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Furanic compounds in different coffee extraction systems: Analysis of the main influencing factors and correlation with acrylamide

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ABSTRACT

This study investigates how different coffee types representative of distinct roast profiles and brewing methods jointly affect the occurrence of furanic compounds and acrylamide in brewed coffee. Coffees were prepared using eight extraction methods (AeroPress, Clever, Chemex, French Press, Moka, Pure Brew, Turkish and V60). Five furanic compounds (furfural, furfuryl acetate, 5-methylfurfural, furfuryl alcohol and 5-hydroxymethylfurfural) were quantified in coffee powders and brews by HS-SPME-GC–MS, while acrylamide was determined by UHPLC–MS/MS. Moka and Turkish brews consistently exhibited the highest concentrations of furanic compounds, whereas paper-filtered pour-over methods (V60 and Chemex) showed the lowest levels. Pearson correlation analysis revealed coffee-dependent relationships between furanic compounds, acrylamide and extraction parameters with the strongest associations observed in dark-roasted coffee, reflecting advanced Maillard reaction chemistry. Overall, these results demonstrate that contaminant levels arise from the combined effects of intrinsic coffee chemistry and brewing mechanics and support targeted mitigation strategies: such as roast selection and brewing method optimization.

1. Introduction

Coffee's widespread popularity can be attributed to its appealing taste, aroma and stimulating properties. Consequently, there is a growing interest in researching coffee quality, extending beyond taste and aroma evaluation to include an assessment of potential toxicological effects (Hall et al., 2022). The roasting process introduces various thermal reactions in coffee beans, including the Maillard reaction, sugar caramelization, Strecker degradation and pyrolysis (Tarigan et al., 2022; Zhu et al., 2022). These processes result in the formation of compounds responsible for coffee's sensory attributes, yet some of these compounds pose potential health risks (Aguiar et al., 2016; Taş & Gökmen, 2017). Among these extensively investigated compounds, furans are prevalent contaminants in thermally processed foods, formed through the thermal degradation of carbohydrates and amino acids. They are derivatives of furan, categorized by the International Agency for Research on Cancer (IARC) as Group 2B (possibly carcinogenic to humans). Furfuryl alcohol is classified as Group 2B by IARC as well (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2017). Moreover, furfural, a compound produced during heat processes like roasting, has been classified, in Group 3, indicating that "the substance is not classifiable as to its carcinogenicity to humans" (Liu et al., 2023; EFSA, 2017).

Another concerning compound is the acrylamide, classified as Group 2 A "probably carcinogenic to humans" by the IARC (Kocadağlı & Gökmen, 2022; Koszucka et al., 2020), it forms during the Maillard reaction at temperatures above 120 °C (Gökmen, 2023). The European Food Safety Authority (EFSA) has highlighted the potential health concern on gene mutations promoting cancer development, due to relatively low Margin of Exposure (MoE) values (Çebi, 2024). According to the literature, ground coffee has been reported to exhibit significant levels of furanic compounds and acrylamide among coffee products, while their contents in coffee cup depend on the adopted extraction method. In addition, also the roasting parameters, including time and temperature, have an impact on the chemical composition of coffee brews. In fact, high roasting temperatures and times were associated with increased levels of specific furanic compounds and decreased acrylamide levels (Acquaticci et al., 2023; Córdoba et al., 2021; Yu et al., 2021). Despite the negative health effects of these compounds, their concentrations and formation mechanisms across different coffee extraction systems remain underexplored. This paper aims to address this gap by conducting a comprehensive analysis of these analytes such as furfural, furfuryl acetate, 5-methylfurfural, furfuryl alcohol and 5-

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(hydroxymethyl)furfural (5-HMF), in various coffee extraction systems, applied to different coffees. The study encompassed different coffee extraction methods, including more traditional (Moka, Turkish), pour over (Clever, Chemex and V60), full immersion (French Press, AeroPress) and mechanized approaches (Pure Brew). Moreover, potential correlation between the contents of furanic substances, acrylamide and some extraction parameters has been evaluated to select a coffee extraction system which could minimize potential health risks associated with coffee consumption.

2. Experimental section

2.1. Chemicals and reagents

Pure standards of furfural (CAS 98–01-1), furfuryl acetate (CAS 623–17-6), 5-methylfurfural (CAS 620–02-0), furfuryl alcohol (CAS 90–00-0), 5-(hydroxymethyl)furfural (5-HMF) (CAS 67–47-0) and HPLC-grade ethanol were purchased from Sigma Aldrich (Milan, Italy). The stock solutions of target volatile compounds were prepared by mixing 10 mg of pure standards with 10 mL of HPLC-grade ethanol (1000 mg/L). Standard working solutions at different concentration were prepared by diluting the stock solutions in ultrapure water. Acrylamide (AA, for molecular biology ≥99%, HPLC, C_3H_5NO, molecular weight 71.08 g/mol, CAS No 79–06-1) and 2,3,3-d_3-acrylamide (AA-d_3) standard solution, 500 mg/mL in acetonitrile (analytical standard, CAS 122775–19-3) was purchased from Sigma Aldrich (St. Louis, MO, USA). The individual stock solution of AA was prepared by dissolving the pure standard compound in ultra-pure water at a concentration of 1000 mg/L and stored in glass-stoppered bottles at −18 °C. Afterwards, standard working solutions at various concentrations were prepared daily by appropriate dilution of the stock solution with water. A solution of AA-d_3 was combined with standard working solutions of native AA prepared at various concentrations to obtain a concentration of 500 ng/mL. Bond Elut-Accucat, 200 mg, 3 mL cartridges for solid-phase extraction (SPE) were bought from Agilent Technology (Santa Clara, CA, USA), while Oasis HLB 200 mg, 6 mL cartridges were purchased from Waters (Milford, MA, USA). Deionized water was further purified using a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). Before high-performance liquid chromatography–tandem mass (HPLC-MS/MS) analysis, all samples were filtered with a PhenexTM RC 4 mm 0.2 μm syringeless filter.

2.2. Coffee samples

Eight filter coffee extraction methods were tested with three distinct coffee types: Gardelli Specialty's natural, non-classic anaerobic Ethiopia Uraga (light roasting); Gardelli Specialty's washed Kenya Thiriku (medium roasting); Roasted Blond 100% Starbucks Arabica (dark roasting).

The selected coffees differed not only in roasting degree, but also in origin and post-harvest processing. Therefore, the study was designed to evaluate commercially representative coffee samples associated with different roast profiles rather than to isolate the sole effect of roasting degree under controlled conditions. The coffee varieties were chosen to represent a realistic spectrum of "filter" and "specialty" coffees, reflecting typical consumer preferences. All coffee samples were prepared by professional baristas, with coffee ground obtained using a professional grinder (Atom Brew Pro - Eureka). Nerea water was used for all preparations, selected for its balanced mineral composition (161 mg/L dry residue). A standard procedure was followed for each of the eight brewing techniques, maintaining consistent parameters, while preserving the unique characteristics of each method. Three replicates were conducted for each brewing method (Table 1S). The same coffee brew samples were analyzed for the acrylamide contents in a previous work and the standard procedures adopted to prepare coffee beverages are described in that paper (Santanatoglia, Alessandroni, et al., 2023). Briefly, the summary of the eight coffee preparation methods is reported in the following subsections.

2.2.1. AeroPress

This method uses two nested cylinders. The AeroPress® Micro Filter is pre-wet and placed at the bottom. Coffee grounds are measured, and a blooming phase involves pouring 60 mL of water, stirring three times and repeating the process with additional water. Pressure is applied for 40 s, using a coffee-to-water ratio of 15:225.

2.2.2. Chemex

Chemex is made of a transparent hourglass shaped carafe, involves moistening the bonded filter before placing it in the cone. Hot water (93 °C) is poured over the coffee grounds in two stages, with a brewing ratio of 20:300.

2.2.3. Clever

Clever consists of plastic cone with a valve, it starts by pouring 300 g of 93 °C water over coffee grounds, mixing for 10 s and allowing steeping for 3 min before filtering. The brewing ratio is 20:300.

2.2.4. French press

This method uses a cylindrical pot with a plunger. Ground coffee is steeped with water, with turbulence introduced at 1-, 2- and 3-min intervals. After 4 min, the filter is pressed to separate solids from the liquid, following a 20:300 ratio.

2.2.5. Moka

The Moka pot consists of a base container, a funnel filter and a top chamber. It brews coffee with 250 g of water and 25 g of grounds. A Bialetti Moka Express, 6-cup size, was used for the preparation.

Table 1
Levels (mean ± standard deviation) of furanic compounds and acrylamide in different samples of coffee powder (light, medium and dark) obtained by GC–MS analysis, expressed in mg/kg. Different superscript letters (^{a,b,c}) denote significant differences ($p < 0.05$) among different coffee roasting levels.

Sample	Furfural	Furfuryl acetate	5-Methyl furfural	Furfuryl alcohol	5-HMF	Acrylamide
LIGHT Specialty natural Ethiopia	325.67 ± 3.41^{c}	12.07 ± 3.36^{c}	112.57 ± 2.41^{c}	1124.22 ± 3.12^{c}	12.26 ± 1.11^{b}	423.00 ± 6.21^{b}
MEDIUM Specialty washed Kenya	1618.41 ± 3.28^{a}	117.84 ± 2.11^{b}	416.77 ± 3.58^{b}	2972.33 ± 4.23^{a}	5.60 ± 1.12^{a}	361.20 ± 11.25^{c}
DARK Blond 100% Starbucks	1284.84 ± 6.05^{b}	189.45 ± 5.16^{a}	815.34 ± 4.14^{a}	2650.57 ± 8.81^{b}	5.08 ± 1.34^{a}	497.00 ± 15.42^{a}

2.2.6. Pure brew

This method uses the VA388 Black Eagle Maverick espresso machine with a fine-mesh basket. Coffee is brewed with a 20:260 ratio at 93 °C.

2.2.7. Ibrik coffee (Turkish coffee)

Turkish coffee is prepared using a traditional cezve, this method combines 8 g of coffee with 80 g of water at 100 °C. The mixture is brought to a boil twice, following a 1:10 ratio.

2.2.8. V60

V60 consisted of a three-part dripper system, the V60 requires pre-wetting a paper filter and placing coffee grounds on top. Water (93 °C) is poured in two stages: 60 mL for pre-infusion and another 100 mL after 30 s, using a 20:300 brewing ratio.

2.3. Headspace solid-phase microextraction (HS-SPME)

Furanic compounds in both ground and brew coffee were analyzed using headspace-solid phase microextraction coupled with gas chromatography–mass spectrometry (HS-SPME-GC–MS). For ground coffee, 3 g of sample were weighted directly into a 20 mL vial and sealed with a screw cap equipped with a PTFE/silicone septum, without the addiction of additional solvents. Vials were equilibrated at 60 °C, and the subsequent extraction and analysis followed the same procedure applied to brew samples, with 3 mL of the coffee sample.

The analysis followed a method previously established by Acquaticci et al., 2023. Briefly, the SPME fiber was conditioned for 10 min at 250 °C before being inserted into the vial's headspace at a speed of 20 mm/s and a penetration depth of 40 mm. The extraction process was carried out at 60 °C for 30 min, after which the fiber was introduced into the injector port at a speed of 100 mm/s and a penetration depth of 40 mm. Desorption of analytes occurred at 250 °C for 1 min and the fiber was subsequently conditioned again at 250 °C for 10 min.

2.4. GC–MS furanic compounds analysis

Furanic compounds in both ground and brewed coffee samples were analyzed using headspace solid-phase microextraction coupled with gas chromatography–mass spectrometry (HS-SPME-GC–MS). The analytical procedure was adapted from a previously developed method for volatile Maillard-derived compounds with modifications specifically optimized for coffee matrices and furanic analytes. For ground coffee analysis, 3 g of freshly ground sample were directly weighed into a 20 mL headspace vial and tightly sealed with a screw cap equipped with a PTFE/silicone septum, without the addition of solvents or salts, in order to avoid dilution effects and preserve the native volatile profile of the sample. For brewed coffee analysis, 3 mL of coffee beverage were transferred into 20 mL vials under the same conditions. A Divinylbenzene/Carbon-Wide Range/Polydimethylsiloxane (DVB/C-WR/PDMS) fiber (Supelco, Bellefonte, PA, USA) was selected because of its high affinity toward low-molecular-weight volatile compounds and furan derivatives, as previously reported (Acquaticci et al., 2023) for thermally processed food matrices. HS-SPME was selected as a suitable solvent-free extraction technique for highly volatile furanic compounds, minimizing matrix interference and analyte loss while allowing efficient enrichment directly from the sample headspace. Extraction conditions were selected according to previous optimization studies on volatile Maillard-derived compounds and represented a compromise between extraction efficiency and prevention of thermal artefact formation. In particular, moderate extraction temperatures were employed to avoid excessive thermal degradation or artificial formation of furanic compounds during analysis. Before extraction, samples were equilibrated at 60 °C. The SPME fiber was conditioned at 250 °C for 10 min according to manufacturer recommendations and subsequently exposed to the vial headspace at a speed of 20 mm/s with a penetration depth of 40 mm. The extraction was carried out at 60 °C for 30 min. These conditions were selected to maximize headspace equilibrium of volatile furans while limiting competitive adsorption phenomena on the fiber coating. After extraction, the fiber was introduced into the GC injector port at a speed of 100 mm/s with a penetration depth of 40 mm. Thermal desorption was performed at 250 °C for 1 min in splitless mode. Following each analysis, the fiber was reconditioned at 250 °C for 10 min to minimize carry-over effects and ensure analytical repeatability. All analyses were performed in triplicate to ensure analytical reproducibility and repeatability of the measurements.

GC–MS analysis.

GC–MS analyses were carried out using an Agilent 8890 gas chromatograph coupled with a PAL RTC 120 autosampler and an Agilent 5977B mass selective detector (MSD) equipped with an electron ionization (EI) source (Agilent Technologies, Santa Clara, CA, USA). The injector temperature was set at 250 °C and an Ultra Inert splitless straight liner specifically recommended for SPME applications (0.75 mm i.d., Agilent 5190–4048) was employed. Helium was used as carrier gas at a constant flow rate of 1 mL/min. The chromatographic separation of target analytes was achieved using a DB-WAX capillary column (60 m × 250 μm i.d. × 0.25 μm film thickness). The oven temperature program started at 35 °C and was maintained for 3 min, then increased to 200 °C at 5 °C/min and finally raised to 250 °C at 15 °C/min, held for 5 min. The total run time was approximately 44.3 min. The transfer line temperature was maintained at 250 °C, while ion source and quadrupole analyzer temperatures were set at 230 °C and 150 °C, respectively. The ion species selection and optimization for each analyte were carried out using authentic analytical standards. Data acquisition was performed in Selected Ion Monitoring (SIM) mode in order to improve analytical sensitivity and selectivity toward target furanic compounds while reducing background noise. Detection was divided into specific time windows to further enhance sensitivity. For each analyte, the most abundant ion was used for quantification, while additional qualifier ions were employed for compound confirmation. Retention times, monitored ions and acquisition windows are reported in Table 2S. Compound identification was based on comparison with NIST retention times and characteristic mass fragments. Mass spectral information was additionally compared with available spectral libraries when appropriate. Data acquisition and processing were carried out using MSD ChemStation Software (Agilent Technologies, Version G1701DA D.01.00). All analyses were performed in triplicate and results were expressed as mean ± standard deviation.

2.5. UHPLC-MS/MS acrylamide analysis

Data on acrylamide in coffee brew were reported in a previous paper by Santanatoglia, Angeloni, et al., 2023 and those findings were used for the correlation study. On the other hand, the levels of acrylamide in the three ground coffees were measured in the present work following a previously developed and validated method (Santanatoglia, Cespi, et al., 2023; Schouten et al., 2023). The analysis utilized an Agilent 1290 Infinity Series UHPLC system paired with a 6420 Triple Quadrupole mass spectrometer from Agilent Technologies (Santa Clara, CA, USA), equipped with an electrospray ionization (ESI) source operating in positive polarity. The analytical column was a Kinetex Hilic (100 mm length, 4.6 mm i.d., 2.6 μm particle size) from Phenomenex (Torrance, CA, USA), preceded by a KrudKatcher ULTRA HPLC in-line filter (2.0 μm depth, 0.004 in i.d.). The mobile phase comprised water (A) and acetonitrile (B), each containing 0.1% formic acid and was delivered at a flow rate of 0.8 mL/min in gradient elution mode. The gradient profile was as follows: 0–2.5 min at 85% B; 2.5–3.5 min, 85–70% B; 3.5–5.5 min, 70% B; 5.5–6.5 min, 70–60% B; and 6.5–10 min, 60% B. The injection volume was set at 2 μL. The drying gas temperature was maintained at 350 °C with a gas flow of 12 L/min, the nebulizer pressure was 45 psi, and the capillary voltage was 4000 V. Data acquisition was performed in “Multiple Reaction Monitoring” (MRM) mode (Table 3S).

Table 2
Levels (mean ± standard deviation) of furanic compounds in different coffee samples, expressed in mg/L. Different superscript letters (^{a,b,c,d,e,f,g}) denote significant differences ($p < 0.05$) among different coffee extraction methods.

Roasting level	Extraction method	Furfural	Furfuryl acetate	5-Methyl furfural	Furfuryl alcohol	5-HMF	SUM of FURANIC COMPOUNDS
LIGHT Specialty natural Ethiopia	AEROPRESS	16.91 ± 1.80^{b}	12.20 ± 0.92^{b}	6.70 ± 0.69^{b}	18.82 ± 2.61^{c}	0.48 ± 0.11^{e}	55.11 ± 6.11^{b}
	CLEVER	7.63 ± 1.26^{e}	6.25 ± 0.81^{d}	3.02 ± 0.48^{d}	15.83 ± 2.35^{d}	1.02 ± 0.02^{c}	33.76 ± 4.87^{e}
	CHEMEX	6.76 ± 1.48^{e}	5.88 ± 1.04^{d}	2.58 ± 0.52^{d}	10.67 ± 2.42^{e}	0.48 ± 0.11^{e}	22.82 ± 4.81^{f}
	FRENCH PRESS	8.90 ± 0.02^{d}	7.32 ± 0.03^{c}	3.54 ± 0.02^{d}	18.17 ± 0.08^{c}	1.88 ± 0.06^{b}	39.81 ± 0.05^{d}
	MOKA	37.51 ± 2.95^{a}	29.72 ± 1.55^{a}	14.93 ± 1.21^{a}	44.10 ± 4.79^{a}	5.32 ± 1.04^{a}	131.58 ± 11.43^{a}
	PURE BREW	5.50 ± 1.28^{e}	5.74 ± 1.43^{d}	2.30 ± 0.55^{d}	11.05 ± 2.70^{e}	0.75 ± 0.19^{d}	25.34 ± 5.85^{f}
	TURKISH	10.99 ± 0.55^{c}	4.35 ± 0.56^{e}	4.33 ± 0.09^{c}	23.41 ± 0.59^{b}	2.31 ± 0.50^{b}	45.39 ± 0.93^{c}
	V60	8.68 ± 0.17^{d}	7.50 ± 0.26^{c}	3.47 ± 0.06^{c}	17.09 ± 0.07^{c}	0.61 ± 0.02^{e}	37.36 ± 0.43^{d}
MEDIUM Specialty washed Kenya	AEROPRESS	18.09 ± 4.24^{c}	5.83 ± 1.21^{c}	5.05 ± 1.22^{c}	18.82 ± 2.61^{d}	3.88 ± 0.74^{b}	51.67 ± 3.73^{c}
	CLEVER	12.60 ± 1.05^{e}	4.06 ± 0.24^{d}	3.47 ± 0.35^{d}	15.84 ± 2.35^{e}	1.16 ± 0.25^{d}	37.14 ± 4.24^{e}
	CHEMEX	15.41 ± 0.03^{d}	4.92 ± 0.04^{d}	4.18 ± 0.07^{d}	11.96 ± 2.82^{c}	2.06 ± 0.02^{c}	38.54 ± 2.70^{d}
	FRENCH PRESS	11.73 ± 2.50^{e}	4.12 ± 0.90^{d}	3.22 ± 0.69^{d}	18.17 ± 0.07^{f}	2.97 ± 0.73^{b}	40.20 ± 4.86^{f}
	MOKA	24.63 ± 0.29^{a}	8.37 ± 0.24^{a}	6.98 ± 0.09^{b}	44.10 ± 4.78^{a}	4.81 ± 0.97^{a}	88.88 ± 3.28^{a}
	PURE BREW	13.41 ± 0.26^{e}	4.81 ± 0.23^{d}	3.76 ± 0.03^{d}	10.88 ± 2.62^{d}	3.38 ± 0.46^{b}	36.24 ± 2.58^{d}
	TURKISH	24.19 ± 5.61^{a}	7.78 ± 1.48^{a}	7.14 ± 1.78^{a}	23.41 ± 0.59^{b}	5.41 ± 1.14^{a}	67.93 ± 10.50^{a}
	V60	22.54 ± 4.91^{b}	7.06 ± 1.45^{b}	6.21 ± 1.48^{b}	17.09 ± 0.07^{c}	1.48 ± 0.37^{d}	54.83 ± 8.12^{b}
DARK Blond 100% Starbucks	AEROPRESS	12.92 ± 1.46^{c}	29.17 ± 1.44^{c}	8.55 ± 1.01^{e}	31.51 ± 5.94^{d}	n.d.	82.14 ± 9.85^{d}
	CLEVER	5.82 ± 1.12^{e}	15.03 ± 2.29^{f}	4.16 ± 0.95^{f}	26.57 ± 5.02^{e}	0.13 ± 0.03^{c}	51.72 ± 9.39^{e}
	CHEMEX	13.99 ± 0.27^{c}	29.45 ± 0.44^{c}	8.63 ± 0.15^{d}	30.56 ± 0.75^{d}	0.78 ± 0.07^{b}	83.41 ± 1.68^{c}
	FRENCH PRESS	14.47 ± 2.43^{c}	26.19 ± 1.70^{d}	9.41 ± 1.36^{c}	34.11 ± 5.57^{c}	n.d.	84.18 ± 11.05^{c}
	MOKA	28.56 ± 0.55^{a}	33.82 ± 0.03^{a}	19.00 ± 0.78^{a}	73.71 ± 4.29^{a}	n.d.	155.09 ± 5.58^{a}
	PURE BREW	8.00 ± 1.81^{d}	18.91 ± 2.95^{e}	5.37 ± 1.23^{c}	35.09 ± 5.54^{c}	0.32 ± 0.07^{c}	67.69 ± 11.59^{d}
	TURKISH	21.34 ± 3.10^{b}	30.64 ± 5.41^{b}	10.76 ± 2.22^{b}	61.19 ± 7.54^{b}	1.22 ± 0.02^{a}	125.15 ± 11.13^{b}
	V60	4.80 ± 0.24^{f}	13.53 ± 0.71^{g}	3.21 ± 0.17^{e}	18.62 ± 1.60^{f}	0.15 ± 0.043^{c}	40.31 ± 2.76^{f}

Table 3
Levels (mean ± standard deviation) of acrylamide (AA) in eight different filter coffee extraction methods, for three diverse coffee beans obtained by HPLC-MS/MS analysis, expressed in ng/mL.

Sample	LIGHT Specialty natural Ethiopia	MEDIUM Specialty washed Kenya	DARK Blond 100% Starbucks
AEROPRESS	107.85 ± 5.57^{c}	56.72 ± 2.43^{f}	37.79 ± 2.72^{d}
CHEMEX	102.55 ± 1.13^{c}	61.63 ± 2.97^{e}	44.65 ± 1.95^{c}
CLEVER	45.81 ± 2.31^{f}	47.68 ± 1.23^{g}	24.73 ± 2.98^{f}
FRENCH PRESS	46.089 ± 1.52^{f}	172.26 ± 6.52^{a}	28.45 ± 1.41^{e}
MOKA	174.68 ± 32.33^{a}	122.03 ± 2.43^{b}	170.06 ± 42.05^{a}
PURE BREW	62.34 ± 5.82^{e}	67.66 ± 2.58^{e}	29.72 ± 1.39^{e}
TURKISH	79.37 ± 1.86^{d}	81.90 ± 0.01^{d}	49.02 ± 3.71^{b}
V60	126.68 ± 25.70^{b}	111.74 ± 1.91^{c}	40.42 ± 1.78^{c}
AVERAGE VALUE	**93.12 ± 9.41**	**90.20 ± 2.51**	**53.10 ± 7.25**

2.6. Brewing characteristics evaluation

To evaluate the extraction properties, the Total Dissolved Solids (TDS%) value was measured, and extraction yield was calculated. TDS% serves as an indicator of the brew's strength, defining the concentration of soluble solids in the final beverage, so it was measured with a refractometer (VST LAB Coffee III Refractometer, USA). The extraction yield, also known as the "extraction percentage" (EY%), quantifies the fraction of soluble solids extracted from the coffee grounds (Frost, Ristenpart, & Guinard, 2020; Santanatoglia et al., 2023c) (Table 1S). These values were incorporated by Lockhart into the "Coffee Brewing Control Chart" (Lockhart, 1957) an important tool in professional coffee training and a benchmark standard for home brewing certifications. This chart is divided into nine regions: vertical divisions categorize brews as "strong" or "weak" based on TDS%, while horizontal divisions classify them as "bitter" or "underdeveloped" based on EY%. The Specialty Coffee Association's "Golden Cup Standard" aligns with the central range on this chart, setting ideal brewing conditions with TDS values between 1.15% and 1.35% and EY values from 18% to 22%.

2.7. Particle size analysis

For each extraction method, a professional barista selected an optimal coffee powder grain size to achieve the desired brewing result. A portion of the ground coffee was analyzed using the Mastersizer 3000 Aero Series (Malvern PANalytical Ltd., UK) (**Table 4S**). A vacuum extraction unit (KARCHER Professional NT 45/1 Tact, Germany) removes the samples from the aerodry.

2.8. Statistical analysis

All analyses for each coffee sample were performed in triplicate ($n = 3$) and values were expressed as mean ± standard deviation. The one-way analysis of variance (ANOVA) post-hoc Tukey's test was applied to study the differences in furans levels among differently extracted coffee brews. To assess the correlation between coffee molecules, three databases were prepared according to the different types of samples (light, medium and dark). They contained data on the five furanic compounds (furfural, furfuryl alcohol, furfuryl acetate, 5-HMF and 5-methylfurfural), pH, EY% and TDS%, and acrylamide concentration previously analyzed on the same coffee samples (Santanatoglia et al. 2023). Data were Pareto scaled before each statistical analysis to have more suitable values despite the huge differences in selected parameters. A Pearson correlation analysis was conducted using MetaboAnalyst 5.0 tool (https://www.metaboanalyst.ca/), $p < 0.05$ was used as the criterion for statistical significance.

3. Results and discussion

3.1. Furanic compounds and acrylamide content in coffee powders

Firstly, the content of furans and acrylamide was assessed in the three coffee powders. The results are in Table 1. In general, the presence of these undesirable compounds emerged as related to the coffee type and the roasting process. In the light-roasted coffee (Specialty natural Ethiopia Uraga),

the overall lowest concentrations for most furanic compounds were observed, with furfural at 325.67 ± 3.41 mg/kg and furfuryl alcohol at 1124.22 ± 3.12 mg/kg, while 5-HMF showed a comparatively higher

value (12.26 ± 1.11 mg/kg) than in medium and dark roasts. These relatively lower values for furfural and furfuryl alcohol can be attributed to the limited progression of Maillard reactions and sugar degradation at this roast level and with this coffee type (Moon & Shibamoto, 2009; Schouten et al., 2021). For the medium-roasted coffee (Specialty washed Kenya Thiriku), furfural (1618.41 ± 3.28 mg/kg) and furfuryl alcohol (2972.33 ± 4.23 mg/kg) reached their highest concentrations. This result reflects the intermediate thermal conditions, which enhance the Maillard reaction and promote the formation of these volatile compounds. The 5-HMF content (5.60 ± 1.12 mg/kg) at this stage suggests that its formation is reduced compared with the light roast and is not favored under these conditions, consistent with previous findings indicating its limited temperature dependency (Macheiner et al., 2020). In the dark-roasted coffee (Blond 100% Starbucks Arabica), furfuryl acetate (189.45 ± 5.16 mg/kg), 5-methylfurfural (815.34 ± 4.14 mg/kg) and acrylamide (497.00 ± 15.42 mg/kg) exhibited significant increases. This rise aligns with the prolonged exposure to high temperatures, intensifying sugar degradation and secondary Maillard reactions (Del Castillo et al., 2002). However, furfural (1284.84 ± 6.05 mg/kg) and furfuryl alcohol (2650.57 ± 8.81 mg/kg) showed a slight decline from their medium-roast peak values, likely due to increased volatility and degradation at extreme roasting conditions (Dybing et al., 2005). Acrylamide formation followed a distinct trend: high concentration was found in light-roasted coffee (423 ± 6.21 mg/kg), decreasing in medium (361.2 ± 11.25 mg/kg) before rising again in dark-roasted coffee (497.00 ± 15.42 mg/kg). This behaviour is attributed to the dual effects of temperature on acrylamide precursors. At the initial stages of roasting, acrylamide forms due to the reaction between asparagine and reducing sugars (Vezzulli et al., 2022). As roasting progresses, acrylamide levels drop due to thermal degradation. However, in dark roasts, prolonged exposure to high temperatures can trigger additional secondary reactions that regenerate acrylamide, contributing to its re-elevation (Lantz et al., 2006). These results highlight the critical role of roasting in modulating furanic compounds and acrylamide levels. The findings reinforce the importance of optimizing roasting profiles to balance desirable coffee flavors while minimizing potential health risks. The observed trends are aligned with previous literature (Moon & Shibamoto, 2009; Anese et al., 2015).

3.2. Furanic compounds quantification in extracted coffee beverages by HS-SPME-GC–MS

This section explores how different brewing methods and coffee types impact the concentration of furanic compounds, providing a detailed analysis based on the results presented in Table 2.

3.2.1. Specialty's natural, non-classic anaerobic Ethiopia Uraga, by Gardelli – Light roasted coffee

For light roast Specialty Natural Ethiopia Uraga coffee, the Moka beverage exhibited the highest total concentration of furanic compounds at 131.58 ± 11.43 mg/L, significantly differing from all other methods ($p < 0.05$), primarily driven by high levels of furfuryl alcohol (44.10 ± 4.79 mg/L), furfural (37.51 ± 2.95 mg/L) and furfuryl acetate (29.72 ± 1.55 mg/L). The AeroPress coffee followed with a total of 55.11 ± 6.11 mg/L, with 16.91 ± 1.80 mg/L of furfural and 18.82 ± 2.61 mg/L of furfuryl alcohol. The Turkish method also showed a considerable furanic compound extraction capacity (45.39 ± 0.93 mg/L), where furfural (10.99 ± 0.55 mg/L) and furfuryl alcohol (23.41 ± 0.59 mg/L) were the major contributors. Pour-over methods such as V60 and Chemex extracted significantly lower amounts of furanic compounds, with 37.36 ± 0.43 mg/L and 22.82 ± 4.81 mg/L as total concentrations respectively. This lower extraction efficiency in pour-over methods can be attributed to the absence of pressure during extraction and the use of paper filtration, which can retain volatile compounds more effectively (Mestdagh et al., 2017; Santanatoglia et al., 2023b).

3.2.2. Specialty's washed, Kenya Thiriku, by Gardelli – Medium roasted coffee

For medium roast Specialty Washed Kenya Thiriku coffee, a similar trend was observed with Moka coffee exhibiting the highest concentration of total furanic compounds at 88.88 ± 3.28 mg/L, with furfuryl alcohol (44.10 ± 4.78 mg/L), furfural (24.63 ± 0.29 mg/L) and furfuryl acetate (8.37 ± 0.24 mg/L), significantly differing from the all the other methods, except for Turkish. This can be attributed to the combination of high pressure and temperature, which facilitates the release of volatile compounds from the coffee matrix (Cheong et al., 2013). The Turkish method closely followed with a total of 67.93 ± 10.50 mg/L, with furfural (24.19 ± 5.61 mg/L) and furfuryl alcohol (23.41 ± 0.59 mg/L) as main contributors. The AeroPress method emerged as able to extract a total of 51.67 ± 3.73 mg/L, while the Chemex beverages yielded 38.54 ± 2.70 mg/L, with 15.41 ± 0.03 mg/L of furfural and 11.96 ± 2.82 mg/L of furfuryl alcohol. Interestingly, Pure Brew showed the lowest total furanic compounds content (36.24 ± 2.58 mg/L), due to its reduced levels of furfural (13.41 ± 0.26 mg/L) and furfuryl alcohol (10.88 ± 2.62 mg/L).

3.2.3. Roasted blond 100% Arabica, by Starbucks – Dark roasted coffee

Also, for dark roast Starbucks Arabica coffee, the Moka was confirmed to be the most capable method in furanic compound extraction (155.09 ± 5.58 mg/L), with significant contributions from furfuryl alcohol (73.71 ± 4.29 mg/L) and furfuryl acetate (33.82 ± 0.03 mg/L), significantly differing from all the other analyzed cups. This phenomenon further underscores the impact of pressure and prolonged extraction times on furanic compound formation (Cordoba et al., 2019). The Turkish method was second, with a total of 125.15 ± 11.13 mg/L, where furfuryl alcohol and furfuryl acetate concentrations were 61.19 ± 7.54 mg/L and 30.64 ± 5.41 mg/L. The French Press, Chemex and AeroPress samples resulted very similar in total concentrations of furanic compounds, with similar distribution of the single molecules with furfuryl alcohol as the main contributor (34.11 ± 5.57 mg/L, 30.56 ± 0.75 mg/L and 31.51 ± 5.94 mg/L, respectively).

The V60, with total concentration of 40.31 ± 2.76 mg/L, emerged as the less capable method to extract furanic compounds from dark roasted coffee.

3.3. Influence of brewing methods and types of coffee on furanic compounds

The obtained results underscore the importance of coffee type, brewing method and roasting level in determining the concentrations of furanic compounds in the final coffee cup. Across all the three different types of coffee, the Moka method consistently extracted the highest amounts of these compounds, with total furanic compound concentrations reaching 155.09 ± 5.58 mg/L in dark roast (Starbucks Arabica coffee), 88.88 ± 3.28 mg/L in medium roast (Specialty Washed Kenya Thiriku coffee) and 131.58 ± 11.43 mg/L in light roast (Specialty Natural Ethiopia Uraga coffee). These high values are likely due to the elevated pressure and extended coffee/water contact time during brewing, which enhance the release of volatile compounds (Cordoba et al., 2019). In contrast, pour over methods such as V60, Chemex and Clever resulted in significantly lower furanic compound concentrations, indicating that these methods may offer safer coffee preparation options in terms of furanic compound exposure. For instance, in dark roast (Starbucks Arabica coffee), the V60 method extracted only 40.31 ± 2.76 mg/L, while Chemex resulted in 83.41 ± 1.68 mg/L. These lower concentrations can be attributed to shorter brewing times and the absence of pressure, limiting the extraction of these compounds (Rahn & Yeretzian, 2019; Yu et al., 2021). While Amanpour and Selli (2016) reported higher concentrations of furfural in Turkish and French Press coffees, likely due to the longer contact time between water and coffee grounds during brewing. Our findings show that Turkish coffee yielded 125.15 ± 11.13 mg/L in dark roast (Starbucks Arabica coffee) and 67.93

± 10.50 mg/L in medium roast (Specialty Washed Kenya Thiriku coffee), supporting the idea that extended brewing time leads to increased furanic compound extraction. Although pressure seems to play a more crucial role. Furthermore, brewing by espresso machine has been found to cause significant loss of most furanic compounds, except for furfural (Chaichi et al., 2015). The increasing concentration of furanic compounds with darker roasts, particularly in the Roasted Blond 100% Arabica by Starbucks, can be attributed to higher roasting temperatures, which promote greater thermal degradation of carbohydrates and amino acids, leading to the formation of these compounds (Acquaticci et al., 2023; Liu et al., 2023).

Particle size distribution likely contributed to the observed extraction differences among brewing methods (**Table 4S**). Turkish coffee and Moka preparations, characterized by finer grinding conditions (approximately 252–684 μm), generally showed higher extraction yields and higher concentrations of furanic compounds. In contrast, coarser grinding conditions used for Chemex and AeroPress (>1200 μm) were associated with lower extraction of several analytes. This observation agrees with previous studies demonstrating that reduced particle size increases surface area and mass transfer phenomena during brewing.

The elevated levels observed in Moka and Turkish coffee are consistent with previous studies reporting enhanced extraction of thermally generated contaminants in high-temperature and pressure-assisted brewing systems. Conversely, paper-filtered brewing methods such as V60 and Chemex generally exhibited lower concentrations, likely due to reduced extraction efficiency and partial retention of volatile compounds by the paper filter matrix. Previous investigations by Engelhardt et al. (2023), Yu et al. (2021) and Santanatoglia et al. (2023a) similarly highlighted substantial variability in furanic compound occurrence depending on roasting degree, brewing parameters, extraction pressure, and filtration system.

Although coffee powders differed in their furanic compound content, the final concentrations detected in brewed coffee were also influenced by the extraction method. Paper-filtered brews generally showed lower levels, whereas Moka and Turkish coffee promoted higher transfer of furanic compounds into the beverage, highlighting the importance of brewing conditions in determining contaminant occurrence.

3.4. Furanic compounds correlation with acrylamide content in the coffee cup

The correlation of the concentrations of furanic compounds and acrylamide in coffee samples is of particular interest. Acrylamide concentration data in the same kind of coffee brews were previously published in Santanatoglia et al., (2023) (Table 3) and those findings were used for the correlation study. The same coffee brew samples and experimental batches were considered in the present investigation. A Pearson correlation was carried out to understand the impact of the roasting process and extraction parameters on the concentrations of these compounds potentially harmful to health (Fig. 1). The findings are reported and discussed in the following sections.

3.4.1. Specialty's natural, non-classic anaerobic Ethiopia Uraga, by Gardelli – Light roasted coffee

In Specialty Natural Ethiopia Uraga, some correlations were observed between furanic compounds and acrylamide (Fig. 1A, **Tables 5S** and **6S**). The pH showed strong negative correlations with 5-HMF ($r = -0.697$, $p < 0.001$) and furfuryl alcohol ($r = -0.574$, $p < 0.01$), indicating that lower pH values are associated with higher levels of these two compounds. This suggests that the more acidic environment characteristic of light-roasted coffees may enhance the release or formation of specific furanic derivatives. This relationship may be explained by the role of acidic conditions in promoting carbohydrate dehydration reactions and Maillard-derived pathways leading to the formation of furanic compounds, particularly 5-HMF. Previous studies

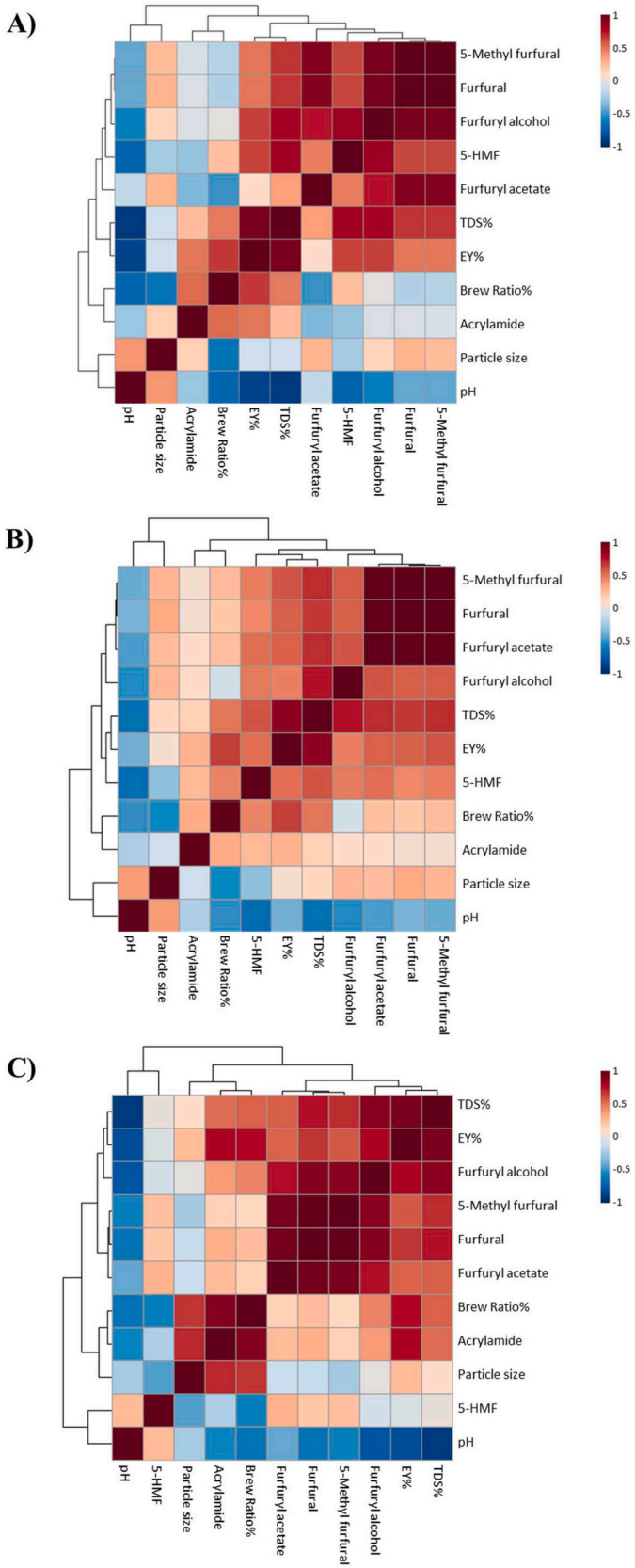

Fig. 1. Furanic compounds, acrylamide and extraction parameters Pearson correlation graphic results. A) Light roasted samples (Specialty natural Ethiopia) B) Medium roasted samples (Specialty washed Kenya) C) Dark roasted samples (Blond 100% Starbucks).

have shown that acid-catalysed degradation of hexoses enhances 5-HMF generation, while the extraction of organic acids during brewing can simultaneously decrease pH and favour the release of thermally generated furanic derivatives (Lee et al., 2019). Therefore, the observed correlation may reflect both the influence of acidity on reaction pathways and the co-extraction of acidic and Maillard-derived compounds. Nevertheless, because correlation analysis does not demonstrate causality, these mechanisms should be considered plausible interpretations rather than direct evidence of cause–effect relationships.

A similar but weaker trend was also observed for furfural and 5-methylfurfural ($r = -0.41$), although these correlations were less pronounced. Overall, all five furanic compounds were positively intercorrelated, reflecting their shared origin from Maillard and sugar-degradation pathways and their structural similarity.

Extraction yield (EY%) showed a moderate correlation with furfuryl alcohol and 5-HMF ($r = 0.64$ for both), suggesting that a more efficient extraction process may increase the concentration of these compounds. Additionally, TDS% exhibited a strong negative correlation with pH ($r = -0.898$, $p < 0.001$), indicating that higher total dissolved solids are associated with lower pH values. This supports the hypothesis that higher extraction efficiency leads to a greater release of acidic compounds, which may contribute to furan formation. Regarding acrylamide, no strong correlations were observed with furanic compounds, suggesting that acrylamide formation may follow different mechanisms compared to furans, in this case.

3.4.2. *Specialty's washed, Kenya Thiriku, by Gardelli – Medium roasted coffee*

In Specialty Washed Kenya, the correlation pattern was dominated by strong interrelationships among furanic compounds (Fig. 1B, **Tables 7S** and **8S**). Furfuryl acetate, furfural, and 5-methylfurfural showed extremely high positive correlations ($r > 0.98$), suggesting that these compounds are generated and released through closely interconnected thermal degradation pathways. Furfural and 5-methylfurfural are well-known products of carbohydrate degradation and Maillard reactions, while furfuryl acetate derives from the esterification of furfuryl alcohol, another key furanic intermediate formed during roasting. Their highly coordinated behaviour across brewing methods indicates that extraction efficiency affects these compounds in a similar manner, likely because they share comparable physicochemical properties and originate from common roasting-induced precursor pools. Therefore, the observed correlations probably reflect both a shared formation chemistry during roasting and a parallel extraction behaviour during brewing. These three compounds behaved almost identically across the different brewing methods. 5-HMF also showed significant positive correlations with several furanic compounds, such as furfural ($r = 0.430$, $p < 0.05$) and furfuryl acetate ($r = 0.513$, $p < 0.01$), indicating co-formation at this intermediate roasting stage.

Regarding brewing parameters, TDS% and EY% exhibited a strong positive correlation ($r = 0.862$, $p < 0.001$), reflecting the expected increase of dissolved solids as extraction efficiency rises. Both parameters were also strongly correlated with most furanic compounds, supporting the idea that increased extraction intensity enhances the release of Maillard-derived molecules. Conversely, acrylamide did not show significant correlations with EY%, TDS%, or individual furanic compounds, suggesting that its extraction in medium-roasted coffee is governed by mechanisms partially independent from those driving furanic compound release.

3.4.3. *Roasted blond 100% Arabica, by Starbucks – Dark roasted coffee*

In the dark roast (Blond 100% Arabica, Starbucks), the strongest correlations of the dataset were observed (Fig. 1C, **Tables 9S** and **10S**), reflecting the thermal degradation and advanced Maillard progression characteristic of dark roasting. Acrylamide showed extremely strong positive correlations with 5-HMF ($r = 0.708$, $p < 0.001$). Although these compounds are generated through distinct reaction pathways, both originate from advanced thermal processing and share common precursors associated with carbohydrate degradation and Maillard chemistry (Hemmler et al., 2017). In dark-roasted coffee, the accumulation of roasting-derived products is more pronounced, and brewing methods capable of extracting larger amounts of soluble solids may simultaneously increase the transfer of both compounds into the beverage. Therefore, the observed correlation is likely driven by their common dependence on roast-induced chemical transformations and extraction efficiency rather than by a direct mechanistic relationship between acrylamide and 5-HMF formation. A strong positive correlation was registered also between acrylamide and brew ratio % ($r = 0.894$, $p < 0.001$), indicating that brewing conditions involving higher solute concentration are strongly associated with increased acrylamide content in dark-roasted beverages.

Acrylamide was also strongly correlated with EY% ($r = 0.778$, $p < 0.001$), confirming that higher extraction efficiency intensifies acrylamide release into the cup. A network of very strong correlations was also found among the furanic compounds. Furfural, furfuryl alcohol, furfuryl acetate and 5-methylfurfural all exhibited r values between 0.75 and 0.99, supporting the hypothesis that dark roasting promotes the simultaneous formation of multiple furanic compounds through interconnected Maillard and carbohydrate degradation pathways. At this roasting stage, the extensive thermal conversion of sugars and amino acid-derived intermediates generates a complex pool of furanic products that are subsequently extracted in a coordinated manner during brewing (Wang et al., 2025). The similarity of their extraction patterns across brewing methods may therefore reflect both common chemical origins and comparable extraction behaviour.

The pH displayed the strongest negative correlations in the entire dataset, particularly with TDS% ($r = -0.896$, $p < 0.001$), EY% ($r = -0.809$, $p < 0.001$) and furfuryl alcohol ($r = -0.787$, $p < 0.001$). This pattern suggests that extraction intensity is a key factor shaping the chemical profile of dark-roasted coffee brews. Higher extraction yields promote the transfer of a broader range of soluble constituents from the roasted coffee matrix, including acidic compounds that contribute to lower pH values as well as Maillard-derived products such as furfuryl alcohol. The strong inverse relationship between pH and furfuryl alcohol may therefore reflect the simultaneous extraction of acidity-related compounds and furanic derivatives rather than a direct mechanistic link between them. In dark-roasted coffees, where thermal degradation reactions are more extensive, this co-extraction effect appears particularly pronounced, resulting in the strongest correlation network observed among all datasets.

4. Conclusions

This study provides a comprehensive evaluation of how coffee type, roasting chemistry and brewing mechanics influence the formation and extraction of furanic compounds and acrylamide in brewed coffee. Across the three coffee types tested, marked differences in precursor availability and roast-induced chemical profiles led to distinct patterns of contaminant formation and co-extraction. Light-roasted Ethiopia exhibited the lowest levels of most furanic species in both powder and brews, with acidity acting as a key modulator, as shown by the negative correlations between pH and compounds such as 5-HMF and furfuryl alcohol. In this coffee, acrylamide and furanic compounds followed independent extraction behaviours. In the medium-roasted Kenya, furanic compounds displayed the strongest inter-correlations, consistent with a predominance of Maillard- and sugar-degradation pathways at intermediate roast development. By contrast, the dark-roasted Starbucks Arabica showed the highest furanic concentrations and the most pronounced correlation networks; here acrylamide significantly correlated with 5-HMF, EY% and brew ratio, indicating that intense roasting combined with high-extraction brewing conditions favours its release. Brewing method remained a dominant extraction variable across coffee types. Moka and Turkish consistently yielded the highest concentrations

of furanic compounds, driven by elevated temperature, pressure and extended contact time. Paper-filtered pour-over brews (V60, Chemex) produced substantially lower levels, while full-immersion methods (Clever, French Press, AeroPress) showed intermediate extraction profiles. Overall, this work demonstrates that contaminant levels in brewed coffee arise from the interplay between intrinsic coffee chemistry and extraction parameters. The occurrence of furanic compounds and acrylamide in coffee beverages depends on the interaction between roast profile, intrinsic coffee chemistry and extraction conditions. While paper-filtered brewing methods generally reduced the extraction of several furanic compounds, no single roast profile can be considered universally optimal for minimizing all contaminants simultaneously.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2026.119964.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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