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Mitigation Strategies of Furan in Coffee Beans by Irradiation Process

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ABSTRACT

Furan is a volatile compound presence in coffee due to thermal processing and its classified as possibly carcinogenic to human. In recent years, different technological strategies to prevent or mitigate furan formation in foods have been performed. The present work as a part of long term program aims to reduce the toxic substances resulted due to roasting process by using γ-rays. The present investigation studied the furan content in different types of coffee beans (green, light and dark roasted beans) before and after irradiated with different doses (5.0,10.0 and 20.0 kGy) of γ- irradiation. The results obtained proved that green coffee beans were less content in furan which increased linearly by thermal process, whereas irradiation doses decreased linearly with high significant correlation coefficient (R2). Therefore, γ- irradiation doses (5.0,10.0 and 20.0kGy) were used for decontamination of molds in collected green coffee beans for decontamination at 10 -20 kGy than using roasted beans (as reported before by same workers). In this respect, the irradiated green coffee beans become more safety with low furan besides free of mould contamination. The present work recommended that using low-dose (10kGy) of γ- irradiation are the ideal solution to reduce the toxic substances besides decontamination, disinfestations of green coffee beans as safe alternative of using harmful chemical for human consumption besides decreasing furan content.

Keywords: Irradiation, Furan, Coffee, Thermal processing, Roasted beans.

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INTRODUCTION

Coffee is one of the most popular drink in the world. Beneficial health effects to coffee, mainly due to its high content of antioxidant components. Thermal processing during roasting activate Millard reaction products of flavor as non-volatile compounds like acrylamide or volatile as furan. US Food and Drug Administration [1] reported that furan compound exist in different thermally treated foods. Unfortunately, furan is classified as possibly carcinogenic (Group 2B) to human in food [2, 3, 4, 5]. Furan (C_4H_4O) is a small organic molecule with high volatility (Fig.1).

Figure (1). Structure of Furan.

Furan and its derivatives recognized as contributors to the sensory properties of a wide variety of foods as coffee flavor. High levels of furan are part of coffee flavor volatiles, were found in roasted coffee beans, ranged from 239 to 5050 ng g^{-1} [6]. Therefore, it has been estimated that coffee consumption may be the highest contributor to furan exposure from dietary sources for adults [7, 8 9]. The same compound can produce in unprocessed foods even under mild (40°C) thermal conditions [10]. It has been shown that furan-induced by thermal treatments from simple carbohydrates, ascorbic acid, amino acids, fatty acids, or a mixture of these compounds [11].

The possible approaches for mitigation of furan in post processing coffee involved irradiation, vacuum treatment, suitable heating and high-pressure processing without flavor-affecting [12, 13]. Positive results for reducing Acrylamide in coffee beans by irradiation were obtained by Egyptian authors [14]. On the contrary, another study in juices indicated that irradiation increased furan [15]. Irradiation of food became more easily and application on a commercial scale of more than 50 countries for decontamination purposes specially to control pathogens [14].

No, available data for reducing furan levels by γ- rays in coffee beans. Therefore, the present work aimed to study the possibility of reducing furan in green and roasted coffee beans at safety low doses.

MATERIALS AND METHODS

Sampling

Fifty samples of imported Arabica coffee (green beans) (*Coffee Arabica* Linn. ,*Rubiaceae*) were randomly collected from different locations of Egyptian markets-Cairo. Each sample (250gm) was packaged in sterile polyethylene bag, sealed to keep in dry storage room even analysis.

Roasting process

Green coffee bean samples were roasted using electrical oven at 200^{0}C by common machine of coffee-private shop for two periods the first time (10 min.) to get light coffee. Whereas, the second time (20 min.) to get deep roasted or dark coffee. After roasting, beans were cooled by oven switch off even room temperature.

Irradiation process

The irradiation process was carried out at National Centre for Radiation Research & Technology (NCRRT). Samples were irradiated with γ- rays at different doses 0.0, 5.0,10.0 and 20.0 kGy. The irradiation process was performed at room temperature using a γ-source Co^{60} at dose rate of ~ 4.0 kGy/h. The irradiation source had been calibrated by the National Physical Laboratory (NPL, Teddington, UK) using the dichromate dosimetry system.

HS-GC/MS furan analysis

Samples were prepared and analyzed by gas chromatography-mass spectrometry (GC/MS) with head space, sampling was used to detect furan in selected-ion monitoring mode (SIM) using ions: m/z 39 and 68 [1]. The reagents involved Furan standard minimum purity 99% (Fluka) and stored in (-20°C) freezer. Also, water purified by water purification system (Milli-Q) and Methanol (HPLC grade). Furan was determined by HS GC–MS. Individual stock standard solutions of furan were prepared by transferring each pure analyze via a micro syringe through the septum of 20 mL headspace vials containing methanol. GC/MS/MS (Agilent 7890N GC with Agilent 7000 MSD with Dynamic headspace), auto-sampler, GC column: HP-5, 15 m, 0.32 mm I.D., 20 µm film were used.

Standards preparation

Ten µL of stock furan solution was diluted to 10 mL in methanol to give a standard solution of 1 µg/mL. From this stock solution 10, 50 & 100 ppb furan concentrations were prepared for working standard solutions and sealed in headspace vials. The stock standard should be stored in a 4°C refrigerator to minimize loss of furan by evaporation. The standard curve was plotted as in Fig.2.

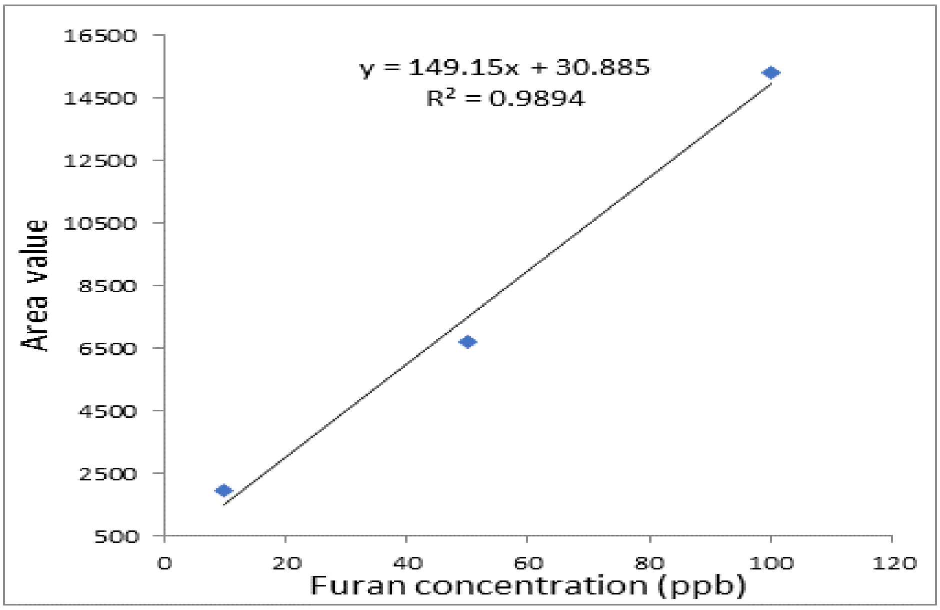

Figure (2). Furan calibration curve.

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

Whereas, the 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. In addition, selected ion monitoring (SIM) was used at ions (m/z): 39, 68 (furan) and dwell time 100 ms each ion. Headspace operating conditions: equilibration temperature 60°C, equilibration time 15 min, volume of headspace gas sampled 500 µl. GC-MS operating conditions used carrier gas helium, constant flow 1.0 ml min^{-1}, oven temperature profile. The obtained MS chromatogram of peak at RT~ 4.5 (m/z of furan compound) was recorded in (Fig.3).

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 (R_T) for the test portions should agree with the average RTs for the calibration standards by ± 2 percent, considering m/z 39/68. 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 (Fig.4).

Statistical analysis

Differences among model system were determinate by analysis of variance and using Excel program; a Microsoft computer software to get value of R^2. All values were average of three replicates with standard deviation.

Degradation rate (%)=furan content of control treatment-treated sample /control treatments X100.

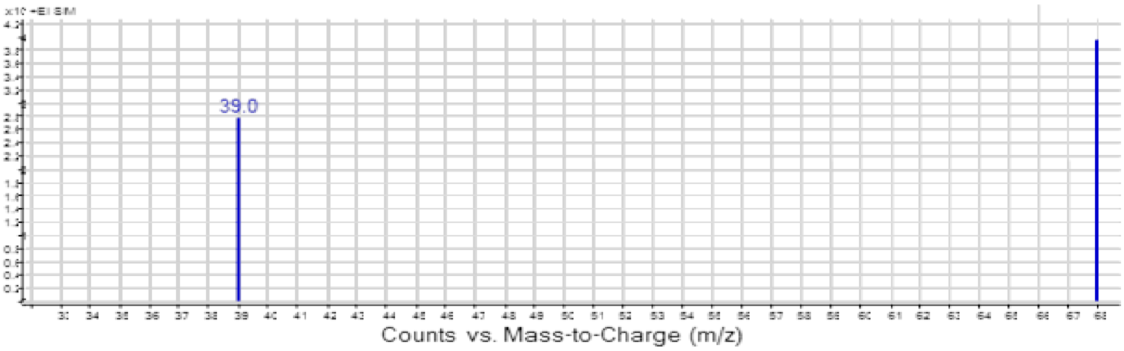

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Figure (3). The obtained MS chromatogram of peak at RT~ 4.5 (m/z of furan compound).

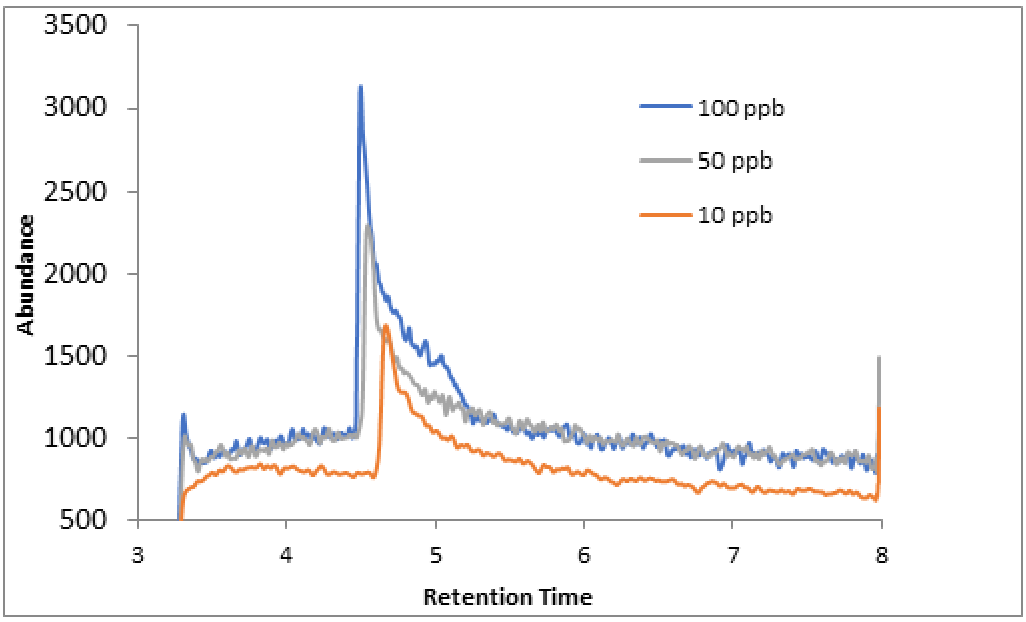

Figure (4). HS- GC/MS chromatograms for furan standards.

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RESULTS AND DISCUSSION

Furan has been demonstrated to be formed in a variety of heat processed foods such as coffee and jarred foods, including baby food containing meat or vegetables (Table 1). It is a potential health concern which classified as 'possibly carcinogenic to humans' [2, 16]. Either, furan or its derivatives were recognized as contributors to the sensory properties of a wide variety of foods. [17] reported that the highest furan levels in foods and exposure assessment, in a total of 5,050 analytical results in 20 countries was 6,407 µg kg^{-1}. The obtained results showed the role enhancement of furan by thermal treatment. Although the mechanism of furan formation in food is not completely understood, it can be synthesized from vitamin C, amino acids, reducing sugars, organic acids, and polyunsaturated fatty acids in the presence of heat [18, 19]. The presence investigation proved that irradiation reduced dramatically the concentration of furan.

Temperature dependence of furan

Furan determination in foods by HS-GC-MS is considered the simpler and accurate method as showed by many workers recently [20]. Many investigators showed that highest furan content is present in coffee beans before preparing the final coffee brew. Among all such products tested, the highest furan content was reported in roasted coffee beans with an average of 3,660 µg/kg. This is at the lower end of the average values reported by [21] for furan in roasted coffee bean. As shown in Table (2), Furan coffee beans, increase as 216% and 329% at 10 and 20 min naturally in green coffee (183.5 µg.kg^{-1}) before thermal process, it may be produced due to drying process of green beans after harvest. Whereas, high temperature at 200^{0}C increased furan content especially at 20 min to produce light and dark, respectively. The furan rate increase was express as rate percentages which was depend on temperature and time of roasting. That relationship was linear with high significant values of the correlation ship coefficient (R^2), as shown in Table (2) and Fig. (5). [22, 23] showed that darker roast colors and longer roast times had a tendency to result in higher levels of furan.

Table 1. Furan concentrations found in some foods commodities on the Swiss Market (according to REINHARD *et al.* 2004 and Swiss Federal Office of Public Health)

Sample description	Furan value (PPB)		Median (PPB)	Number of samples
	minimum	maximum		
Baby food in small glass jars	1	153	12	102
Fruit and vegetable juices for babies and young children	1	40	3	4
Coffee (drink)	13	146	74	9
Hot chocolate and malt beverage	< 2	< 2		2
Canned or jarred vegetables	< 2	12	3	15
Canned soups	19	43		2
Canned fruits	< 1	6		2
Tin containing meat	4	4		1
Tin containing meat and pasta	14	14		1
Sugo, tomato and Chilli sauces	< 4	39	6	13
Soy sauce, hydrolysed vegetable protein	18	91	50	7
Vegetables, fresh	< 1	< 2	< 1	7
Bread and toast	< 2	30	< 2	7
Whole milk UHT	< 0.5	< 0.5		1
Plum beverage	6	6		1
Beetroot juice with fruit juices (organic)	1	1		1
Potato flakes for mashed potatoes (flakes, not prepared)	< 5	< 5		1

Table 2. Effect of irradiation doses on Furan content of coffee (µg. kg^{-1})

Irradiation dose (kGy)	Green beans	Light roasted beans (10.min /200°C)	Dark roasted beans (20 min./200°C)
Control	183.5±17.0	581.6±15.0 (+216%)	789.2±15.4(+329%)
5.0	101.3±15.0(-45%)	204.6±10.0 (-65%)	244.3±14.4(-69%)
10.0	96.2±13.0(-48%)	177.8±8.0 (-69%)	211.1±12.2(-73%)
20.0	90.1±11.5(-51%)	156.6±9.0 (-73%)	205.5±11.2(-74%)

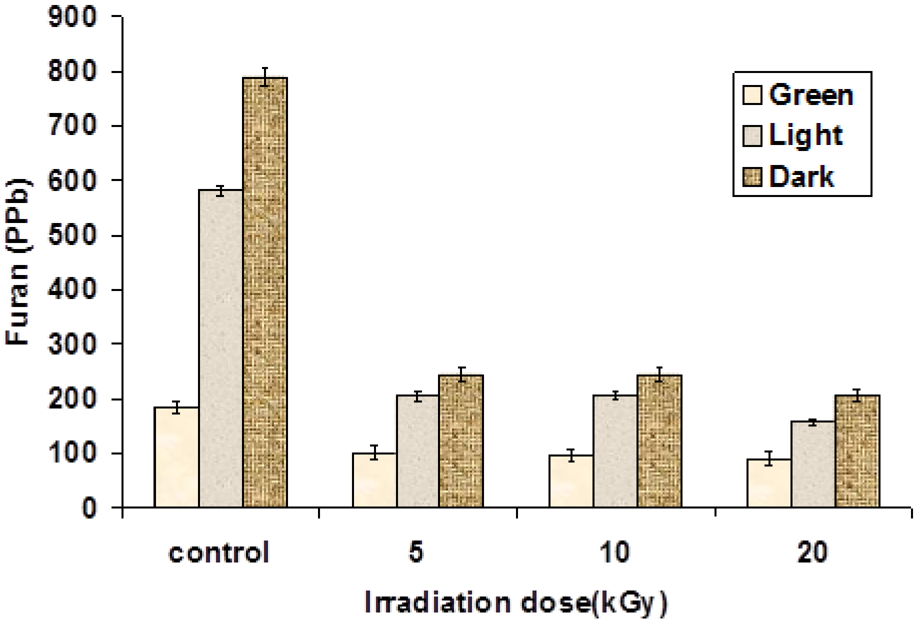

Figure (5). Effect of irradiation doses on Furan content of coffee. (µg.kg^{-1})

The combination effect of thermal, irradiation was clearly as shown in Fig. (6). The linear equation showed that producing rate of furan per one degree temperature as calculated from linear equations, for control green beans during roasting process to (113 µg.kg^{-1}) then decreased dramatically to 39,35,54 (µg.kg^{-1}) after irradiation with 5.0,10.0 and 20.0 kGy. These results proved the possibility of irradiation to mitigate furan formation in coffee.

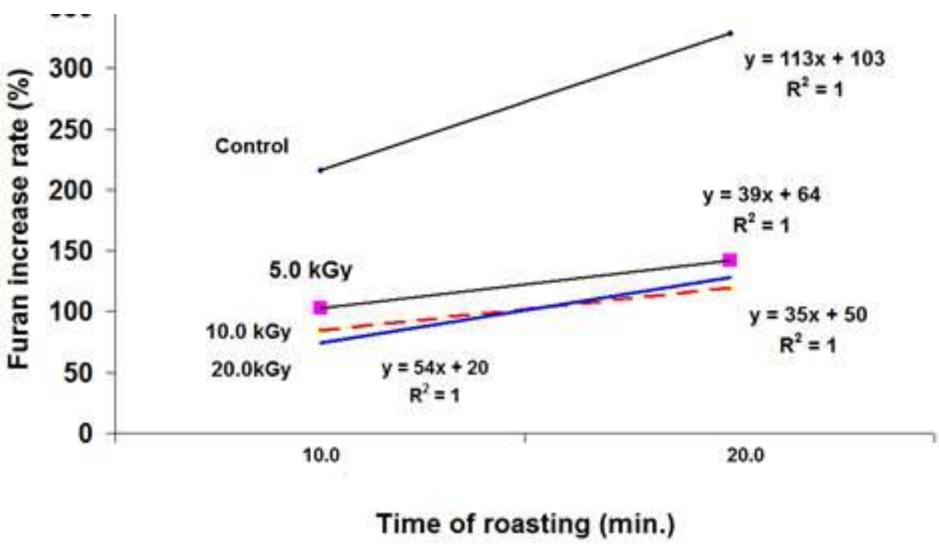

Figure (6). Linear relationship between furan rate (%) increase and thermal process at 200^{0}C.

Effect of irradiation on furan levels

Mitigation of furan in foods is difficult because the mechanism for its formation in food is unclear. Due to the fact that furan is volatile, it is thought that concentrations can be reduced by heating food in open containers or leaving ready-to-eat foods open to air after preparation [24, 25]. Currently, there are no FDA regulations specific to the level of furan in food. It's necessary to mention that many factors effect on furan content in food especially, original sources, preparing coffee drinks [14] or presence of antioxidants [26].

Most of past studies of increasing furan by irradiation were conducted in model systems using pyrolysis-GC-MS, besides it was juices with high water content [15]. But in our trial the water content was 20% in green coffee beans. Irradiation doses were more effective in reducing the formation of furan (Table 2), its recorded that 183.5 µg.kg $^{-1}$ decreased to 101.3µg.kg^{-1} (-45%), to 96.2. µg.kg^{-1} (-48%), to 90.0. µg.kg^{-1} (-51%) after irradiation with 5.0 ,10.0 and 20.0 kGy, respectively. The same trends were observed in roasted coffee beans after irradiation either at 10 min or 20 min. These data were plotted in the linear correlation ship as shown in Fig (6) with high significant (R^2). The linear equation showed that the high degradation rate of furan by irradiation in roasted coffee beans than green beans. Calculated as the rate of slope, it was 113 for green beans, but decreased 39, 35 and 54 after irradiation with 5.0,10.0 and 20.0, respectively. That is proved the rapidly of degradation of furan by irradiation. That is the first time to get positive trend by irradiation for reducing furan as toxic substances in green coffee beans. A high value was recorded before by many workers. The highest concentration was found in a coffee sample (11294 µg kg^{-1}), and the lowest content of furan was found in fruit juice (0.51 µg kg^{-1}) [20]. Also**,** some workers showed that concentrations of furan present in food and coffee ranged from undetectable to approximately 175 µg/kg but raise in coffee powders up to 5000 µg/kg on a dry weight basis [25].

The combination effect of thermal and irradiation was clearly as shown in Fig. (6). The linear equation showed that producing rate of furan per one degree temperature as calculated from linear equations, for control green beans during the roasting process to (113 µg.kg^{-1}) then decreased dramatically to 39,35,54 (µg.kg^{-1}) after irradiation with 5.0,10.0 and 20.0 kGy. These results proved the possibility of irradiation to mitigate furan formation in coffee.

CONCLUSIONS

Furan is one of a group carcinogenic substances that can form when foods and drinks are subject to heat treatment due to the reaction between carbohydrates, unsaturated fatty acids and ascorbic acids or its derivatives (Maillard reaction). Considering that the population could be highly exposed to furan since it is present in several foodstuffs. Irradiation can decrease furan content even safe levels less than 1 µg/kg-bw/d. This level of toxicity of furan were recommended by international agencies, [27]. From a scientific perspective; it is can be explained that irradiation role in reduction of precursor concentration in the raw materials (green coffee beans), through degradation the chain of Maillard reaction. That is can occur through block precursor as reducing sugars, ascorbic acid, amino acids, fatty acids, or a mixture of these above compounds produces a decreasing in the final furan content of roasted coffee.

Finally, the strategy of reducing furan can involve thermal after irradiation process of green beans as proved in our data by using 10 kGy to remove many toxic substances as acrylamide and Ochratoxin A besides Furan, thus, irradiation of green coffee beans is easily for application besides considered as feasible alternative to produce healthier drink, with lower amounts of food processing contaminants.

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