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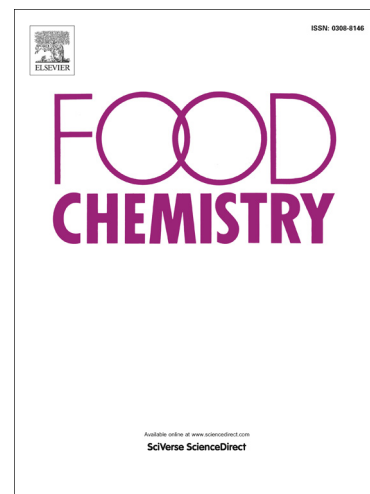
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1 **Impact of consumer behavior on furan and furan-derivative exposure during coffee consumption.**

2 **A comparison between brewing methods and drinking preferences**

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8 **Chemical compounds:**

9 Furan (PubChem CID: 8029); 2-methylfuran (PubChem CID: 10797); 3-methylfuran (PubChem CID: 13587);

10 2,3-dimethylfuran (PubChem CID: 34337); 2,5-dimethylfuran (PubChem CID: 12266); Furan-d_4 (PubChem CID:

11 2733420)

12 **Abstract**

13 This study examined the influence of consumer behavior on furan, 2-methylfuran, 3-methylfuran, 2,5-

14 dimethylfuran and 2,3-dimethylfuran exposure in coffee. Coffees brewed using a filter, fully automatic,

15 capsule machine or reconstituted instant coffee were found to have a significant different cup

16 concentrations of furan derivatives. Coffee brewed with the fully automatic machine contained the highest

17 furan and furan derivative concentrations (99.05 µg/L furan, 263.91 µg/L 2-methylfuran, 13.15 µg/L 3-

18 methylfuran and 8.44 µg/L 2,5-dimethylfuran) whereas soluble coffee did not contain detectable levels,

19 thereby contributing least to a consumer's dietary exposure. Furan and furan derivative concentrations were

20 found to decrease significantly upon cooling, reducing consumer exposure by 8.0-17.2 % on average once the

21 coffee reached drinking temperature 55-60 °C, in ceramic cups. Serving coffee in a ceramic or disposable cup

22 were found to influence the cooling dynamics of the coffee but did not statistically influence the consumers

23 exposure at a given temperature.

24

25   **1. Introduction**

26   Furan, 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran and 2,3-dimethylfuran, hereafter collectively called

27   furan derivatives, **Table S1**, have been known to be present in coffee since the 1960s and 1970s (Maga &

28   Katz, 1979; Stoffelsma, Sipma, Kettenes, & Pypker, 1968). Nevertheless, it was only since the mid-nineteen

29   nineties, when the International Agency for Research on Cancer (IARC, 1995) classified furan as type 2B,

30   *possibly carcinogenic to humans*, that determining consumer's exposure became necessary. Ubiquitously

31   present in thermally processed foods, furan exposure studies revealed that coffee contributes most

32   significantly to an adult's dietary exposure (Fromberg, Mariotti, Pedreschi, Fagt, & Granby, 2014; Mariotti,

33   Granby, Rozowski, & Pedreschi, 2013; Scholl, Scippo, De Pauw, Eppe, & Saegerman, 2012; Waizenegger,

34   Winkler, Kuballa, Ruge, Kersting, Alexy, et al., 2012).   Moreover, coffee is one of the only foods known where

35   2-methylfuran levels consistently exceed those of furan (Becalski, Hayward, Krakalovich, Pelletier, Roscoe, &

36   Vavasour, 2010), revealing that coffee also significantly contributes to a consumer's dietary exposure to 2-

37   methylfuran. Methylfurans appear to be metabolized, at least in part, in a similar manner to furan, resulting

38   in highly reactive intermediates leading to a similar toxicity (Becalski, Hayward, Krakalovich, Pelletier, Roscoe,

39   & Vavasour, 2010). Due to a shared metabolic pathway, methylfurans are considered to contribute to furan

40   toxicity (Becalski, Hayward, Krakalovich, Pelletier, Roscoe, & Vavasour, 2010). Despite coffee being a

41   significant dietary source of furan derivatives, in 2016 the IARC completed their reassessment on the

42   potentially carcinogenic effects of coffee, reclassifying it as type 3, "*not classifiable as to its carcinogenicity to*

43   *humans"*, based on insufficient evidence to justify coffee's previous classification as type 2B, "*possibly*

44   *carcinogenic"* (IARC, 2016).

45   Initially absent in green coffee beans, furan derivatives are generated upon roasting from the thermal

46   degradation of endogenous components (Becalski & Seaman, 2005; Limacher, Kerler, Davidek, Schmalzried,

47   & Blank, 2008; Locas & Yaylayan, 2004; Van Lancker, Adams, Owczarek-Fendor, De Meulenaer, & De Kimpe,

48   2011; Yaylayan, 2006). Model studies conducted under simulated roasting conditions indicate that furan

49   and its derivatives originate from similar precursors in separate but parallel pathways (Limacher, Kerler,

50   Davidek, Schmalzried, & Blank, 2008). Furan was found to preferentially form directly from carbohydrate

51   degradation (Limacher, Kerler, Davidek, Schmalzried, & Blank, 2008; Van Lancker, Adams, Owczarek-Fendor,

52   De Meulenaer, & De Kimpe, 2011), where arabinose, the most liable carbohydrate moiety within green

53   coffee beans (Bradbury, 2008), served as a particularly efficient precursor (Limacher, Kerler, Davidek,

54   Schmalzried, & Blank, 2008). Whereas 2-methylfuran forms predominantly from the condensation of

55   carbohydrate moieties generated during the Maillard reaction (Limacher, Kerler, Davidek, Schmalzried, &

56   Blank, 2008), origins of 3-methyl-, 2,5-dimethyl- and 2,3-dimethyl-furan have yet to be established.

57   The concentrations generated during roasting are not directly predictive of the consumers' exposure.

58   Instead, concentrations of furans in the cup will depend upon the coffee's composition, processing and

59   brewing method, amongst numerous other factors (Altaki, Santos, & Galceran, 2011; La Pera, Liberatore,

60   Avellone, Fanara, Dugo, & Agozzino, 2009; Mariotti, Granby, Rozowski, & Pedreschi, 2013; Morehouse,

61   Nyman, Mcneal, Dinovi, & Perfetti, 2008; Waizenegger, et al., 2012).   Furan has been found to decrease by

62   approximately 90% from bean to cup (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010), due

63   to its high volatility, reflective of its low boiling point, 32 °C. Little information, however, is available

64   regarding cup concentrations of furan's higher boiling methyl derivatives (see **Table S1**). Initial furan

65   derivative concentrations within freshly brewed coffee may be decreased further during cooling, as

66   suggested by Guenther (Guenther, 2012), reducing consumers' exposure.

67   Previous studies demonstrate varying degrees of furan loss upon coffee cooling. Goldmann *et al.*

68   (Goldmann, Perisset, Scanlan, & Stadler, 2005) as well as Zoller and associates (Zoller, Sager, & Reinhard,

69   2007) observed that consumer furan exposure was reduced by approximately 45-50% when the coffee was

70   cooled for an hour, whereas Guenther *et al.* (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz,

71   2010) reported a 10% loss within the same time period. Moreover, Mesìas and Morales (Mesias & Morales,

72   2014) findings suggest that furan loss is also dependent upon stirring before consumption. Their findings

73   demonstrate that passive cooling is 10% more efficient than brief manual stirring, which decreases furan

74   content by 64%, whereas continuous mechanical stirring will reduce furan exposure by 94% within five

75   minutes (Mesias & Morales, 2014). Han and colleagues (Han, Kim, & Lee, 2017) observed a 2-22% decrease

76   in furan over five minutes, reporting furan loss was dependent on coffee type, water temperature, storage

77 temperature and the presence or absence of a lid. These authors observed that while furan loss was greatest

78 from coffees cooled without a lid, using a higher temperature to prepare or store the coffee led to higher

79 furan levels within the freshly brewed cup (Han, Kim, & Lee, 2017).   The higher furan levels found within

80 canned coffee stored at 60 °C were offset by the greater rate of furan loss upon can opening, resulting in

81 approximately equivalent furan exposure between the two storage temperatures after five minutes (Han,

82 Kim, & Lee, 2017). Interestingly, their results demonstrate that preparing instant coffee at a higher

83 temperature, 100 °C instead of 85 °C, led to higher concentrations, suggesting *in situ* formation of furan

84 (Han, Kim, & Lee, 2017).

85 The present study aims to investigate consumer exposure to furan and its methyl derivatives resulting from

86 typical coffee preparation and drinking behaviour. Furan loss over cooling was assessed in four typical coffee

87 brews, including fully automatic, filter, instant and capsule systems, which were prepared in either a ceramic

88 or lidded disposable cup.

89 **2.   Materials and Methods**

90 **2.1. Chemicals**

91 The following chemicals were used without further purification: furan (≥99%), d_4-furan (≥99%), 2,5-dimethyl

92 furan (99%), 2,3-dimethyl furan (99%) purchased from Sigma-Aldrich (Schnelldorf, Germany); 3-methylfuran

93 (>98%) purchased from Thermo Fisher Scientific (Geel, Belgium); methanol (≥99.9%) purchased from

94 Honeywell (Bucharest, Romania). Commercially available 100% Arabica blend medium roasted Tchibo coffee

95 as well as Cafissimo capsule "strong" coffee 100% Arabica (Hamburg, Germany). Nescafé Gold Blend instant

96 coffee (United Kingdom).

97 2.2. **Standards preparation**

98 Furan standard containing furan (40 μL), 2-methylfuran (120 μL), 3-methylfuran (10 μL), 2,3-dimethylfuran

99 (10 μL) and 2,5-dimethylfuran (10 μL) were prepared fresh daily in 20 mL headspace vial as a methanol

100 stock solution. 250 μL of the furan derivative stock solution was then added through the septum into a 20

101 mL headspace vial containing 20 mL of Milli-Q water. d_4-furan internal standard was prepared according to

102 the Food and Drug Administration (USFDA) guidelines (USFDA, 2004).   Limit of quantitation (LOQ) and limit

103   of detection (LOD) were calculated according to the following equations for each compound, in each matrix,

104   and are included in the supplementary material (**Table S2**).

105   LOD = (3 x SD)/slope (ng/mL)

106   LOQ = (10 x SD)/slope (ng/mL)

107   **2.3. Sample preparation**

108   Coffee was received approximately one week after roasting and immediately stored at -20 °C. A single 1 kg

109   bag was thawed every day for two hours before use to achieve room temperature.

110   ***2.3.1.   Whole bean furan content:*** Whole beans were kept at -20 °C before grinding. Coffee was ground at

111   three grind sizes on Mahlkönig EK43/1 (Hamburg, Germany), 3 (D[3,4] 327 ± 4 µm), 6 (D[3,4] 540 ± 1 µm) and

112   9 (D[3,4] 760 ± 11 µm). Standard addition was performed on two water to coffee mixtures, 0.05 g coffee in

113   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.

114   ***2.3.2.   Filter Coffee:*** A Moccamaster KBG 741 AO (Amerongen, Netherlands) was used for the purpose of

115   this study.   Coffee was ground on a Mahlkönig EK43/1 (Hamburg, Germany) using a grind size typical for

116   filter coffee (grinder setting 9 D[3,4] (766 ± 12 µm)). Five grams of coffee were used to clean the grinder

117   before the brewing sample was ground. Within three minutes of grinding, 48 ± 0.29 g of coffee was weighed

118   into a No. 4 Moccamaster filter (Amerongen, Netherlands) resting within the respective machine's brewing

119   basket. The basket was then returned to the respective machine that had been previously filled with 900 mL

120   of water (Total hardness: 80 ppm $CaCO_3$. Alkalinity: 45 ppm $CaCO_3$). Brewing was immediately commenced

121   after replacement of the brewing basket and allowed to complete to the last drop before the carafe was

122   removed from the hotplate. The full brewing time was 4 min 48 ± 18 s. 125 ± 2.25 g of coffee was poured

123   into the respective container (ceramic cup or disposable cup) before a temperature sample was taken.   A

124   fresh pot of coffee was brewed for every temperature measurement.

125   ***2.3.3.   Fully Automatic:*** A Schaerer Coffee Art Plus (Zuchwil, Switzerland) was used, programmed and

126   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 ±

127   6 µm)) of coffee. An unmeasured cup of coffee was brewed before each series in order to rinse and heat up

128   the system.

129   **2.3.4.**   **Capsule:** Cafissimo Classic coffee machines (Wallisellen, Switzerland) were used in the current study

130   to brew the capsule coffees. Average weight of the coffees was 125 ± 2 g with an extraction time of 41.4 ±

131   0.2 s. A blank capsule was prepared before each series of experiments to heat up the system.

132   **2.3.5.**   **Instant coffee:** 2 g of instant coffee was dissolved in 125 g of 100 °C water.

133   2.3.6.   **Sampling:** Sampling was identical, irrespective of the brewing method. Once the coffee was within

134   the disposable cup (Verpackungsteam GmbH, Rohrbach, Germany) or ceramic cup (Cucina & Travola Prima,

135   Migros, Switzerland) the temperature was immediately monitored by a testo 735 thermocouple (Germany)

136   placed within the cup 2 cm above the bottom.

137   Cooling studies refer to a series of studies performed on all brewing methods. These studies investigate the

138   effect of cooling temperature after brewing on the content of furans within the coffee cup. Samples were

139   taken from independently brewed coffees at specific temperatures within the range 75 - 50 °C for black

140   coffee. The temperature was monitored with the thermocouple for the cooling studies until the desired

141   temperature was obtained, 75, 70, 65, 60, 55 or 50 °C. Ambient temperature was stable at 22 °C. Once the

142   desired temperature was achieved, a 5 mL Supelco gastight syringe, previously rinsed with cold water, was

143   used to aliquot 5 mL of sample into a previously cooled 20 mL Gerstel headspace vial (Sursee, Switzerland).

144   The vial was then immediately closed and stored on ice until further handling. This procedure aimed at

145   minimizing furan loss between sampling and measurements. The densities of these coffees were also

146   monitored in order to ensure that 5 mL aliquots were approximately equivalent to 5 g samples normally

147   taken for coffee.

148   Quantification: residual coffee was used as a matrix for the calibration curve background, which entailed

149   allowing it to cool to 35 °C. The temperature of the background was controlled to promote compositional

150   consistency of the matrix between runs (days and bags of coffee). Once the coffee had cooled to 35 °C, it

151   was transferred to a Duran Schott bottle and cooled to 4 °C to ensure furan retention in the matrix before

152   further handling.

153   Once the coffee had undergone additional cooling in the fridge for an hour, a standard addition curve was

154   generated according to the FDA protocol for furan(USFDA, 2004). Standard addition curves were plotted

155 using peak area ratios at characteristic retention times for 2-methylfuran (m/z 82/72), 3-methylfuran (82/72)

156 and 2,5-dimethylfuran (96/72) with R^2 value > 0.98, against their respective concentrations. From the

157 standard addition curve, the background furan derivative concentration was determined. The background

158 concentration of these furans were then added to the known content, used to generate the standard

159 addition curve, in order to generate the calibration curve (concentration in ng/mL versus their respective m/z

160 ratios) within the coffee matrix. The calibration curve was then used to quantitate the furan concentrations

161 within the cooling series.

162 ***2.4. Headspace Gas chromatography-Mass spectrometry (HS-GC/MS):***

163 A Gerstel MultiPurpose Sampler (Sursee, Switzerland) Agilent 7890A gas chromatograph coupled to an

164 Agilent 5975C inert XL quadrupole detector (Delaware, USA) was used for HS-GC/MS analysis.   Samples were

165 incubated at 60 °C for 30 minutes with continual agitation, 10 s *on* and 1 s *off*. One milliliter of sample was

166 collected from the headspace vial and delivered at a rate of 0.5 mL/s into a splitless inlet heated to 240 °C.

167 The initial temperature of the column was set at 50 ˚C, increasing to 225 ˚C at a rate of 10 ˚C/min, which was

168 held for 12.5 min. A constant flow of 1.7 mL/min was used during the analysis. The transferline temperature

169 was held at 225 ˚C. The ion source was maintained at 230 ˚C. The mass range analysed was 35–150 amu. The

170 column was a Supel-Q PLOT column (30 m length, 0.32 mm i.d., and 0.15 μL film thickness). The identity and

171 purity of the chromatographic peaks were determined by comparison with commercially available standards

172 as well as using NIST V 2.0 and MSD ChemStation software.

173 ***2.5. Statistical Analysis***

174 RStudio (Version 1.0.152, 2017) was used to run Shapiro-Wild normality tests, studentized Breusch-Pagan

175 tests, Scheirer Ray Hare tests as well as Dunn's tests to determine whether brewing method, cooling

176 temperature and serving vessel had a significant influence on furan, 2-methylfuran, 3-methylfuran and 2,5-

177 dimethylfuran concentration or percent loss, for a confidence interval of 95%.

178 **3.   Results and Discussion**

179   Coffee used in the current study was 100% Arabica medium roasted in a single batch, with the exception of

180   the soluble coffee that came from a commercially available product. A portion of the whole beans were

181   processed and packaged separately for capsule coffee. Once the coffee was received, within two weeks of

182   roasting, the coffee was stored at -20 °C for the duration of the study.

183   **3.1. Content of furans within dry coffee**

184   Initial concentrations of furans demonstrated a clear loss during processing. Whole beans contained the

185   highest content of furans, ranging from 17.25 mg of 2-methylfuran to 0.83 mg of 3-methylfuran per kilogram

186   of coffee, whereas less than half these concentrations were found within capsule and instant coffees, **Table**

187   **1.**

188 **Table 1:** Furan derivative concentrations within dry coffee samples

Product	Concentration in mg/kg							Reference
	Furan	2-methylfuran	3-methylfuran	2-ethylfuran	2-pentylfuran	2,5-dimethylfuran	2,3-dimethylfuran	
Current Study								
Whole beans	6.67	17.25	0.83	n.d.	n.d.	1.07	<LOD	a
Capsules	2.14	5.22	<LOD	n.d.	n.d.	0.48	<LOD	a
Instant	0.74	2.50	0.27	n.d.	n.d.	0.22	<LOD	a
EFSA								
Roasted bean	2.16-11.00	-	-	-	-	-	-	b
Roasted ground	0.48-6.90	-	-	-	-	-	-	b
Not specified	1.04-6.59	-	-	-	-	-	-	b
Instant	0.06-2.20	-	-	-	-	-	-	b
Whole beans	2.50-3.90	2.40-6.60	-	-	-	-	-	c
Whole beans	3.51-6.10	-	-	-	-	-	-	d
Ground coffee	0.72-2.80	4.89-13.10	0.03-0.62	-	-	-	-	e
Ground coffee	1.40-2.20	1.10-4.30	-	-	-	-	-	c
Coffee	0.05-2.82	0.12-5.98	-	<0.10	<LOD	0.03-0.47	-	f
Decaffeinated	1.64-3.45	6.57-13.50	0.27-0.63	-	-	-	-	e
Cartridge	2.11-2.66	9.44-13.10	0.43-0.56	-	-	-	-	e
Instant	0.40-1.50	0.40-2.40	-	-	-	-	-	c
Instant	0.05-0.74	0.20-6.20	0.01-0.27	-	-	-	-	e
Instant decaffeinated	0.03-0.90	0.13-6.15	0.01-0.21	-	-	-	-	e

Pads	1.40-2.00	1.50-2.10	-	-	-	-	-	[c]

[a] – current study; [b] –P25 to maximum values taken from **Table 5** of the EFSA, 2011 report (European Food Safety, 2011); [c] – (Test, 2004); [d] – (Kuballa, Stier, & Strichow, 2005); [e] – (Becalski, Halldorson, Hayward, & Roscoe, 2016); [f] – (Fromberg, Mariotti, Pedreschi, Fagt, & Granby, 2014); n.d. – not determined

190   Guenther and colleagues(Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010) observed

191   a relationship between furan concentration and roast degree, ranging from 2.00 to7.00 mg furan/kg

192   coffee, suggesting that the coffee used in the present study is of a darker roast than intended.

193   Nevertheless, Guenther *et al*. (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010)

194   demonstrated that a coffee's furan concentration is dependent not only on the roast profile, but also

195   the green beans used, both of which were different between the Guenther and associates'

196   (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010) and the current study.

197   The furan concentrations obtained in the present study for whole beans (6.67 mg/kg), capsules (2.14

198   mg/kg) and instant coffee (0.74 mg/kg) all fall within the ranges reported by EFSA (European Food

199   Safety, 2011) for Roasted bean (2.16-11.00 mg/kg), not specified (1.04-6.59 mg/kg) and instant

200   coffee (0.06-2.20 mg/kg), respectively.

3.2. Content of furans within freshly brewed coffee

202   Using the concentration of furans within the whole bean, a theoretical concentration was calculated

203   based on the quantity of coffee used in the brewing method and the coffee yield, also known as brew

204   (**Table S3**). This theoretical value is representative of a 100% extraction of the furan derivatives from

205   the coffee grounds, based on the solubilities presented in the EFSA report (Knutsen, Alexander,

206   Barregård, Bignami, Brüschweiler, Ceccatelli, et al., 2017), as well as 100% retention of these

207   compounds within the coffee brew.

208   Filter and capsule coffees, **Table S3**, were found to have a furan extraction efficiency of 11.9 and

209   11.2% respectively, supporting Guenther and colleagues (Guenther, Hoenicke, Biesterveld, Gerhard-

210   Rieben, & Lantz, 2010) as well as Kuballa *et al*.'s (Kuballa, Stier, & Strichow, 2005) findings for filter

211   coffee where approximately 10% of furan found in the whole beans was found within the brew.

212   Capsule coffees lose 65.7% of their furan during grinding and packaging of the whole bean in capsule

213   processing, retaining only 34.3% of the concentration within the capsule. From the 34.3% retained

214   within the capsule, 67.4% is lost during brewing, resulting in 32.6% of the furan content of the

215 capsule coffee being found within the cup, or 11.2% of the furan content initially found in the whole

216 beans. The loss between freshly ground coffee and capsule furan content is not attributed to the

217 particle size, P[3,4] 492 μm, but rather to processing, seeing as 6.5 mg/kg (calculated from **Figure S1**),

218 **Table 1**, would have been anticipated for this grind size.

219 Our findings support those of Kuballa's *et al.*'s (Kuballa, Stier, & Strichow, 2005), that brewing coffee

220 with a fully automatic machine extracts furans more efficiently than filter methods. Nevertheless,

221 our fully automatic method demonstrated a twofold higher extraction efficiency compared to filter

222 methods in contrast to Kuballa's and colleagues' (Kuballa, Stier, & Strichow, 2005) fully automatic

223 method that was often greater than three times as efficient to their filter systems.

224 Similar to the parent furan, approximately 78-88% of 2-methyl- and 3-methylfurans' theoretical cup

225 concentration escapes during brewing, resulting in 12-22% remaining within the cup, **Table S3**.

226 Release of 2,5-dimethylfuran is even more efficient, where only 6-11% of the concentration within

227 the coffee beans is retained within the brew, **Table S3**. Regardless of the furan derivatives, coffees

228 brewed with a fully automatic machine retains twice the furan content, of the original beans, than

229 filter or capsule methods.

230 Initial comparison between levels of furans found within the current study and those previously

231 reported within literature for various brewing methods are in agreement, **Table 2**. In the current set

232 of experiments, freshly brewed black coffees were found to have a temperature of 75 °C when

233 prepared with all brewing methods with the exception of capsule coffee prepared in a ceramic cup,

234 which had an initial temperature of 65°C. Furan levels within freshly brewed coffee with a fully

235 automatic (99.1 ± 6.4 μg/L), filter (47.3 ± 5.7 μg/L), or capsule machine (33.5 ± 3.0 μg/L), served in a

236 ceramic cup, were all within the range reported by EFSA for roasted ground brew (0-228 μg/L), with a

237 mean furan content between 39-42 μg/L (European Food Safety, 2011). The levels of furan reported

238 herein are also consistent with those found by Altaki *et al.* (Altaki, Santos, & Galceran, 2011) for

239 filter, (20-78 μg/L) and espresso machines (43-146 μg/L).

240   Altaki *et al.* (Altaki, Santos, & Galceran, 2011) report higher furan concentrations within capsule

241   systems, 68-244 µg/L, than were found in the current study, 20-30 µg/L. This difference is partly due

242   to Altaki and colleagues' (Altaki, Santos, & Galceran, 2011) use of 5.5 and 7 g of coffee to prepare 40

243   or 110 mL of coffee respectively, whereas in the current study, 6 g coffee was used to brew 125 mL

244   of coffee. Calculating back to the furan content within the grinds for Altaki and associates (Altaki,

245   Santos, & Galceran, 2011) capsule systems contain an average of 1.24 ± 0.30 mg furan/kg coffee,

246   resulting in a concentration of 59 µg/L for the coffee ratio brewed in the current study. The higher

247   theoretical concentration that would have been obtained using Altaki *et al.* (Altaki, Santos, &

248   Galceran, 2011) capsule system suggests either that the capsule system used is twice as efficient at

249   extracting furan than the system used in the current study, or that the concentration of furan in the

250   capsule grinds was higher. If 1.24 mg/kg coffee represented 30% of the furan in the grinds, as

251   observed in the current study, the capsule system used by Altaki *et al*. (Altaki, Santos, & Galceran,

252   2011) would have contained 5.58 mg furan/kg coffee. A higher furan retention within the capsule

253   coffee would speak for the efficiency of the capsule manufacturing process and retention of the

254   volatiles of the capsules examined by Altaki and colleagues (Altaki, Santos, & Galceran, 2011).

255   Furan derivatives were not detected in the instant coffee chosen for these series of experiments,

256   resulting in the lowest exposure levels. The absence of furan is in agreement with levels of furan

257   found within instant coffee according to EFSA (European Food Safety, 2011). The absence of furan in

258   freshly brewed instant coffee allows for its exclusion from further investigation and discussion

259   concerning the influence of the cooling and serving vessel.

260   **Table 2:** Furan derivative concentrations within brewed coffee

Product	Concentration in µg/L					
	Furan	2-methylfuran	3-methylfuran	2,5-dimethylfuran	2,3-dimethylfuran	Reference

Current Study

Fully Automatic[a]	74-99	188-264	10-13	7-8	<LOD	[b]
Filter[a]	47-53	138-128	7-6	4	<LOD	[b]
Instant [a]	<LOD	<LOD	<LOD	<LOD	<LOD	[b]
Capsule[c]	20-33	58-103	5	3	<LOD	[b]

EFSA

Instant	0-10	-	-	-	-	[f]
Roasted bean	6-360	-	-	-	-	[f]
Roasted ground	0-228	-	-	-	-	[f]
Not specified	0-248	-	-	-	-	[f]
Whole beans	93-125	-	-	-	-	[g]
Ground coffee	41-158	-	-	-	-	[g]
Coffee	178	670	-	41	-	[h]
Coffee	93-129	-	-	-	-	[i]
Filter coffee[d]	8-66	-	-	-	-	[j]
Filter	20-78	-	-	-	-	[k]
Filter coffee – machine[e]	9-33	-	-	-	-	[j]
Filter coffee – manual[e]	17-24	-	-	-	-	[j]
French press[e]	33-66	-	-	-	-	[j]
Decaffeinated coffee	7-121	24-365	1-12	-	-	[l]
Medium roast	25-70	109-287	5-10	-	-	[l]
Espresso	35-352	135-1260	7-39	-	-	[l]
Espresso[d]	28-60	-	-	-	-	[j]
Espresso	43-146	-	-	-	-	[k]
Canned	25-36	-	-	-	-	[i]
Instant coffee	6-44	-	-	-	-	[g]

14

Instant	7-12	-	-	-	-	[i]
Pads	63-101	-	-	-	-	[g]
Capsule	68-244	-	-	-	-	[k]

[a] – Black coffee in both ceramic or ToGo cup at 75°C; [b] – current study; [c]- Black coffee in both ceramic or ToGo cup at 65°C; [d] – brewed from purchased coffee grounds; [e] brewed from freshly ground whole beans; [f]- (European Food Safety, 2011); [g]- (Test, 2004); [h]- (Shen, Liu, Jia, Jiang, Nie, Xie, et al., 2016); [i]- (Han, Kim, & Lee, 2017); [j]- (Kuballa, Stier, & Strichow, 2005); [k]- (Altaki, Santos, & Galceran, 2011); [l]- (Becalski, Halldorson, Hayward, & Roscoe, 2016); n.d. – not determined

261 Consistent with previous studies, 2-methylfuran concentrations exceeded those of the parent furan

262 (Becalski, Halldorson, Hayward, & Roscoe, 2016). Concentrations of 2-methylfuran obtained within

263 fully automatic and filter coffees (188-264 µg/L) and (138-128 µg/L) respectively, remained within

264 the ranges previously reported by Becalski and colleagues (Becalski, Halldorson, Hayward, & Roscoe,

265 2016), **Table 2**. Levels of 2-methylfuran obtained in the current study for capsule systems (58-103

266 µg/L) are only comparable to levels reported by Becalski and associates (Becalski, Halldorson,

267 Hayward, & Roscoe, 2016) for decaffeinated coffee. Absence of corroborative literature on 2-

268 methylfuran is reflective of the emerging interest in methylfurans, resulting in this being one of the

269 first investigations to report 2-methyl- and 3-methyl-furan content within capsule coffee. While 2-

270 methylfuran levels obtained for capsule systems are lower than for other brewing methods, 3-

271 methylfuran concentrations remain within the previously reported literature values independently of

272 the brewing method employed, **Table 2**.

273 Presence of 2,5-dimethylfuran (41 µg/L) has periodically been reported in brewed coffee (Shen, et

274 al., 2016). Concentrations found in the current study ranged from 3-8 µg/L depending upon the

275 brewing method used, **Table 2**. No detectable levels of 2,3-dimethylfuran were found within any of

276   the coffee samples in the current study (LOD ranging between 0.10-1.99 ng/mL depending upon the

277   coffee matrix examined).

278   The following sections aim to examine the influence of different consumer habits on furan derivative

279   exposure.

280   **3.3. Impact of brewing method on furan derivative exposure**

281   The initial consumer choice when drinking a coffee is the type of coffee to be prepared. Types of

282   coffee distinguish themselves from one another by a multitude of different factors including the

283   extraction equipment, brew ratio (ratio of coffee yield to grounds used), grind size of the coffee as

284   well as water temperature and extraction duration. For the purposes of these experiments, four

285   typical coffee preparations were chosen to determine consumer exposure to furans. Instant coffee

286   examined in the current study did not contain any detectable levels of furans, resulting in the lowest

287   coffee exposure levels possible. Instant coffee was the only coffee used in this study that originated

288   from a different coffee source; all other coffees prepared came from a single batch of roasted coffee.

289   Coffees were prepared using either a fully automatic, filter or capsule machine. While the capsules

290   used contained the same coffee beans as those used for the fully automatic and filter coffee

291   preparations, they were industrially packaged.

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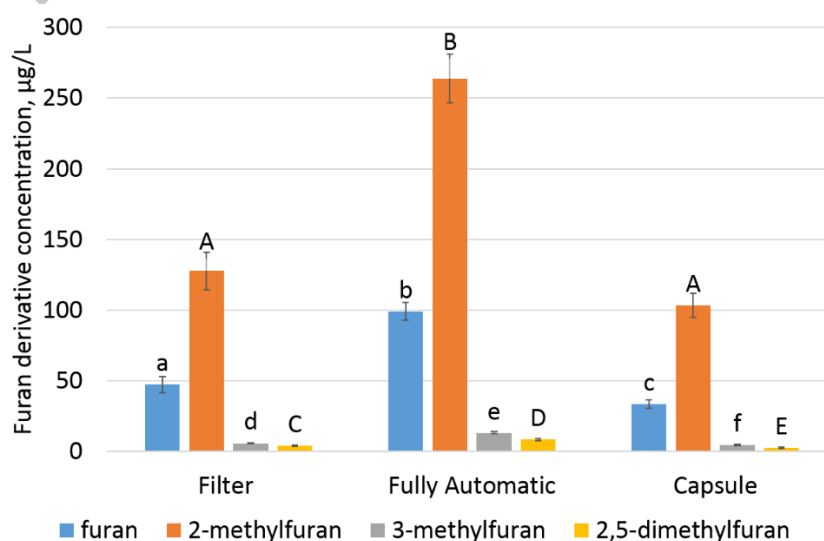
293   **Figure 1:** Dependence of coffee furan composition on brewing method

294   (refer to **Table S4** for statistical summary)

295   Consumer brew preferences have a significant influence on their furan exposure. EFSA findings

296   report that adults are chronically exposed to on average 0.17 - 0.54 µg/kg b.w./day (Knutsen, et al.,

297   2017) of the parent furan, which translates to a daily exposure of between 11.9 – 37.8 µg furan/day

298   for a 70 kg adult. Freshly brewed coffee, in this study, was found to result in a furan content of

299   between 4.2 and 12.4 µg per cup (**Table S4**). One cup of coffee freshly brewed with a fully automatic

300   machine (12.4 µg furan/125mL cup, at 75°C), has the capacity to exceed the average lower exposure

301   threshold of 11.9 µg furan/day (Knutsen, et al., 2017), whereas one would have to consume two cups

302   of filter coffee (5.9 µg furan/125mL cup, at 75°C) or three of capsule coffee (4.1 µg furan/125mL cup,

303   at 65°C) to exceed the lower threshold reported by EFSA. This demonstrates the significant

304   influence, viewed statistically, that the brewing method has over the consumer's daily exposure.

305   Coffee furan concentration has been associated in the literature with its lipid content (Arisseto,

306   Vicente, Ueno, Tfouni, & Toledo, 2011; Van Lancker, Adams, Owczarek, De Meulenaer, & De Kimpe,

307   2009). In 2009, Van Lancker and associates (Van Lancker, Adams, Owczarek, De Meulenaer, & De

308   Kimpe, 2009) demonstrated the ability of lipids to retain furan by measuring d_4-furan retention

309   within various lipid systems. Moreover, these authors compared deuterated furan's retention within

310   normal and defatted coffee matrices demonstrating furan loss when the coffee was de-fatted. In

311   addition, Pavesi Arisseto and colleagues (Arisseto, Vicente, Ueno, Tfouni, & Toledo, 2011) suggest

312   that Arabica's greater lipid content is responsible for its greater furan retention within the beverage,

313   in contrast to Robusta varieties that are more susceptible to generate furan during roasting yet are

314   less inclined to transfer furans into the brew. Interestingly, Glöss and colleagues (Glöss,

315   Schönbächler, Klopprogge, D'Amrosio, Chatelain, Bongartz, et al., 2013) as well as Ratnayake and

316   associates (Ratnayake, Hollywood, Ogrady, & Stavric, 1993) compared the lipid content of coffee

317   between a variety of brewing methods, demonstrating that filter coffee has the lowest lipid content

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318   when compared to any other preparation method. Ratnayake *et al.* (Ratnayake, Hollywood, Ogrady,

319   & Stavric, 1993) demonstrated that the lipids are mainly (90%) retained in the grounds, whereas the

320   retention in the filter paper itself only accounts for just over nine percent, and only approximately

321   0.4% of the fat will be found within the brew. Ratnayake and colleagues (Ratnayake, Hollywood,

322   Ogrady, & Stavric, 1993) also determined that the lipid composition remained the same,

323   independently of where the lipids were retained. If these authors (Glöss, et al., 2013; Ratnayake,

324   Hollywood, Ogrady, & Stavric, 1993) are correct, then the reduced furan content, and possibly furan

325   release, observed within filter coffee may be attributed to the partial removal of coffee lipids during

326   brewing. This suggests that the brewing method influences the furan content of the coffee through

327   its ability to extract lipids. Furthermore, lipid content of the coffee, potentially enhanced by the

328   addition of cream, may significantly influence a consumer's exposure to coffee furans.

329   Numerous brew parameters are varied in the generation of a specific type of coffee that may

330   influence furan derivative content. One of the main parameters likely to influence the concentration

331   of furans within the final cup is the brew ratio. The brew ratio is an indirect expression of the extract

332   concentration by comparing the brew yield, in grams, to the mass of grounds used during

333   preparation. In the current experiment, brew ratios typical of the brewing method were used: 16.5

334   for filter, 13.9 fully automatic and 20.8 for capsules. Concentrations of furans observed in **Figure 1**

335   reflect the same trend anticipated from dilution, reflected by the brew ratio. High brew ratios

336   reflect a higher dilution, whereas low brew ratios reflect a higher concentration. Nevertheless, brew

337   ratio is not directly proportional to furan derivative content and therefore can only give a relative

338   indication of a consumer's furan derivative exposure. The indicative nature of the brew ratio with

339   respect to furan derivative exposure suggests that other brewing parameters influence the final cup

340   concentration.

341   In the current investigation, meticulous attention was paid to each step within the brewing

342   procedure due to their potential impact on the coffee's furan derivative concentration. The highest

343   furan derivative concentrations were found in fully automatic machines that employ an enclosed

344   grinding and extraction module. Furthermore, the fully automatic machine used the finest mean

345   particle size, 366 μm of all brewing procedures employed in this study, which should have promoted

346   furan release (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010). However, coffee

347   was brewed within 10.6 ± 0.3 s after grinding, minimizing furan loss promoted by grinding. Filter

348   coffee with a coarser mean particle size 766 μm took significantly longer to brew: 3 - 4 minutes,

349   which is likely to have contributed to the lower furan derivative content measured. Probing into cup

350   furan concentration's dependence on particle size (760, 540 and 327 μm), in filter coffee, a weak

351   correlation was found (results not shown), suggesting that furan's concentration has a stronger

352   dependence with respect to other brewing parameters, such as the time interval between grinding

353   and extraction.   Most coffee prepared is ground well in advance of extraction, as mentioned by EFSA

354   in their report, where over 90% of the products reported were analyzed as purchased (European

355   Food Safety, 2011). Considering the high volatility of furan, this will potentially reduce the furan

356   content significantly during storage (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz,

357   2010) affecting the consumers' final exposure.

358   In addition to monitoring the time between grinding and extraction, the duration of extraction was

359   also recorded. Similar to their grinding interval, filter machines had a significantly longer extraction

360   time 4.0 ± 0.2 minutes when compared to their fully automatic counterparts, 18.9 ± 0.3 s.

361   Nevertheless, associating extraction time with a higher or lower furan content is complex, due to the

362   brewing setup. La Pera and colleagues (La Pera, Liberatore, Avellone, Fanara, Dugo, & Agozzino,

363   2009) found that over 60% of furan is extracted within the first minute of brewing when water is

364   close to boiling, as in the current set of experiments (92 - 96 °C).   Therefore, if the initial coffee

365   extract was richest in furan, then letting it incubate on the filter machine hotplate for the entire

366   extraction period, 4 minutes, would reduce the consumer's exposure by driving the furan out of the

367   brew.   In addition to the potential loss of furan during the carafe's incubation, various authors

368   (Goldmann, Perisset, Scanlan, & Stadler, 2005; Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, &

369   Lantz, 2010) have observed a 10% decrease in furan content when coffee was poured, which was

370   only done with filter coffee.

371   Interestingly, concentrations of all furan derivatives shared a similar ratio between brewing methods.

372   Coffee brewed with the fully automatic machine consistently contained approximately twice the

373   concentration of all furan derivatives when compared to filter coffee, whereas filter coffee contained

374   approximately 1.5 times the content found in capsule coffee in the current study. The consistent

375   ratios found between brewing methods is also a reflection of a constant ratio within a brewing

376   method between furan derivatives, **Table S5**. 2-methylfuran was consistently found at more than

377   three times the furan concentration, which has also been observed in previous studies (Becalski &

378   Seaman, 2005), with the exception of Fromberg and colleagues (Fromberg, Mariotti, Pedreschi, Fagt,

379   & Granby, 2014). In contrast, concentrations found for 3-methylfuran and 2,5-dimethylfuran were

380   only 12 - 14% and 8 - 9% of the furan concentration, respectively. Percent 3-methylfuran levels

381   found within this study are consistent with those presented in the EFSA (Knutsen, et al., 2017). Given

382   a constant ratio between individual furans, the brewing method primarily influences the extent of

383   exposure to furans, where capsules present the least exposure followed by coffees prepared using a

384   filter and fully automatic machine.

385   **3.4. Influence of cooling temperature on furan derivative loss in ceramic cups**

386   Coffees brewed for this study were initially between 65 – 75 °C, classifying them as very hot

387   beverages and therefore also a type 2B, *possibly carcinogenic,* product according to IARC (IARC,

388   2016).   Those who drink their coffee at these high temperatures are therefore more susceptible

389   to developing esophageal cancer (IARC, 2016), than those that wait for their coffee to cool.

390   Furan derivative exposure was also found to be greatest immediately after brewing, decreasing

391   significantly upon cooling, **Table 3**, independently of brewing method and furan derivatives.

392   Continuous furan derivative loss upon cooling in a ceramic cup can partially be attributed to the

393   evaporation of the beverage, **Figure S2**, where approximately 3.2 g of coffee is lost over 20

394   minutes.
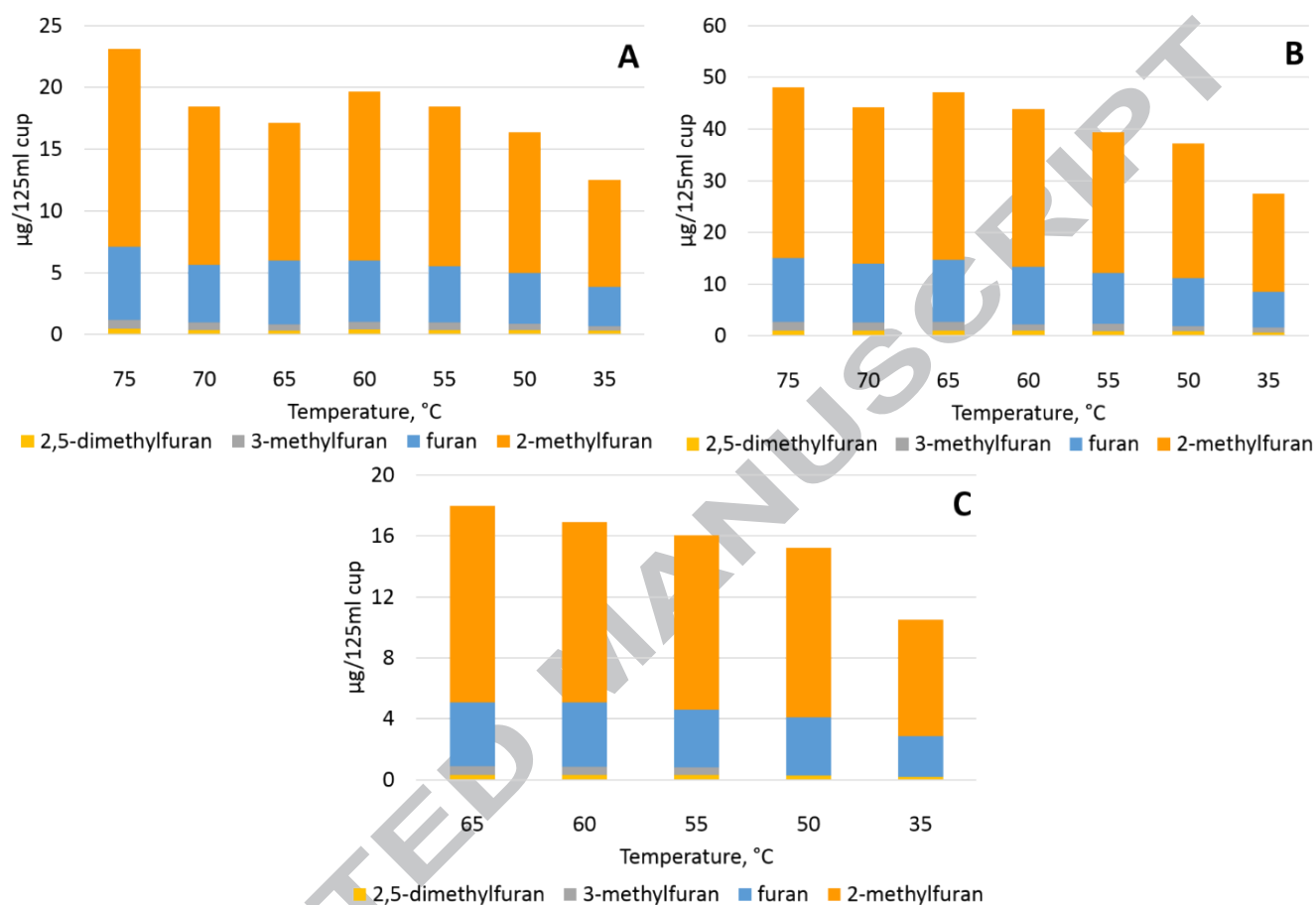
395

396   **Figure 2:** Concentrations of (blue) furan, (orange) 2-methylfuran, (grey) 3-methylfuran and (yellow)

397   2,5-dimethylfuran in coffee brewed from a (A) filter, (B) fully automatic or (C) capsule machine

398   served in a ceramic cup (refer to **Table 3** statistical summary)

399   Furan and 2-methylfuran account for 95% of a consumer's exposure to furan, **Figure 2**. While coffee

400   is often consumed at 60 °C independently of its strength (Lee & O'Mahony, 2002), this temperature is

401   reached at different rates depending on the coffee brewed. In the current experiments, capsule

402   coffee, cooled in a ceramic cup, reached 55-60 °C in approximately 2.9 minutes, whereas filter coffee

403   required an additional minute and a half, while coffee prepared with a fully automatic machine

404   needed six additional minutes. As anticipated, rapid cooling, experienced by capsule coffee, resulted

405   in the smallest furan loss, on average 8.0%, before consumer consumption. Lengthier cooling

21

406   periods for fully automatic and filter coffees resulted in a greater average loss of 14.3 and 17.2%, at

407   55-60 °C respectively.   Han and colleagues (Han, Kim, & Lee, 2017) report a 20% reduction in furan

408   from an open vessel of filter coffee after five minutes, which aligns well with our findings where a

409   22.4% reduction was found within six minutes, corresponding to a temperature of 55 °C. 2-

410   methylfuran, 3-methylfuran and 2,3-dimethylfuran were all found to decrease in a proportional

411   manner, for example all by between 20 - 22% at 55 °C, for filter and capsule coffees.   Rate of loss for

412   furan derivatives in fully automatic machines seem to be dependent on the furan derivatives;

413   however, this has to be corroborated by additional studies.

414   The significant retention of furans, 85%, by coffee brewed with a fully automatic machine, despite

415   the longer cooling period of nine minutes, suggests the presence of a barrier to the release of furans.

416   This barrier, as previously discussed, may be due to the greater lipid extraction efficiency anticipated

417   by brewing with a fully automatic machine, or may also be due to the formation of a visible crema

418   layer upon brewing, which is the formation of a foam layer on the surface of the coffee upon brewing

419   and which may present a physical barrier to furan loss.

420   **Table 3:** Statistical results for Dunn pairwise comparison of furan derivative concentrations of over

421   cooling temperatures

	Temperature, °C						
	75	**70**	**65**	**60**	**55**	**50**	**35**
furan	A	ab	ab	bc	cd	cd	D
2-methylfuran	A	AB	BC	BCD	CDE	DE	E
3-methylfuran	E	ef	fg	gh	gh	h	h
2,5-dimethylfuran	F	F	FG	GHI	HI	HI	I

422   The parent furan content of a cup, 125 mL, of coffee cooled to 55-60 °C does not exceed the daily

423   exposure threshold reported by EFSA, 11.9-37.8 μg/day (Knutsen, et al., 2017) for a 70 kg adult,

424   independent of brew method, **Table S6**; nevertheless, cumulative furan exposure does, **Figure 2**. All

425   coffees served in a ceramic cup and cooled to 55-60 °C, irrespective of brewing method, exceed the

426   lower chronic exposure threshold established by EFSA (Knutsen, et al., 2017), with coffee brewed

427   using a fully automatic machine exceeding the upper threshold.

428   **3.5. Impact of coffee container on furan derivative loss: ceramic versus disposable cups**

429   Coffee is commonly consumed from either a ceramic or disposable cup. Han and associates (Han,

430   Kim, & Lee, 2017) investigated the impact of open and closed systems, using paper cups, on furan

431   reduction upon coffee cooling demonstrating that closed vessels lose less furan over five minutes

432   than their open system counterparts. While Han *et al.*'s (Han, Kim, & Lee, 2017) findings are

433   corroborated by the results presented in the current study, their results are strictly time-dependent,

434   neglecting a potential temperature-dependent consumer drinking bias. Lee and O'Mahony's (Lee &

435   O'Mahony, 2002) established that consumers preferentially drink their coffee at around 60 °C,

436   however filter coffee cooled in an open ceramic cup for five minutes will have cooled to almost 55

437   °C, while coffee in a lidded disposable cup will have barely cooled to 65 °C. The rate of cooling

438   therefore is likely to have a significant influence on a consumer's drinking behavior and consequently

439   their furan exposure. Coffee consumed from a ceramic cup will reach a drinking temperature, 60 °C,

440   more rapidly after brewing, approx. 3 minutes in the case of filter coffee, than a disposable cup,

441   approx. 9 minutes, possibly resulting in more immediate consumption. If the coffee is consumed at

442   60 °C, instead of after five minutes of cooling, disposable cups contribute a statistically equivalent

443   furan exposure when compared to their ceramic counterparts for all brewing methods, according to

444   Dunn's *post hoc* test, **Figure 3** and **Table S4**. Therefore, time-dependent differences in exposure

445   found in the literature for open and closed systems may be a reflection of different temperatures,

446   which is a function of the cup dynamics.

447   Coffee served in a disposable cup maintains a desirable drinking temperature for a longer period of

448   time, cooling at a rate of approx. 1 °C/min for filter coffee (R^2 = 0.9954), possibly leading to a more

449   gradual consumption of the beverage. Interestingly, while the rate of cooling in disposable cups

450   revealed a nearly linear relationship between temperature and time, ceramic cups demonstrate a

451   greater rate of initial cooling. Preliminary experiments with regard to heat dissipation, **Table S7**,

452   demonstrates that pre-heating a cup has minimal influence on the first five minutes of cooling,

453   whereas selection of cup geometry may have a more significant effect. In addition to the cup

454   materials influencing the rate of cooling, coffees cooled in an open system were found to lose over

455   2.5% of their weight over 20 minutes or approx. 30 °C of cooling, whereas closed systems lost less

456   than 0.4% over the same time period or approx. 30 °C of cooling (**Figure S2**).

457   The potential influence of cup choice on cooling rate and thereby consumer drinking behavior

458   emphasizes the importance of examining the dependence of furan derivative exposure on

459   temperature.
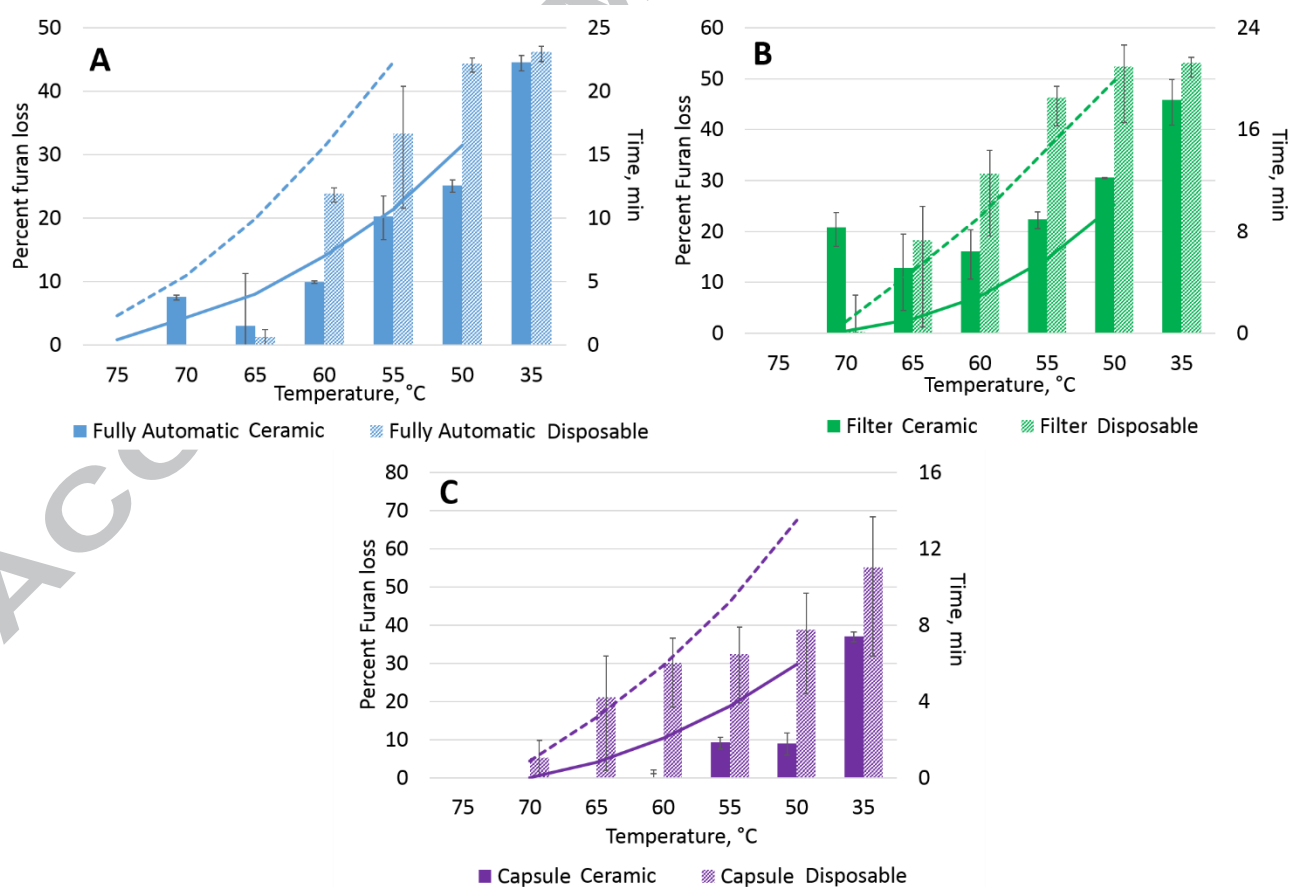
460

461   **Figure 3**: Furan loss in coffee upon cooling comparison between ceramic and disposable cups

462   prepared from either a fully automatic (A), filter (B) or capsule (C) machine (refer to **Table S8** and **S9**

463   for statistical summary)

464   Similar results were obtained for all furan derivatives and are included in the supplementary

465   materials (**Figures S3-S5**).

466   **Conclusions**

467   Furan and 2-methylfuran account for 95% of the furan derivatives found within coffee. While whole

468   beans contain the highest furan levels, less than 21% of these furan derivatives will be extracted into

469   the cup.   The extraction efficiency of furan derivatives is dependent upon prior processing steps and

470   the brewing method employed. Filter coffee was found to result in the lowest level of furan

471   derivative extraction, approximately 10% of furans were found within the brew in contrast to coffee

472   brewed with a fully automatic machine that was twice as efficient. Capsule coffees demonstrated

473   the highest extraction efficiency, at 32.6%. However, the furan content within the brew is

474   significantly influenced by the loss during capsule manufacturing, of 34.3%. The compounded loss

475   during capsule manufacturing and brewing resulted in the consumer being exposed to approximately

476   11% of the furan theoretically transferable into the brew, based on the brew ratio. The initial

477   concentration of furans within a brew are therefore dependent on the brewing method as well as the

478   amount of coffee being extracted and the brew yield. This initial concentration of furans within the

479   brew decreases significantly upon cooling, with longer times being associated with a greater loss.

480   Cooling rate is dependent upon brewing method where capsule coffees cooled most rapidly,

481   followed by filter and finally coffee brewed with a fully automatic machine. Coffee brewed with a

482   fully automatic machine did not lose as much furan (14.3%) as its filter (17.2%) machine counterpart,

483   despite requiring twice as long to cool. The limited furan derivative loss undergone by coffee brewed

484   with a fully automatic machine was attributed to the higher lipid content of these coffees as well as

485   the formation of a crema layer that could serve as a physical barrier to the loss of furans. Finally,

486   while serving vessels appeared to have a significant influence on furan loss, this was found to not be

487   statistically significant. Serving vessels were found to influence the cooling rate but not the furan

488   exposure at a given temperature.

489   **Acknowledgements**

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594 **Highlights**

595   • Brewing method has a significant influence on furan and furan derivative exposure

596   • Drinking temperature influences furan and furan derivative exposure

597   • Cup choice affects cooling dynamics but not temperature dependent furan exposure