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Impact of consumer behavior on furan and furan-derivative exposure during coffee consumption. A comparison between brewing methods and drinking preferences

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ABSTRACT

This study examined the influence of consumer behavior on furan, 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran and 2,3-dimethylfuran exposure in coffee. Coffees brewed using a filter, fully automatic, capsule machine or reconstituted instant coffee were found to have a significant different cup concentrations of furan derivatives. Coffee brewed with the fully automatic machine contained the highest furan and furan derivative concentrations (99.05 µg/L furan, 263.91 µg/L 2-methylfuran, 13.15 µg/L 3-methylfuran and 8.44 µg/L 2,5-dimethylfuran) whereas soluble coffee did not contain detectable levels, thereby contributing least to a consumer's dietary exposure. Furan and furan derivative concentrations were found to decrease significantly upon cooling, reducing consumer exposure by 8.0–17.2 % on average once the coffee reached drinking temperature 55–60 °C, in ceramic cups. Serving coffee in a ceramic or disposable cup were found to influence the cooling dynamics of the coffee but did not statistically influence the consumers exposure at a given temperature.

1. Introduction

Furan, 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran and 2,3-dimethylfuran, hereafter collectively called furan derivatives, Table S1, have been known to be present in coffee since the 1960s and 1970s (Maga & Katz, 1979; Stoffelsma, Sipma, Kettenes, & Pypker, 1968). Nevertheless, it was only since the mid-nineteen nineties, when the International Agency for Research on Cancer (IARC, 1995) classified furan as type 2B, *possibly carcinogenic to humans*, that determining consumer's exposure became necessary. Ubiquitously present in thermally processed foods, furan exposure studies revealed that coffee contributes most significantly to an adult's dietary exposure (Fromberg, Mariotti, Pedreschi, Fagt, & Granby, 2014; Mariotti, Granby, Rozowski, & Pedreschi, 2013; Scholl, Scippo, De Pauw, Eppe, & Saegerman, 2012; Waizenegger et al., 2012). Moreover, coffee is one of the only foods known where 2-methylfuran levels consistently exceed those of furan (Becalski et al., 2010), revealing that coffee also significantly contributes to a consumer's dietary exposure to 2-methylfuran. Methylfurans appear to be metabolized, at least in part, in a similar manner to furan, resulting in highly reactive intermediates leading to a similar toxicity (Becalski et al., 2010). Due to a shared metabolic pathway, methylfurans are considered to contribute to furan toxicity (Becalski et al., 2010). Despite coffee being a significant dietary source of furan derivatives, in 2016 the IARC completed their reassessment on the potentially carcinogenic effects of coffee, reclassifying it as type 3, "*not classifiable as to its carcinogenicity to humans",* based on insufficient evidence to justify coffee's previous classification as type 2B, "*possibly carcinogenic"* (IARC, 2016).

Initially absent in green coffee beans, furan derivatives are generated upon roasting from the thermal degradation of endogenous components (Becalski & Seaman, 2005; Limacher, Kerler, Davidek, Schmalzried, & Blank, 2008; Locas & Yaylayan, 2004; Van Lancker, Adams, Owczarek-Fendor, De Meulenaer, & De Kimpe, 2011; Yaylayan, 2006). Model studies conducted under simulated roasting conditions indicate that furan and its derivatives originate from similar precursors in separate but parallel pathways (Limacher et al., 2008). Furan was found to preferentially form directly from carbohydrate degradation (Limacher et al., 2008; Van Lancker et al., 2011), where arabinose, the most liable carbohydrate moiety within green coffee beans (Bradbury, 2008), served as a particularly efficient precursor (Limacher et al., 2008). Whereas 2-methylfuran forms predominantly from the condensation of carbohydrate moieties generated during the Maillard

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reaction (Limacher et al., 2008), origins of 3-methyl-, 2,5-dimethyl- and 2,3-dimethyl-furan have yet to be established.

The concentrations generated during roasting are not directly predictive of the consumers' exposure. Instead, concentrations of furans in the cup will depend upon the coffee's composition, processing and brewing method, amongst numerous other factors (Altaki, Santos, & Galceran, 2011; La Pera et al., 2009; Mariotti et al., 2013; Morehouse, Nyman, Mcneal, Dinovi, & Perfetti, 2008; Waizenegger et al., 2012). Furan has been found to decrease by approximately 90% from bean to cup (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010), due to its high volatility, reflective of its low boiling point, 32 °C. Little information, however, is available regarding cup concentrations of furan's higher boiling methyl derivatives (see Table S1). Initial furan derivative concentrations within freshly brewed coffee may be decreased further during cooling, as suggested by Guenther (2012), reducing consumers' exposure.

Previous studies demonstrate varying degrees of furan loss upon coffee cooling. Goldmann, Perisset, Scanlan, and Stadler (2005) as well as Zoller, Sager, and Reinhard (2007) observed that consumer furan exposure was reduced by approximately 45–50% when the coffee was cooled for an hour, whereas Guenther et al. (2010) reported a 10% loss within the same time period. Moreover, Mesias and Morales (2014) findings suggest that furan loss is also dependent upon stirring before consumption. Their findings demonstrate that passive cooling is 10% more efficient than brief manual stirring, which decreases furan content by 64%, whereas continuous mechanical stirring will reduce furan exposure by 94% within five minutes (Mesias & Morales, 2014). Han, Kim, and Lee (2017) observed a 2–22% decrease in furan over five minutes, reporting furan loss was dependent on coffee type, water temperature, storage temperature and the presence or absence of a lid. These authors observed that while furan loss was greatest from coffees cooled without a lid, using a higher temperature to prepare or store the coffee led to higher furan levels within the freshly brewed cup (Han et al., 2017). The higher furan levels found within canned coffee stored at 60 °C were offset by the greater rate of furan loss upon can opening, resulting in approximately equivalent furan exposure between the two storage temperatures after five minutes (Han et al., 2017). Interestingly, their results demonstrate that preparing instant coffee at a higher temperature, 100 °C instead of 85 °C, led to higher concentrations, suggesting *in situ* formation of furan (Han et al., 2017).

The present study aims to investigate consumer exposure to furan and its methyl derivatives resulting from typical coffee preparation and drinking behavior. Furan loss over cooling was assessed in four typical coffee brews, including fully automatic, filter, instant and capsule systems, which were prepared in either a ceramic or lidded disposable cup.

2. Materials and methods

2.1. Chemicals

The following chemicals were used without further purification: furan (≥99%), d_4-furan (≥99%), 2,5-dimethyl furan (99%), 2,3-dimethyl furan (99%) purchased from Sigma-Aldrich (Schnelldorf, Germany); 3-methylfuran (> 98%) purchased from Thermo Fisher Scientific (Geel, Belgium); methanol (≥99.9%) purchased from Honeywell (Bucharest, Romania). Commercially available 100% Arabica blend medium roasted Tchibo coffee as well as Cafissimo capsule "strong" coffee 100% Arabica (Hamburg, Germany). Nescafé Gold Blend instant coffee (United Kingdom).

2.2. Standards preparation

Furan standard containing furan (40 µL), 2-methylfuran (120 µL), 3-methylfuran (10 µL), 2,3-dimethylfuran (10 µL) and 2,5-dimethylfuran (10 µL) were prepared fresh daily in 20 mL headspace vial as a methanol stock solution. 250 µL of the furan derivative stock solution was then added through the septum into a 20 mL headspace vial containing 20 mL of Milli-Q water. d_4-furan internal standard was prepared according to the Food and Drug Administration (USFDA) guidelines (USFDA, 2004). Limit of quantitation (LOQ) and limit of detection (LOD) were calculated according to the following equations for each compound, in each matrix, and are included in the supplementary material (Table S2).

$$LOD = (3\times SD)/slope\,(ng/mL)$$

$$LOQ = (10\times SD)/slope\,(ng/mL)$$

2.3. Sample preparation

Coffee was received approximately one week after roasting and immediately stored at −20 °C. A single 1 kg bag was thawed every day for two hours before use to achieve room temperature.

2.3.1. Whole bean furan content

Whole beans were kept at −20 °C before grinding. Coffee was ground at three grind sizes on Mahlkönig EK43/1 (Hamburg, Germany), 3 (D[3,4] 327 ± 4 µm), 6 (D[3,4] 540 ± 1 µm) and 9 (D[3,4] 760 ± 11 µm). Standard addition was performed on two water to coffee mixtures, 0.05 g coffee in 4.95 mL water or 0.1 g coffee in 4.9 mL water. The coffee, vials and water were kept at 4 °C during weighing.

2.3.2. Filter coffee

A Moccamaster KBG 741 AO (Amerongen, Netherlands) was used for the purpose of this study. Coffee was ground on a Mahlkönig EK43/1 (Hamburg, Germany) using a grind size typical for filter coffee (grinder setting 9 D[3,4] (766 ± 12 µm)). Five grams of coffee were used to clean the grinder before the brewing sample was ground. Within three minutes of grinding, 48 ± 0.29 g of coffee was weighed into a No. 4 Moccamaster filter (Amerongen, Netherlands) resting within the respective machine's brewing basket. The basket was then returned to the respective machine that had been previously filled with 900 mL of water (Total hardness: 80 ppm $CaCO_3$. Alkalinity: 45 ppm $CaCO_3$). Brewing was immediately commenced after replacement of the brewing basket and allowed to complete to the last drop before the carafe was removed from the hotplate. The full brewing time was 4 min 48 ± 18 s. 125 ± 2.25 g of coffee was poured into the respective container (ceramic cup or disposable cup) before a temperature sample was taken. A fresh pot of coffee was brewed for every temperature measurement.

2.3.3. Fully automatic

A Schaerer Coffee Art Plus (Zuchwil, Switzerland) was used, programmed and calibrated to deliver 125 g of brew within an 18.9 ± 0.3 s extraction time from 9 g (particle size D[3,4] (366 ± 6 µm)) of coffee. An unmeasured cup of coffee was brewed before each series in order to rinse and heat up the system.

2.3.4. Capsule

Cafissimo Classic coffee machines (Wallisellen, Switzerland) were used in the current study to brew the capsule coffees. Average weight of the coffees was 125 ± 2 g with an extraction time of 41.4 ± 0.2 s. A blank capsule was prepared before each series of experiments to heat up the system.

2.3.5. Instant coffee

2 g of instant coffee was dissolved in 125 g of 100 °C water.

2.3.6. Sampling

Sampling was identical, irrespective of the brewing method. Once the coffee was within the disposable cup (Verpackungsteam GmbH, Rohrbach, Germany) or ceramic cup (Cucina & Travola Prima, Migros,