



**HAL**  
open science

**ANALYSIS OF FURAN IN COFFEE FROM  
DIFFERENT PROVENIENCE BY HEAD-SPACE  
SOLID PHASE MICROEXTRACTION GAS  
CHROMATOGRAPHY-MASS SPECTROMETRY:  
EFFECT OF BREWING PROCEDURES.**

Lara La Pera, Alfredo Liberatore, Giuseppe Avellone, Serena Fanara, Giacomo  
Dugo, Pasquale Agozzino

► **To cite this version:**

Lara La Pera, Alfredo Liberatore, Giuseppe Avellone, Serena Fanara, Giacomo Dugo, et al.. ANALYSIS OF FURAN IN COFFEE FROM DIFFERENT PROVENIENCE BY HEAD-SPACE SOLID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY: EFFECT OF BREWING PROCEDURES.. Food Additives and Contaminants, 2009, 26 (06), pp.786-792. 10.1080/02652030902751712 . hal-00577362

**HAL Id: hal-00577362**

**<https://hal.science/hal-00577362>**

Submitted on 17 Mar 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**ANALYSIS OF FURAN IN COFFEE FROM DIFFERENT PROVENIENCE BY HEAD-SPACE SOLID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY: EFFECT OF BREWING PROCEDURES.**

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2008-392.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	06-Jan-2009
Complete List of Authors:	La Pera, Lara; University of Messina, Food and Environmental Science Liberatore, Alfredo; Laboratorio Bidiagnostica di A. Liberatore & C Avellone, Giuseppe; University of Palermo, Chimica e Tecnologie Farmaceutiche Fanara, Serena; University of Palermo, Chimica e Tecnologie Farmaceutiche Dugo, Giacomo; University of Messina, Food and Environmental Science Agozzino, Pasquale; University of Palermo, Chimica e Tecnologie Farmaceutiche
Methods/Techniques:	Chromatography - GC/MS, Chromatography - Headspace
Additives/Contaminants:	Volatiles
Food Types:	Coffee



1  
2  
3 1 **ANALYSIS OF FURAN IN COFFEE OF DIFFERENT PROVENIENCE BY HEAD-SPACE**  
4  
5 2 **SOLID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS**  
6  
7  
8 3 **SPECTROMETRY: EFFECT OF BREWING PROCEDURES.**  
9  
10 4

11  
12 5 *La Pera Lara<sup>a</sup>, Liberatore Alfredo<sup>c</sup>, Avellone Giuseppe<sup>b</sup>, Fanara Serena<sup>b</sup>, Dugo Giacomo<sup>a</sup>*  
13  
14  
15 6 *Agozzino Pasquale<sup>b</sup>*  
16  
17 7

18  
19 8 *<sup>a</sup> Dip. Scienze degli Alimenti e dell'Ambiente, Università di Messina, Sal. Sperone 31 98166*  
20  
21  
22 9 *Messina*  
23

24 10 *<sup>b</sup> Dip. Chimica e Tecnologie Farmaceutiche, Via Archirafi 32, Università di Palermo 90123*  
25  
26  
27 11 *Palermo*  
28

29 12 *<sup>c</sup> Laboratorio Bodiagnostica di A. Liberatore & C s.a.s., Via M. Vaccaro 4, 90145 Palermo*  
30  
31 13

32  
33  
34 14 **TITLE RUNNING HEADER. Effect of brewing methods on furan in coffee**  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**Abstract**

A simple, sensitive and accurate method for the analysis of furan in roasted coffee has been used based on headspace-solid-phase micro-extraction (HS-SPME) coupled to gas chromatography-mass spectrometry (GC-MS). The extraction was performed using 75  $\mu\text{m}$  carboxen/polydimethylsiloxane fiber. Ionic strength, extraction time and temperature, desorption time were valued as the most important parameters affecting the HS-SPME procedure and  $\text{d}_4$ -furan was used as the internal standard. The linearity range was in the range 0.0075-0.486  $\text{ng g}^{-1}$ , the LOD and LOQ calculated using the signal-to-noise ratio approach were 0.002 and 0.006  $\text{ng g}^{-1}$ , respectively. The inter- and intra-day precision were 8 and 10%, respectively. The concentration of furan found in lots of roasted coffee powder coming from different producing countries ranged from 57.3 to 587.3  $\text{ng g}^{-1}$ . The mean reduction of furan levels observed brewing coffee by either infusion, using a moka pot or an espresso machine were of 57%, 67.5 % and 63.3%, respectively.

**Keywords:** brewing procedures, coffee, furan, SPME-GC/MS.

## INTRODUCTION

Furan ( $C_4H_4O$ ) is a cyclic ether with aromatic character and a low boiling point of 31 °C. The occurrence of furan in thermally-processed food has been reported since 1979 (Maga et al, 1979). The crucial conclusion was that furan is carcinogenic to rats and mice with a clear dose-dependency and probably acting by a genotoxic mechanism. Therefore the International Agency for research on Cancer (IARC) classified furan in the group 2B, as “possibly carcinogenic” to humans (IARC, 1995).

Furan is present in low amounts ( $<200 \text{ ngg}^{-1}$ ) in heat-processed food as a result of thermal degradation of carbohydrates, ascorbic acid, proteins and polyunsaturated fatty acids (Cerny and Davidek, 2003; Locas and Yaylayan, 2004; Becalski and Seaman, 2005; Fan 2005 a, b; Hasnip et al, 2006). Initial findings on the occurrence of furan in heat-processed food sold in jars and cans were published by the Food and Drugs Administration (FDA) in 2004 (FDA 2004 a,b). Great attention was addressed to baby food followed by canned vegetables, fruit, meat and fish, pasta sauces, nutrition drinks, fruit preserves, beers, and coffees.

In 2004 also the European Food Safety Authority (EFSA 2004 a, b) began to collect information on the methods of analysis, occurrence and formation in food, exposure through consumption, and the toxicity of furan. This survey gave evidence that the highest levels of furan were found in coffee: 38 out of 42 samples of brewed coffee were contaminated, with concentration ranging from 3 to 125  $\text{ng g}^{-1}$ , whereas the 100% of 19 samples of coffee powder were contaminated with concentration ranging from 239 to 5050  $\text{ng g}^{-1}$ . It is well known that furans are normal components of coffee flavour volatiles; high levels of furan were found in roasted coffee beans, probably on account of the roasting process where the high temperatures exceed most other food processing procedures.

Few data are actually available in literature about the presence of furan in coffee from different provenience and on the effect of brewing procedure on furan levels in coffee (EFSA 2004 a).

1  
2  
3 56 Nowadays the EFSA is still collecting data on furan levels in different type of foods, including  
4  
5 57 coffee from different producing countries.  
6  
7  
8 58

9  
10 59 The purpose of this research is to give further insight into the effect of brewing on the presence of  
11  
12 60 furan in coffee samples from different origin. The most diffused procedures to brew coffee have  
13  
14  
15 61 been studied: infusion (also called Turkish coffee), using a moka pot and espresso machines (Italian  
16  
17 62 coffee). A rapid, accurate and high sensitive method has been used, able to detect furan levels in  
18  
19 63 coffee lower than  $0.01 \text{ ng g}^{-1}$   
20  
21  
22 64

23  
24 65 The analysis of furan in food is not easy due to its high volatility and low molecular weight and,  
25  
26  
27 66 moreover, it is present in foods at low concentration levels ( $\text{ng g}^{-1}$  or  $\text{pg g}^{-1}$ ). Gas chromatography–  
28  
29  
30 67 mass spectrometry combined with headspace (HS-GC–MS) is the method currently used for the  
31  
32 68 analysis of furan in foods (Goldman et al, 2005; Nyman et al, 2006; Altaki et al, 2007; Nyman et al,  
33  
34  
35 69 2008). In this study the HS-GC–MS method described by Altaki et al. (2007) was employed and  
36  
37 70 re-evaluated for furan analysis in coffee. In particular, the HS-SPME procedure was optimized in  
38  
39  
40 71 terms of extraction time, temperature and ionic strength.  
41  
42 72

## 43 44 73 **MATERIALS AND METHODS**

### 45 46 47 74 **Reagents**

48  
49 75 Furan and  $d_4$ -furan at a purity grade higher than 99.0% were purchased from Sigma-Aldrich (Milan,  
50  
51 76 Italy), methanol was obtained from JT Baker (Deventer, Holland). Stock standard solutions of furan  
52  
53  
54 77 and  $d_4$ -furan were prepared in methanol at a concentration of  $120 \mu\text{g g}^{-1}$ . These solution were  
55  
56 78 stored at  $0 \text{ C}^\circ$  and prepared weekly. Water working standard solutions were prepared daily for  
57  
58  
59 79 dilution of methanolic stock solutions and stored in closed vials at  $4 \text{ C}^\circ$ .  
60  
61 80

## Samples

Samples were cleaned, roasted, cooled, ground, and packaged by a Sicilian company (ZiCaffè, Marsala, Italy). Bags of green coffee beans are machine-opened, dumped into a hopper, and screened to remove debris. The green beans are then transferred by belt to storage hoppers. From the storage hoppers, the green beans are conveyed to the roaster. 240 kg of green coffee were simultaneously roasted. Roasters operated at temperatures of 200°C for 3 min (full roast). Experiments were carried out using 12 lots of 650 kg of roasted coffee coming from different countries (2 from India, 4 from Vietnam, 2 from Cameroun, 1 from Ethiopia, 2 from Brazil, 1 from Salvador). All the studied coffee samples are of “Arabica” type. Furthermore 16 pods made of miscellaneous coffee from two different lots (8 pods from each lot), named A and B, were also analyzed. The degree of grinding of coffee used for the espresso machine (pods) is extra fine (200-250 microns particle size), whereas that used for moka pot and infusion is fine (300-350 microns particle size). The sampling was conducted by the provider; several aliquots of each sample was taken at different site in each lot (ISO 4072-1982).

## Sample preparation procedure: cold extraction

To determine the content of furan powdered coffee, both magnetic assisted extraction (MAE) and ultrasound (USAE) extraction were tested, using cold water. For MAE, 20 g of grounded roasted coffee were mixed with 100 ml of distilled water and placed under magnetic stirring at 20 C° for 20 min. For USAE, 20 g of grounded roasted coffee were mixed with 100 ml of distilled water and placed in a ultrasound bath for 10 min. at 20 C°. In both cases, 20 µl of the mixture were placed in a 4 ml vial together with 10 µl of 0.6 ngg<sup>-1</sup> d<sub>4</sub>-furan and brought to 1.5 ml with distilled water.

## Coffee Brewing

*Infusion:* 10 g of grounded roasted coffee were mixed with 100 mL of hot water (about 80 C°). After five minutes the mixture was filtered trough a metal filter; then 20 µl of the filtrate were

1  
2  
3 106 placed in a 4 ml vial together with 10  $\mu\text{l}$  of 0.6  $\text{ngg}^{-1}$  d<sub>4</sub>-furan and brought to 1.5 ml with distilled  
4  
5 107 water.  
6  
7

8 108 *Brewing with an Italian moka pot:* 100 mL of water were poured in the boiler, then the funnel-  
9  
10 109 shaped metal filter is inserted. 20 g of ground coffee is thereupon added, and the upper part is  
11  
12 110 tightly screwed on the base. By placing the pot on a heat source, the water is brought close to  
13  
14  
15 111 boiling point creating steam in the boiler. The espresso is created when the steam reaches a high  
16  
17 112 enough pressure: it gradually forces the surrounding water up the funnel through the coffee powder  
18  
19 113 and into the upper chamber, where the coffee is collected. The brew was transferred into a 100 mL  
20  
21  
22 114 graduated cylinder, made up to the mark with water and analysed as described earlier  
23

24 115 *Espresso machines* Coffee was prepared according to the manufacturer instructions using 7 g coffee  
25  
26 116 pods. After coffee preparation, the dilution ratio has been calculated using a graduate cylinder.  
27  
28

### 29 117 **Samples fortification**

30  
31 118 Recovery experiments were performed by spiking 20 g of coffee samples containing low amount of  
32  
33 119 furan, with 100  $\mu\text{l}$  of furan standard solutions (prepared by appropriate dilution of the stock  
34  
35 120 solution), to achieve the final spiked amounts of 30, 60, 90  $\text{ng g}^{-1}$ . Spiked samples were left at least  
36  
37 121 1 h at 4°C prior to extraction. To study the between-day precision of the method, the furan sample  
38  
39 122 spiked with 60  $\text{ng g}^{-1}$ , was analysed in triplicate for 3 days; the between-day precision was  
40  
41 123 expressed as relative standard deviation of the obtained measurements.  
42  
43  
44  
45

### 46 124 **HS-SPME procedure**

47  
48 125 The procedure described by Altaki et al (2007) was optimized for coffee analysis. 75  $\mu\text{m}$   
49  
50 126 carboxen/polydimethylsiloxane fibers (CAR-PDMS) (Supelco, Milan, Italy) were used for the  
51  
52 127 extraction of furan by using a manual device. The fiber was exposed to the head space of the 4 ml  
53  
54 128 sample vial, adsorption time and temperature were optimized in the ranges 10-30 min. and 20-35  
55  
56 129 C°, respectively. A constant magnetic stirring was applied. The fiber was conditioned in the  
57  
58 130 injection port of the gas chromatograph at 295 C° under helium flow for 2 h. Desorption was  
59  
60 131 performed at 290 C° for 5 min.



### GC-MS conditions

The analysis of furan in coffee samples were performed using a GC 2010 (Shimadzu, Milan, Italy) equipped with a GCMS QP 2010 mass spectrometer. For furan separation a SGE BPX-VOL column (cyanopropylphenyl polysilphenilene-siloxane), 30 m length, 0.25 mm ID, 1.4  $\mu\text{m}$  film thickness (SGE Europe, Villebon, France) was used. The carrier gas was helium at a flow rate of 0.95 ml/min; the GC oven temperature programme was 35°C (held for 2 min) to 230°C at 20 °C min<sup>-1</sup>, the injector temperature was 290°C and the splitless injection mode was used. Interface and ion source temperature were 220 and 250°C, respectively. The MS spectrometer automatically tuned using perfluorotrybutylamine (PFTBA) according to the manufacturer instruction; after automatic tuning the electron multiplier voltage was set at 1000 V. First, EI full scan data were acquired over the range m/z 35-100 at 0.73 sec per scan to confirm appropriate masses for the selected-ion monitoring mode (SIM). In the SIM mode the current of the following ions was recorded: m/z 68 and 39 for furan, m/z 72 and 39 for d<sub>4</sub>-furan; the ionization energy and emission current were 70 eV and 250  $\mu\text{A}$ , respectively.

### HS-SPME optimization

As Altaki et al reported (2007), a 0.75  $\mu\text{m}$  CAR-PDMS fiber and a SGE BPX-VOL capillary column were chosen for furan analysis in coffee. HS-SPME optimization experiments were carried out using a fortified coffee sample. Three parameters of the SPME procedure were re-validated: extraction temperature, extraction time and ionic strength. The optimum conditions reported by Altaki et al for furan analysis in food were the following: sampling temperature of 20 °C, sampling time 30 min. In this study, the temperature was set at 35 C° and sampling time from 10 to 45 min were tested; the same experiments were performed at 30, 25 and 20 C°. The best analytical response for furan extraction was obtained by fixing sampling temperature at 25C° for 15 min. Furthermore Altaki et al (2007) performed furan analysis in food increasing the ionic strength of the medium by adding NaCl in the concentration of 20% (w.w). To confirm this result also for furan analysis in coffee, different amounts of NaCl in the range 0-30% (w.w.) were added to the sample vial. In this

1  
2  
3 158 study opposite results were obtained (**Fig. 1**): by increasing NaCl amount from 0 to 10% no  
4  
5 159 significant difference were noticed, whereas by increasing NaCl concentration from 10% to 30% a  
6  
7  
8 160 remarkable decrease of the analytical response (expressed as furan/ d<sub>4</sub>-furan area ratio) was  
9  
10 161 observed. Therefore further analysis has been carried out with no addition of salt. As Altaki  
11  
12 162 reported, a desorption time of 5 min at 290 C° in the injection port ensured a complete removal of  
13  
14  
15 163 the analyte from the fibre.

### 17 164 **Method validation**

18  
19  
20 165 The overall analytical method was validated according to the guidelines reported by Green (1996)  
21  
22 166 in terms of specificity, linearity, sensitivity, inter and intra day precision and accuracy. The  
23  
24 167 comparison of the chromatogram of a standard solution of furan with that of a coffee sample  
25  
26 168 (**Figure 2**), gave evidence that no co-elution occurred and a good resolution and peak purity were  
27  
28 169 obtained in the chromatographic conditions described.

29  
30 170 A seven points calibration curve ( $y= 33.28x$ ;  $R^2=0.994$ ) covering the range 0.0075-0.486 ngg<sup>-1</sup> was  
31  
32 171 obtained. The limit of detection (LOD) and the limit of quantitation (LOQ), calculated as 3- and 10-  
33  
34 172 fold the signal to noise ratio, were 0.002 and 0.006 pgg<sup>-1</sup>, respectively.

35  
36 173 The best way to assess accuracy is by analyzing standard reference matrices, but coffee standards  
37  
38 174 certified for furan were not available. The second approach is to compare test results from the new  
39  
40 175 method with results from an existing alternate method that is known to be accurate. Again, for furan  
41  
42 176 analysis, such an alternate method is not available. The third approach, which is the most widely  
43  
44 177 used recovery study, is performed by spiking analyte in blank matrices. However, roasted coffee  
45  
46 178 free from furan contamination was not found. The fourth approach is the technique of standard  
47  
48 179 addition or fortification, which is performed by spiking analyte in coffee sample, containing low  
49  
50 180 amounts of furan, at different concentration levels. Spike and recovery test were performed both for  
51  
52 181 the ultrasound assisted extraction and for the magnetic assisted extraction. The obtained results  
53  
54  
55  
56  
57  
58  
59  
60 182

1  
2  
3 183 showed that the accuracy, expressed as recovery factor, ranged between 92.8 and 102%; no  
4  
5 184 significant differences were observed between the two extraction methods. USAE has been used for  
6  
7  
8 185 further analysis. Intra-day precision was within 8%, expressed as RSD% of nine measurements  
9  
10 186 performed on a standard solution and on a diluted coffee sample both containing  $0.05 \text{ ngg}^{-1}$  of  
11  
12 187 furan.

13  
14 188  
15  
16  
17 189 The between-day coefficient of variation, is a very important parameter when establishing routine  
18  
19 190 methods to be used over extended periods. It was determined by performing extraction and analysis  
20  
21  
22 191 of furan on a coffee sample three consecutive days; five measurements were performed each day.  
23  
24 192 The between-day precision achieved was within 10%, expressed as RSD% .

25  
26 193  
27  
28  
29 194 The method validated in this study (test method) for furan analysis in coffee was compared with the  
30  
31 195 method proposed by Altaki et al (2007). The mathematical relation between methods was estimated  
32  
33  
34 196 by a scatterplot with identity line (**Fig 3**) (Bland and Altman, 1986). The regression line obtained  
35  
36 197 showed a good agreement between the two methods.

## 37 38 198 39 40 41 199 **RESULTS and DISCUSSION**

### 42 43 200 **Furan in coffee samples**

44  
45 201 The analysis of furan has been performed on 12 lots of coffee from different producing countries  
46  
47  
48 202 and on 16 pods made of miscellaneous coffee from two different lots (A and B). The concentration  
49  
50 203 of furan found in the powder ranged from 53 to  $587 \text{ ng g}^{-1}$  and no correlation was observed  
51  
52 204 between furan levels and the zone of provenience (**Fig 4**). In particular the 7.14 % of the 14 lots of  
53  
54  
55 205 grounded coffee presented a mean concentration of furan lower than  $100 \text{ ng g}^{-1}$ , the 50 % ranging  
56  
57 206 from 100 to  $200 \text{ ngg}^{-1}$ , the 21.43% from 200 to  $400 \text{ ng g}^{-1}$  and the 21.43% higher than  $400 \text{ ng g}^{-1}$ .  
58  
59 207 The highest mean levels was measured in coffee lots coming from Brazil ( $527 \pm 85 \text{ ng g}^{-1}$ ), the  
60  
208 lowest in those coming from Cameroun ( $142 \pm 119 \text{ ng g}^{-1}$ ). The concentration of furan found in

1  
2  
3 209 coffee powder of this study were lower than those reported by Altaki et al ( $2279\pm 53 \text{ ng g}^{-1}$ ) and  
4  
5 210 within the range reported by EFSA in 2004 ( $3\text{-}5050 \text{ ng g}^{-1}$ ) and higher than those reported by  
6  
7  
8 211 Hasnip et al (2006),  $28\pm 7 \text{ ng g}^{-1}$ .  
9

### 10 212 **Effect of brewing procedures**

11  
12 213 There have been a few studies to investigate if furan persists in food and particularly in coffee,  
13  
14 214 during normal preparation processes leading to consumption. Kuballa et al. (2005) reported that  
15  
16  
17 215 automatic coffee machines produced brews with the highest levels of furan, because the closed  
18  
19 216 system favours retention of furan; much lower levels were produced by standard home coffee-  
20  
21  
22 217 making machines and by manual brewing. Unfortunately, the data provided by this study were too  
23  
24 218 limited to draw any firm conclusions. Hasnip et al., (2006) gave evidence that furan can be lost  
25  
26 219 during food cooking, presumably by evaporation and by entrainment in the large volumes of steam  
27  
28  
29 220 that are released.  
30

31 221  
32  
33 222 Our study aimed to give further insight into the effect of infusion in hot water (Turkish coffee),  
34  
35  
36 223 moka express and espresso machines brewing (Italian coffee) on the content of furan in coffee. To  
37  
38 224 determine the significance of furan reduction by brewing coffee, a paired t-test was performed.  
39

40  
41 225 The results (**Table 1**) gave evidence that furan in contaminated coffee, was reduced by  $57.0\pm 6.9\%$   
42  
43 226 ( $t < 0.0001$ ) after infusion in hot water ( $80 \text{ C}^\circ$ ) for 5 minutes (Turkish coffee); stronger furan  
44  
45 227 reductions were observed by brewing coffee using a moka pot ( $67.5\pm 15.3\%$ ;  $t < 0.0001$ ) or an  
46  
47  
48 228 automatic espresso machines ( $63.3\pm 7.9\%$ ;  $t < 0.0001$ )(Italian coffee). The stronger reduction  
49  
50 229 observed in the last cases might be due to the higher temperature (near  $100 \text{ }^\circ\text{C}$ ) and pressure  
51  
52  
53 230 reached by a moka pot or a coffee machine respect to the infusion procedure. Even though the  
54  
55 231 moka pot and the coffee machine are closed system, furan can be lost presumably by evaporation  
56  
57 232 when the hot brew is poured into the cup and by entrainment in the large volumes of steam.  
58

### 59 233 **Effect of heating temperature: kinetic of furan disappearing**

1  
2  
3 234 Furan is a volatile molecule, and a portion may evaporate when foods are heated. To have further  
4  
5 235 information about the effect of heating temperature on furan reduction in coffee during brewing  
6  
7  
8 236 procedures, the concentration of furan was measured over time by brewing coffee in hot water at  
9  
10 237 80°C and 98 °C (water at 80°C and 98 °C respectively, was poured onto the coffee powder and the  
11  
12 238 temperature of the brew was maintained over the time of the experiment in a thermostatted bath).  
13  
14  
15 239 These experiments were carried out on coffee powder from the Cameroon, corresponding to 57.3 ng  
16  
17 240 g<sup>-1</sup> of furan. **Figure 5a** gives evidence that at 80°C furan level was reduced by 35 % respect to the  
18  
19 241 concentration measured in the powder after 1 min, and by 60 % after 5 min, confirming the results  
20  
21  
22 242 obtained by infusion brewing procedure. After 10 min furan decrease was of 96 %, whereas by  
23  
24 243 prolonging coffee infusion up to 20 min furan level in the brew was lower than the LOD. Furan  
25  
26 244 reduction of 60 % respect to the concentration measured in the powder was observed by heating  
27  
28  
29 245 coffee 1 min in 98 C° water, in agreement with results obtained by brewing coffee with a moka pot  
30  
31 246 or a express automatic machine (this experiment does not take into account the possible effect of the  
32  
33 247 high pressure reached inside a moka or a espresso machine); prolonging heating time up to 5  
34  
35  
36 248 minutes furan decrease was of 91%; after 10 min furan level in the brew was lower than the LOD.  
37

#### 38 249 **Nutritional consideration: furan in the cup**

39 250  
40  
41 251 This study provides evidence that extra-furan is not formed by usual coffee preparation methods,  
42  
43  
44 252 confirming that the limit temperature of furan formation in coffee had been reached only during the  
45  
46 253 roasting processes of industrial preparation. Whereas significant furan losses were observed after  
47  
48  
49 254 brewing coffee by in infusion, using a moka or an espresso machine.  
50

51 255  
52  
53 256 Due to its carcinogenicity, the EFSA (2004 b) recommended to keep furan levels in food 'ALARA',  
54  
55  
56 257 as low as reasonably achievable. The EFSA estimated that the daily intake of furan from coffee  
57  
58 258 (based on data from 45 samples) was 2.4 to 116 µg/person, making coffee the major dietary source  
59  
60 259 for adults. Due to the scarcity of data available, actually the EFSA has invited researchers to submit

1  
2  
3 260 results about furan content in coffee and beverages (EFSA, 2006). Coffee samples of this research  
4  
5 261 represent a poor alimentary source of furan: 100 mL of brew prepared by infusion with 10 g of  
6  
7  
8 262 powder, provides about 0.3-3 µg/day of furan; the intake of 3 cups of coffee (60 mL total) prepared  
9  
10 263 with 20 g of powder using a moka, provide from 0.72 to 2.6 µg/day of furan, whereas 3 cups of  
11  
12 264 espresso (60 mL total) each prepared using the pods of this study provide about 1-1.9 µg/day of  
13  
14  
15 265 furan.  
16

17 266  
18  
19  
20 267 Reduction of furan in foods and particularly in coffee is likely to be more difficult compared to  
21  
22 268 other process contaminants. The obvious way to reduce heat-induced toxins in food is by changes to  
23  
24  
25 269 the heating regime or by reduction in the content of precursors. Both ways are of limited  
26  
27 270 applicability for coffee because temperatures higher than 200C° are required in roasting procedures  
28  
29 271 and it would be technically difficult to purge coffee of furan whilst retaining all the flavour and  
30  
31  
32 272 aroma substances that the consumer demands (Crews and Castle, 2007). Recently Mark et al (2006)  
33  
34 273 proposed the modification of the atmospheres within heating systems: reduction of atmospheric  
35  
36 274 oxygen reduces the autoxidation of unsaturated fatty acids and also reduces furan formation from  
37  
38  
39 275 several precursors. As technological prevention measures against furan formation are not easy to be  
40  
41 276 applied in the coffee industry, the only way to keep under control the introduction of furan in the  
42  
43  
44 277 food chain through coffee consumption, is a systematic investigations of the product after the  
45  
46 278 roasting procedure.  
47

## 48 279 49 280 **References**

- 51 281  
52 Altaki MS, Santos FJ, Galceran MT. 2007. Analysis of furan in foods by head-space solid phase  
53  
54 282 microextraction gas chromatography-ion trap mass spectrometry Journal of Chromatography A.  
55  
56 283 1146: 103-109  
57  
58  
59 284 Becalski A, Seaman S. 2005. Furan precursors in food: a model study and development of a  
60  
285 simple headspace method for determination of furan. J. AOAC International. 88: 102-106.

- 1  
2  
3 286 Bland JM, Altman DG. 1986. Statistical methods for assessing agreements between two  
4  
5 287 methods of clinical measurement. *Lancet*, 1: 307-310  
6  
7  
8 288 Cerny C, Davidek T. Formation of aroma compounds from ribose and cysteine during the  
9  
10 289 Maillard reaction. 2003. *Journal of Agricultural and Food Chemistry*. 51: 2714-2721.  
11  
12 290 Crews C, Castle L. 2007. A review of the occurrence, formation and analysis of furan in heat-  
13  
14  
15 291 processed foods *Trends in Food Science & Technology*. 18: 365-372  
16  
17 292 EFSA. (2004 a) Report of the CONTAM Panel on provisional findings on furan in food.  
18  
19 293 Annexe corrigendum. Available at  
20  
21  
22 294 [http://www.efsa.europa.eu/etc/medialib/efsa/science/contam/contam\\_documents/760.Par.0002.F](http://www.efsa.europa.eu/etc/medialib/efsa/science/contam/contam_documents/760.Par.0002.F)  
23  
24 295 [ile.dat/furan\\_annex1.pdf](http://www.efsa.europa.eu/etc/medialib/efsa/science/contam/contam_documents/760.Par.0002.F)  
25  
26 296 EFSA. (2004 b). Report of the Scientific Panel on Contaminants in the Food Chain on  
27  
28  
29 297 provisional findings of furan in food. *EFSA Journal*, 137, 1-20, Available at  
30  
31 298 [http://www.efsa.eu.int/science/contam/contam\\_documents/760/contam\\_furan\\_report7-11-](http://www.efsa.eu.int/science/contam/contam_documents/760/contam_furan_report7-11-)  
32  
33 299 [051.pdf](http://www.efsa.eu.int/science/contam/contam_documents/760/contam_furan_report7-11-)  
34  
35  
36 300 EFSA. (2006). Invitation to submit data on furan in food and beverages. Available at  
37  
38 301 [http://www.efsa.europa.eu/en/science/data\\_collection/furan.html](http://www.efsa.europa.eu/en/science/data_collection/furan.html)  
39  
40  
41 302 Fan X. 2005a Impact of ionizing radiation and thermal treatments on furan levels in fruit juice.  
42  
43 303 *Journal of Food Science*. 70: 409-414.  
44  
45 304 Fan X. 2005b. Formation of furan from carbohydrates and ascorbic acid following exposure to  
46  
47  
48 305 ionizing radiation and thermal processing. *Journal of Agricultural and Food Chemistry*. 53:  
49  
50 306 7826-7831.  
51  
52  
53 307 FDA. (2004a). Exploratory data on furan in food. Available at  
54  
55 308 <http://www.cfsan.fda.gov/wdms/furandat.html>  
56  
57 309 FDA. (2004b). Determination of furan in foods. Available at  
58  
59 310 <http://www.cfsan.fda.gov/wdms/furan.html>  
60

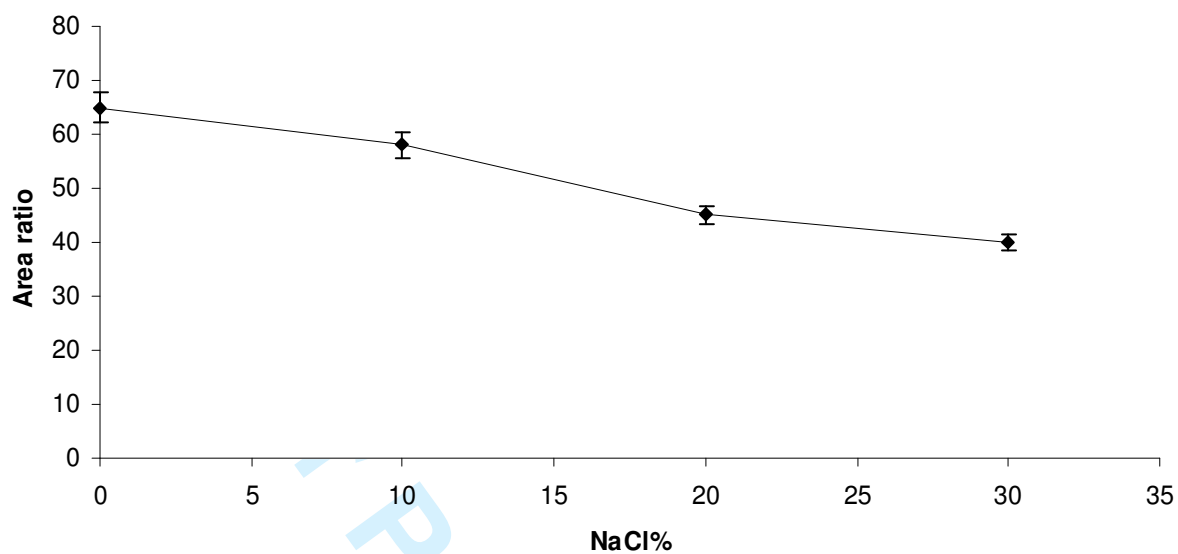
- 1  
2  
3 311 Goldmann T, Perisset A, Scanlan F, Stadler RH. 2005. Rapid determination of furan in heated  
4  
5 312 foodstuffs by isotope dilution solid phase micro-extraction-gas chromatography-mass  
6  
7  
8 313 spectrometry (SPME-GC-MS). *Analyst*, 130: 878-883  
9  
10  
11 314 Green JM. 1996. A Practical Guide to Analytical Method Validation *Analytical Chemistry*, 68:  
12  
13 315 305A-309A  
14  
15  
16  
17 316 Hasnip S, Crews C, Castle L. 2006. Some factors affecting the formation of furan in heated  
18  
19 317 foods. *Food Additives and Contaminants*. 23: 219-227.  
20  
21  
22 318 ISO 4072-1982 (E). Green coffee in bags-Sampling, International Organization for  
23  
24 319 Standardization: Geneva, 1982, pp 1-3.  
25  
26  
27 320 Kuballa T, Stier S, Strichow N. 2005. Furan concentrations in coffee and coffee beverages.  
28  
29 321 *Deutsche Lebensmittel-Rundschau*. 101: 229-235.  
30  
31 322 Locas C P, Yaylayan V A. 2004. Origin and mechanistic pathways of formation of the parent  
32  
33 323 furan-a food toxicant. *Journal of Agricultural and Food Chemistry*. 52: 6830-6836.  
34  
35  
36 324 International Agency for research on Cancer (IARC) Dry cleaning, some chlorinated solvents  
37  
38 325 and other industrial chemicals. In: *Monographs on the evaluation of carcinogenic risks to*  
39  
40  
41 326 *humans 1995, Vol. 63, (pp. 394-407) Lyon: IARC.*  
42  
43 327 Maga J A. Furans in foods. 1979. *Critical Reviews in Food Science and Nutrition*. 4: 355-400.  
44  
45 328 Mark J, Pollien P, Lindinger C, Blank I, Mark T. 2006. Quantitation of furan and methylfuran  
46  
47  
48 329 formed in different precursor systems by proton transfer reaction mass spectrometry. *Journal of*  
49  
50 330 *Agricultural and Food Chemistry*. 54:2786-2793.  
51  
52  
53 331 Nyman P J, Morehouse KM., McNeal TP, Perfetti GA., Diachenko GW. 2006 Single-  
54  
55 332 Laboratory Validation of a Method for the Determination of Furan in Foods by Using Static  
56  
57 333 Headspace Sampling and Gas Chromatography/Mass Spectrometry. *J. of AOAC Int.* 89:1417-  
58  
59 334 1424  
60



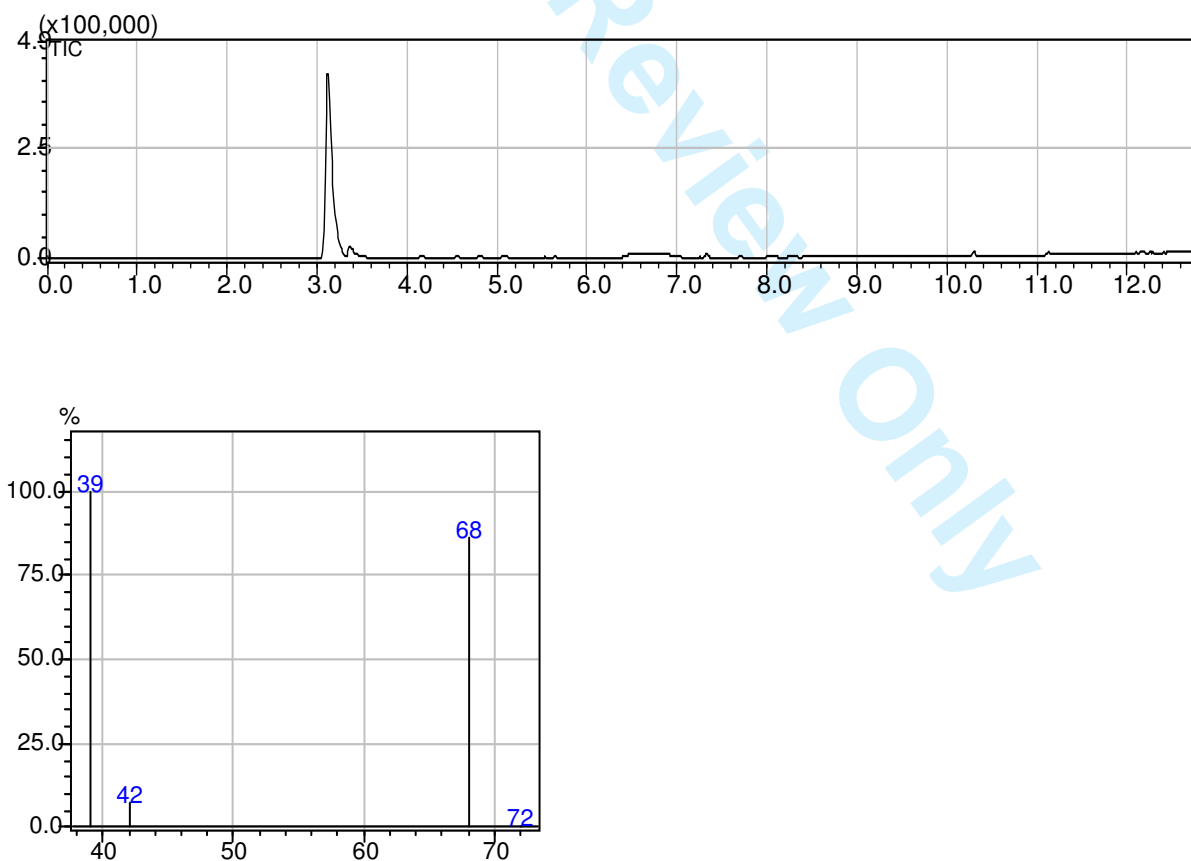
1  
2  
3 335 Nyman P J, Morehouse KM., Perfetti GA., Diachenko GW., Holcomb J R 2008 Single-  
4  
5 336 Laboratory Validation of a Method for the Determination of Furan in Foods by Using  
6  
7  
8 337 Headspace Gas Chromatography/Mass Spectrometry, Part 2—Low-Moisture Snack Foods. J. of  
9  
10 338 AOAC Int. 91: 414 - 421  
11

### 12 13 339 14 15 16 17 340 **Acknowledgements**

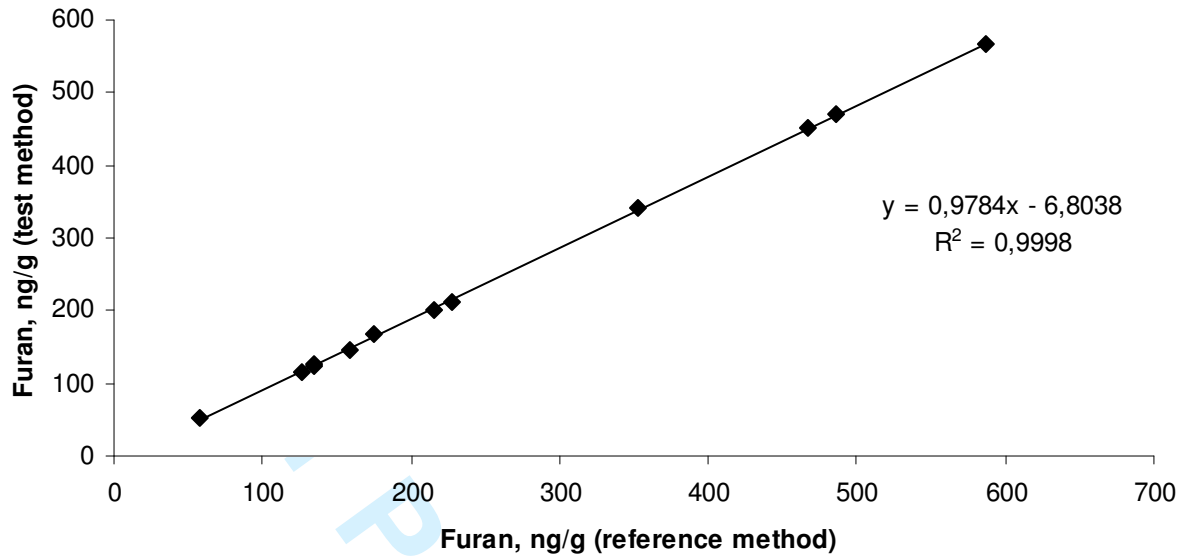
18  
19 341 We thanks Zi-Caffè s.p.a. (Marsala, Trapani) which entirely financed this research.  
20  
21  
22 342  
23  
24 343  
25  
26 344  
27  
28  
29 345  
30  
31 346  
32  
33 347  
34  
35  
36 348  
37  
38 349  
39 350  
40 351  
41  
42  
43 352  
44  
45 353  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



**Figure 1** Effect of ionic strength on furan extraction from coffee ( $t_{\text{sampling}}=15$  min;  $T_{\text{sampling}}=25^{\circ}\text{C}$ )



**Figure 2** Total ion current chromatogram (m/z 68 and m/z 39) of furan in a coffee sample obtained by the GC-MS method described



**Figure 3** Comparison of the proposed method (test) for furan analysis in coffee with that described by Altaki (reference): scatterplot with identity line (agreement line)

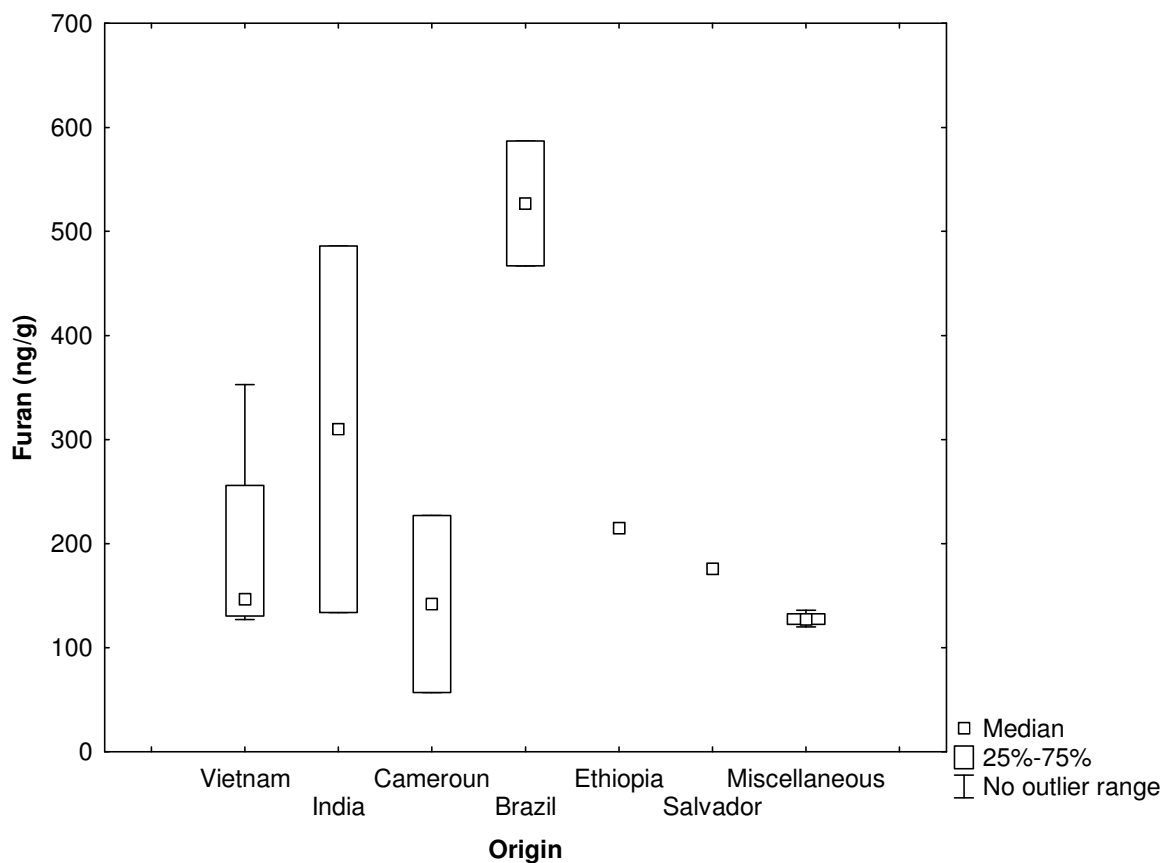
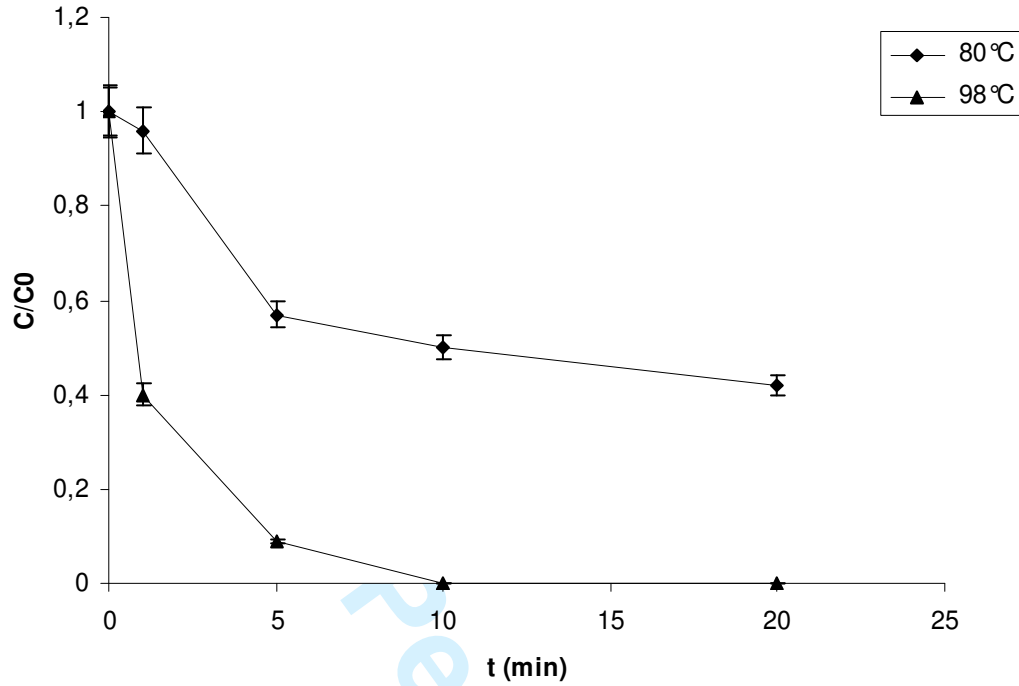


Figure 4 Box-plot of furan concentration found in lots of coffee from different producing countries



a)

**Figure 5 a)** Effect of brewing temperature (80 and 98 °C) on furan concentration in coffee;  $C_0$  represent furan concentration measured in the coffee powder,  $C$  is the concentration found after the brewing procedure .

**Table 1** Furan levels found in coffee powder and in the brew obtained by infusion, using a moka and an espresso machine. Furan concentration in brewed coffee sample is referred to the powder.

<b>Lots of Coffee</b>	<i>POWDER</i> Furan (ngg <sup>-1</sup> )*	<i>MOKA</i> Furan (ngg <sup>-1</sup> )	<i>INFUSION</i> Furan (ngg <sup>-1</sup> )	<i>EXPR. MACH.</i> Furan (ngg <sup>-1</sup> )
<i>Vietnam A</i>	127.0±5.7	81.2±4.9	63.0±1.6	-
<i>Vietnam B</i>	353.3±4.9	54.1±3.9	171.0±3.0	-
<i>Vietnam C</i>	133.7±9.6	66.5±5.6	60.0±4.0	-
<i>Vietnam D</i>	158.7±12.9	36.0±2.2	43.0±3.1	-
<i>India Robusta Monsonato</i>	486.7±41.6	104±7.0	170±5.0	-
<i>India Robusta Cherry</i>	134.1±9.7	60.3±6.2	51.6±4.3	-
<i>Cameroun Robusta</i>	226.3±15.2	131.1±7.8	99.5±3.9	-
<i>Cameroun</i>	57.3±2.9	37.5±3.0	24.5±2.4	-
<i>Santos A</i>	466.7±50.3	72.3±4.8	215.5±10.0	-
<i>Santos B</i>	587.3±32.9	63.8±3.9	305.0±6.0	-
<i>Salvador</i>	175.5±12.3	103.2±6.5	100±6.0	-
<i>Ethiopia Washed</i>	215.5±16.3	60.0±3.3	72.7±6.8	-
<i>Pods from lot A (miscellaneous)** (n=8)</i>	120.0-136.1	-	-	33.1-62.9
<i>Pods from lot B (miscellaneous)** (n=8)</i>	105.5-122.1	-	-	36.3-47.5
<i>MEAN REDUCTION %</i>		<b>67.5±15.3</b>	<b>57.0±6.9</b>	<b>63.3±7.9</b>
<i>t-test</i>		<b>0.0001</b>	<b>0.0001</b>	<b>0.0001</b>

\*Furan level measured in the powder of coffee after cold extraction using ultrasound

\*\*Pods are made of miscellaneous coffee from Zi-Caffé firm