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

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SPECTROMETRY: EFFECT OF BREWING PROCEDURES.**

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TITLE RUNNING HEADER. Effect of brewing methods on furan in coffee

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 μm carboxen/polydimethylsiloxane fiber. Ionic strength, extraction time and temperature, desorption time were valued as the most important parameters affecting the HS-SPME procedure and d_4 -furan was used as the internal standard. The linearity range was in the range 0.0075-0.486 ng g^{-1} , the LOD and LOQ calculated using the signal-to-noise ratio approach were 0.002 and 0.006 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 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.

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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 ng g^{-1} , whereas the 100% of 19 samples of coffee powder were contaminated with concentration ranging from 239 to 5050 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).

Nowadays the EFSA is still collecting data on furan levels in different type of foods, including coffee from different producing countries.

The purpose of this research is to give further insight into the effect of brewing on the presence of furan in coffee samples from different origin. The most diffused procedures to brew coffee have been studied: infusion (also called Turkish coffee), using a moka pot and espresso machines (Italian coffee). A rapid, accurate and high sensitive method has been used, able to detect furan levels in coffee lower than 0.01 ng g^{-1} .

The analysis of furan in food is not easy due to its high volatility and low molecular weight and, moreover, it is present in foods at low concentration levels (ng g^{-1} or pg g^{-1}). Gas chromatography–mass spectrometry combined with headspace (HS-GC–MS) is the method currently used for the analysis of furan in foods (Goldman et al, 2005; Nyman et al, 2006; Altaki et al, 2007; Nyman et al, 2008). In this study the HS-GC–MS method described by Altaki et al. (2007) was employed and re-evaluated for furan analysis in coffee. In particular, the HS-SPME procedure was optimized in terms of extraction time, temperature and ionic strength.

MATERIALS AND METHODS

Reagents

Furan and d_4 -furan at a purity grade higher than 99.0% were purchased from Sigma-Aldrich (Milan, Italy), methanol was obtained from JT Baker (Deventer, Holland). Stock standard solutions of furan and d_4 -furan were prepared in methanol at a concentration of $120 \mu\text{g g}^{-1}$. These solution were stored at 0°C and prepared weekly. Water working standard solutions were prepared daily for dilution of methanolic stock solutions and stored in closed vials at 4°C .

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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⁻¹ d₄-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

placed in a 4 ml vial together with 10 μl of 0.6 ngg^{-1} d₄-furan and brought to 1.5 ml with distilled water.

Brewing with an Italian moka pot: 100 mL of water were poured in the boiler, then the funnel-shaped metal filter is inserted. 20 g of ground coffee is thereupon added, and the upper part is tightly screwed on the base. By placing the pot on a heat source, the water is brought close to boiling point creating steam in the boiler. The espresso is created when the steam reaches a high enough pressure: it gradually forces the surrounding water up the funnel through the coffee powder and into the upper chamber, where the coffee is collected. The brew was transferred into a 100 mL graduated cylinder, made up to the mark with water and analysed as described earlier

Expresso machines Coffee was prepared according to the manufacturer instructions using 7 g coffee pods. After coffee preparation, the dilution ratio has been calculated using a graduate cylinder.

Samples fortification

Recovery experiments were performed by spiking 20 g of coffee samples containing low amount of furan, with 100 μl of furan standard solutions (prepared by appropriate dilution of the stock solution), to achieve the final spiked amounts of 30, 60, 90 ng g^{-1} . Spiked samples were left at least 1 h at 4°C prior to extraction. To study the between-day precision of the method, the furan sample spiked with 60 ng g^{-1} , was analysed in triplicate for 3 days; the between-day precision was expressed as relative standard deviation of the obtained measurements.

HS-SPME procedure

The procedure described by Altaki et al (2007) was optimized for coffee analysis. 75 μm carboxen/polydimethylsiloxane fibers (CAR-PDMS) (Supelco, Milan, Italy) were used for the extraction of furan by using a manual device. The fiber was exposed to the head space of the 4 ml sample vial, adsorption time and temperature were optimized in the ranges 10-30 min. and 20-35 C°, respectively. A constant magnetic stirring was applied. The fiber was conditioned in the injection port of the gas chromatograph at 295 C° under helium flow for 2 h. Desorption was performed at 290 C° for 5 min.

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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 polysilphenilenel-siloxane), 30 m length, 0.25 mm ID, 1.4 µm 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 35C° (held for 2 min) to 230C° at 20 °C min⁻¹, 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 d₄-furan; the ionization energy and emission current were 70 eV and 250 µA, respectively.

HS-SPME optimization

As Altaki et al reported (2007), a 0.75 µm 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-valuated: 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

study opposite results were obtained (**Fig. 1**): by increasing NaCl amount from 0 to 10% no significant difference were noticed, whereas by increasing NaCl concentration from 10% to 30% a remarkable decrease of the analytical response (expressed as furan/ d₄-furan area ratio) was observed. Therefore further analysis has been carried out with no addition of salt. As Altaki reported, a desorption time of 5 min at 290 C° in the injection port ensured a complete removal of the analyte from the fibre.

Method validation

The overall analytical method was validated according to the guidelines reported by Green (1996) in terms of specificity, linearity, sensitivity, inter and intra day precision and accuracy. The comparison of the chromatogram of a standard solution of furan with that of a coffee sample (**Figure 2**), gave evidence that no co-elution occurred and a good resolution and peak purity were obtained in the chromatographic conditions described.

A seven points calibration curve ($y = 33.28x$; $R^2 = 0.994$) covering the range 0.0075-0.486 ngg⁻¹ was obtained. The limit of detection (LOD) and the limit of quantitation (LOQ), calculated as 3- and 10-fold the signal to noise ratio, were 0.002 and 0.006 pgg⁻¹, respectively.

The best way to assess accuracy is by analyzing standard reference matrices, but coffee standards certified for furan were not available. The second approach is to compare test results from the new method with results from an existing alternate method that is known to be accurate. Again, for furan analysis, such an alternate method is not available. The third approach, which is the most widely used recovery study, is performed by spiking analyte in blank matrices. However, roasted coffee free from furan contamination was not found. The fourth approach is the technique of standard addition or fortification, which is performed by spiking analyte in coffee sample, containing low amounts of furan, at different concentration levels. Spike and recovery test were performed both for the ultrasound assisted extraction and for the magnetic assisted extraction. The obtained results

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3 183 showed that the accuracy, expressed as recovery factor, ranged between 92.8 and 102%; no
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5 184 significant differences were observed between the two extraction methods. USAE has been used for
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7 185 further analysis. Intra-day precision was within 8%, expressed as RSD% of nine measurements
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10 186 performed on a standard solution and on a diluted coffee sample both containing 0.05 ngg⁻¹ of
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17 189 The between-day coefficient of variation, is a very important parameter when establishing routine
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19 190 methods to be used over extended periods. It was determined by performing extraction and analysis
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22 191 of furan on a coffee sample three consecutive days; five measurements were performed each day.
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24 192 The between-day precision achieved was within 10%, expressed as RSD% .
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29 194 The method validated in this study (test method) for furan analysis in coffee was compared with the
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31 195 method proposed by Altaki et al (2007). The mathematical relation between methods was estimated
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33 196 by a scatterplot with identity line (**Fig 3**) (Bland and Altman, 1986). The regression line obtained
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36 197 showed a good agreement between the two methods.
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41 199 **RESULTS and DISCUSSION**
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43 200 **Furan in coffee samples**
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45 201 The analysis of furan has been performed on 12 lots of coffee from different producing countries
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47 202 and on 16 pods made of miscellaneous coffee from two different lots (A and B). The concentration
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50 203 of furan found in the powder ranged from 53 to 587 ng g⁻¹ and no correlation was observed
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52 204 between furan levels and the zone of provenience (**Fig 4**). In particular the 7.14 % of the 14 lots of
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55 205 grounded coffee presented a mean concentration of furan lower than 100 ng g⁻¹, the 50 % ranging
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57 206 from 100 to 200 ngg⁻¹, the 21.43% from 200 to 400 ng g⁻¹ and the 21.43% higher than 400 ng g⁻¹.
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59 207 The highest mean levels was measured in coffee lots coming from Brazil (527±85 ng g⁻¹), the
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208 lowest in those coming form Cameroun (142±119 ng g⁻¹). The concentration of furan found in

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

Effect of brewing procedures

There have been a few studies to investigate if furan persists in food and particularly in coffee, during normal preparation processes leading to consumption. Kuballa et al. (2005) reported that automatic coffee machines produced brews with the highest levels of furan, because the closed system favours retention of furan; much lower levels were produced by standard home coffee-making machines and by manual brewing. Unfortunately, the data provided by this study were too limited to draw any firm conclusions. Hasnip et al., (2006) gave evidence that furan can be lost during food cooking, presumably by evaporation and by entrainment in the large volumes of steam that are released.

Our study aimed to give further insight into the effect of infusion in hot water (Turkish coffee), moka express and espresso machines brewing (Italian coffee) on the content of furan in coffee. To determine the significance of furan reduction by brewing coffee, a paired t-test was performed.

The results (**Table 1**) gave evidence that furan in contaminated coffee, was reduced by $57.0 \pm 6.9\%$ ($t < 0.0001$) after infusion in hot water ($80 \text{ }^{\circ}\text{C}$) for 5 minutes (Turkish coffee); stronger furan reductions were observed by brewing coffee using a moka pot ($67.5 \pm 15.3\%$; $t < 0.0001$) or an automatic espresso machines ($63.3 \pm 7.9\%$; $t < 0.0001$) (Italian coffee). The stronger reduction observed in the last cases might be due to the higher temperature (near $100 \text{ }^{\circ}\text{C}$) and pressure reached by a moka pot or a coffee machine respect to the infusion procedure. Even though the moka pot and the coffee machine are closed system, furan can be lost presumably by evaporation when the hot brew is poured into the cup and by entrainment in the large volumes of steam.

Effect of heating temperature: kinetic of furan disappearing

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3 234 Furan is a volatile molecule, and a portion may evaporate when foods are heated. To have further
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5 235 information about the effect of heating temperature on furan reduction in coffee during brewing
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7 236 procedures, the concentration of furan was measured over time by brewing coffee in hot water at
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9 237 80°C and 98 °C (water at 80°C and 98 °C respectively, was poured onto the coffee powder and the
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11 238 temperature of the brew was maintained over the time of the experiment in a thermostatted bath).
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13 239 These experiments were carried out on coffee powder from the Cameroon, corresponding to 57.3 ng
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15 240 g⁻¹ of furan. **Figure 5a** gives evidence that at 80°C furan level was reduced by 35 % respect to the
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17 241 concentration measured in the powder after 1 min, and by 60 % after 5 min, confirming the results
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19 242 obtained by infusion brewing procedure. After 10 min furan decrease was of 96 %, whereas by
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21 243 prolonging coffee infusion up to 20 min furan level in the brew was lower than the LOD. Furan
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23 244 reduction of 60 % respect to the concentration measured in the powder was observed by heating
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25 245 coffee 1 min in 98 C° water, in agreement with results obtained by brewing coffee with a moka pot
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27 246 or a express automatic machine (this experiment does not take into account the possible effect of the
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29 247 high pressure reached inside a moka or a espresso machine); prolonging heating time up to 5
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31 248 minutes furan decrease was of 91%; after 10 min furan level in the brew was lower than the LOD.
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41 250 **Nutritional consideration: furan in the cup**

42 251 This study provides evidence that extra-furan is not formed by usual coffee preparation methods,
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44 252 confirming that the limit temperature of furan formation in coffee had been reached only during the
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46 253 roasting processes of industrial preparation. Whereas significant furan losses where observed after
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48 254 brewing coffee by in infusion, using a moka or an espresso machine.
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53 256 Due to its carcinogenicity, the EFSA (2004 b) recommended to keep furan levels in food ‘ALARA’,
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55 257 as low as reasonably achievable. The EFSA estimated that the daily intake of furan from coffee
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57 258 (based on data from 45 samples) was 2.4 to 116 µg/person, making coffee the major dietary source
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59 259 for adults. Due to the scarcity of data available, actually the EFSA has invited researchers to submit
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results about furan content in coffee and beverages (EFSA, 2006). Coffee samples of this research represent a poor alimentary source of furan: 100 mL of brew prepared by infusion with 10 g of powder, provides about 0.3-3 µg/day of furan; the intake of 3 cups of coffee (60 mL total) prepared with 20 g of powder using a moka, provide from 0.72 to 2.6 µg/day of furan, whereas 3 cups of espresso (60 mL total) each prepared using the pods of this study provide about 1-1.9 µg/day of furan.

Reduction of furan in foods and particularly in coffee is likely to be more difficult compared to other process contaminants. The obvious way to reduce heat-induced toxins in food is by changes to the heating regime or by reduction in the content of precursors. Both ways are of limited applicability for coffee because temperatures higher than 200°C are required in roasting procedures and it would be technically difficult to purge coffee of furan whilst retaining all the flavour and aroma substances that the consumer demands (Crews and Castle, 2007). Recently Mark et al (2006) proposed the modification of the atmospheres within heating systems: reduction of atmospheric oxygen reduces the autoxidation of unsaturated fatty acids and also reduces furan formation from several precursors. As technological prevention measures against furan formation are not easy to be applied in the coffee industry, the only way to keep under control the introduction of furan in the food chain through coffee consumption, is a systematic investigations of the product after the roasting procedure.

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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.

Lots of Coffee	POWDER <i>Furan (ngg⁻¹)*</i>	MOKA <i>Furan (ngg⁻¹)</i>	INFUSION <i>Furan (ngg⁻¹)</i>	EXPR. MACH. <i>Furan (ngg⁻¹)</i>
<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>		67.5±15.3	57.0±6.9	63.3±7.9
<i>t-test</i>		0.0001	0.0001	0.0001

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

**Pods are made of miscellaneous coffee from Zi-Caffè firm