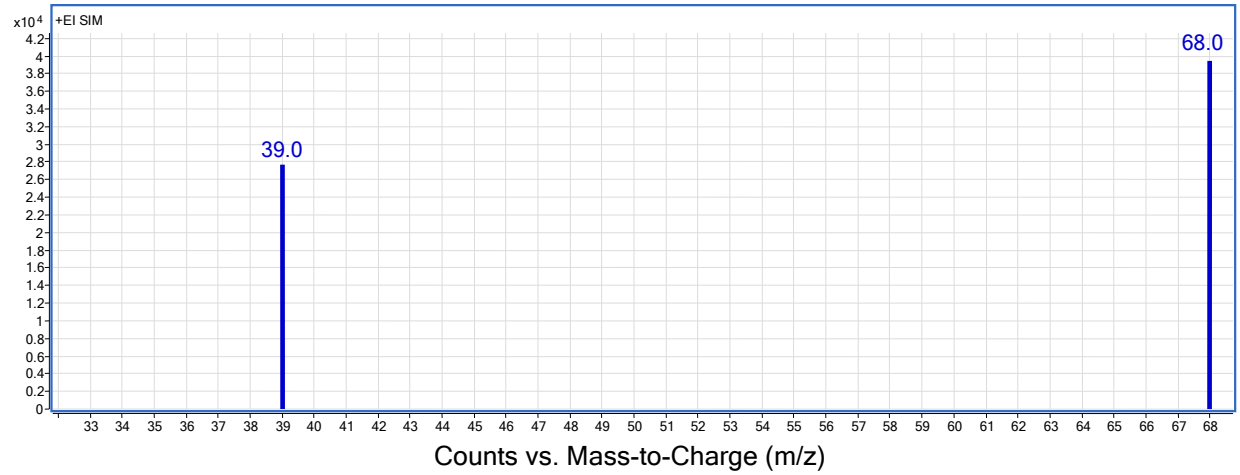

Fig. (2): The obtained MS chromatogram of peak at RT~ 4.5 min (m/z of furan compound)

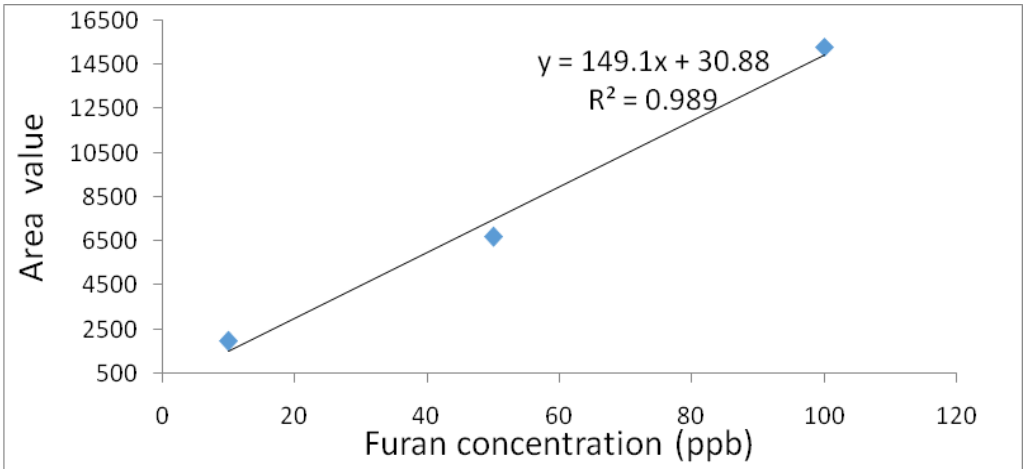

Fig. (3): Furan Standard Curve

Table (1) displays the different levels of furan in different food samples. It is cleared that all chosen samples are shown positive results for furan concentration. Coffee samples showed high content of furan in comparison to other products and that may due to coffee beans are rich in carbohydrates and amino acids and therefore when subjected to the high temperature roasting process, higher levels of furan are formed. Furan levels in food depend on heat treatments and vary depending on the product being processed. For example, beans are generally fried at a lower temperature and for a shorter time compared to roasting of coffee beans which involves higher temperatures (e.g. > 200ºC) and comparatively longer periods of time depending on whether a medium roast, medium to dark roast or dark roast coffee is required. Also, Table (1) show the daily intake of each kind of samples which have been calculated according to Codex Committee on Food Additives and Contaminants (CCFAC, 1989). This revealed that, coffee is the major contributor to furan exposure in the adult population. Morehouse et al., (2008) also identified coffee as the major source of furan in the adult diet in the USA.

It is worth to mention that JECFA, 2010 reported the following ranges for national mean levels of furan in foods with the highest contamination levels: roasted coffee (powder), 814–4590 µg/kg; instant coffee (powder), 90–783 µg/kg; brewed roasted coffee, 34–113 µg/kg; jarred baby foods, 19–96 µg/kg; soy sauce, 16–52 µg/kg; canned fish, 6–76 µg/kg; and baked beans, 27–581 µg/kg.

Great concern should be taken to avoid consumption a lot of food which contains

some levels of furan especially babies and infant foods whereas - according to a preliminary recommendation of the National Toxicology Program (NTP) - the acceptable daily intake (ADI) of 1 μg/kg body weight a day should not be exceeded. However once furan formed it cannot evaporate from processed food contained in an airtight sealed pack until the container is opened. Residual furan that may be present in the food after first opening the container may also evaporate over time. As furan is a volatile substance, it appears that furan levels can be reduced in some foods through volatilization e.g. by heating and stirring canned/jarred foods in an open saucepan. So, five samples have been chosen for heat treatments after opening the container at three degrees (50º, 60º & 70º C) and for four different periods (5, 10, 15 & 20 min).

Table (1): Furan content in different samples with its relative standard deviation and calculated daily intake

Sample	Furan conc.(ppb) before treat.	Furan conc.(ppb) after 5 min.	Furan conc.(ppb) after 10 min.	Furan conc.(ppb) after 15 min.	Furan conc.(ppb) after 20 min.
bean	13.7	8.8	7.3	6.6	6.3
white beans	14.8	8.7	7.5	6.8	6.1
sauces	7.4	3.7	2.9	2	1.7
sausages	13.4	8.3	6.9	6.2	5.9
beef	21.1	11.8	9.4	8.5	7.1

The results of treatment at 50º, 60º & 70º C are illustrated in Tables (2, 3 & 4) respectively. From these results, it is clear that heating reduced the level of furan in the tested food samples in all treatment and that attributed to heating food samples with stirring allow partial volatilization and dissipation of furan.Furan content reduced to about 38-50% of the original content for 50 º C at 5 min and the loss percent raised to about 55-71% at 20 min. At 60 º C, furan content reduced to about 47-56% of the original content at 5 min and the loss percent raised to about 62-78% at 20 min. And at 70º C, furan content reduced to about 53-59% at 5 min and the loss percent raised to about 70-89% at 20 min.

Table (2): Furan content in some samples after heat treatment at 50ºC and at different period

Sample	Range of furan concentration (ppb)	± RSD	Daily intake
Bean	9.55 – 13.7	0.18	0.87-1.02
sweet corn	18 – 23.2	0.17	0.64-0.83
white beans	12.1 – 14.8	0.15	0.94-1.16
sauces	4.8 – 7.4	0.3	0.47-0.73
infant formula	13.1 – 16.6	0.16	0.12-0.15
sausages	8.5 – 13.4	0.31	0.83-1.21
beef	17 – 21.1	0.15	1.6-2.03
baby food	25.7 – 34.7	0.21	0.23-0.33
snacks	6.4 – 8.3	0.18	0.53-0.69
Light-colored coffee	482.7 – 512.6	0.05	2.0-2.2
Dark coffee	702 - 789.2	0.1	2.8-3.2

Table (3): Furan content in some samples after heat treatment at 60ºC and at different period

Sample	Furan conc.(ppb) before treat.	Furan conc.(ppb) after 5 min.	Furan conc.(ppb) after 10 min.	Furan conc.(ppb) after 15 min.	Furan conc.(ppb) after 20 min.
Bean	13.7	8.4	7.1	6.2	5.3
white beans	14.8	7.9	7	6	4.9
Sauces	7.4	3.2	2.1	1.5	0.9
Sausages	13.4	8.4	7	5.9	5
Beef	21.1	10.2	8.9	7.7	6.1

Table (4): Furan content in some samples after heat treatment at 70°C and at different period

Sample	Furan conc.(ppb) before treat.	Furan conc.(ppb) after 5 min.	Furan conc.(ppb) after 10 min.	Furan conc.(ppb) after 15 min.	Furan conc.(ppb) after 20 min.
bean	13.7	7.3	6	5.1	4.3
white beans	14.8	6.9	5.8	5	4.4
sauces	7.4	3	2	1.3	0.8
sausages	13.4	8.1	7	5.8	5
beef	21.1	9.8	8.1	7.1	6

Above results revealed the decreasing of furan content for all heat treatment and as long as time of heat exposure increases the furan content decrease through volatilize tion. Then, the extent of furan loss is related to the temperature of the product and time of exposure to heat which agrees with Goldmann et al. (2005) who reported the decrease of furan concentrations over time upon heating in open jars, thus leading to 85% loss. While, Kim et al. (2009) found that heating canned meats to 50-70 ºC reduced furan levels 26 to 46 percent.

Conclusion

More concern should be taken for exhausting canned or jarred foods, which undergo high thermal treatment while manufacturing, especially baby and infant foods because of its furan content. Also, this study may be helpful in establishing approaches to lower the exposure of the population to furan from the consumption of coffee which contains the highest furan levels in comparison to other products. Furan is not stable in foods after or opening the commercial products then it is recommended to heat canned or jarred foods before consumption. Heating the food after opening the container at about 60-70 ºC for few minutes with stirring would be enough for evaporate most of furan content.

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