LWT - Food Science and Technology 175 (2023) 114471

Contents lists available at ScienceDirect

LWT

journal homepage: www.elsevier.com/locate/lwt

A comprehensive comparative study among the newly developed Pure Brew method and classical ones for filter coffee production

Agnese Santanatoglia [a,b], Giovanni Caprioli [a,*], Marco Cespi [a], Dario Ciarlantini [b], Luca Cognigni [b], Lauro Fioretti [b], Filippo Maggi [a], Ahmed M. Mustafa [a,b], Franks Nzekoue [a], Sauro Vittori [a,b]

[a] School of Pharmacy, University of Camerino, 62032, Camerino, Italy
[b] Research and Innovation Coffee Hub, Via Emilio Betti 1, 62020, Belforte del Chienti, Italy

ARTICLE INFO

Keywords:
Brewing methods
Caffeine
Coffee roasting
Extraction yields
Filter coffee
GC-MS
PCA
Specialty coffee
UHPLC-MS/MS

ABSTRACT

Pure Brew represents a real innovation because it allows one to obtain a fast-filter coffee with an espresso machine without the need for the barista to purchase additional equipment. This study investigated the difference between Pure Brew, French Press, V60 and AeroPress in terms of physical and chemical characteristics, extraction yields, volatile compounds by GC-MS and bioactive molecules by UHPLC-MS of resulting coffee, studying also powder particle size. Finally, main results showed that Pure Brew is comparable to other methods available on the market, but also showed the highest levels of caffeine (598.28 ± 8.84 and 556.13 ± 1.22 μg/mL) and total bioactive compounds (1726.8 ± 22.4 and 1407.89 ± 9.53 μg/mL) in medium and dark roasted coffee, compared to the other brewing methods. Pure Brew also displayed the most positive results in extraction yields, it falls into the ideal extraction percentage (18–22%) at the three different degrees of roasting, versus the other brewing methods. At the light roast, for Pure Brew were discovered the most olfactometrically impactful molecules of the study at GC-MS, 5-Methyl 2-furancarboxaldehyde, Furfural, and 2-Furanmethanol, connected with positive remarks, associated with almond and sweet.

1. Introduction

Coffee is one of the most popular brewed beverages in the world, due to its complex aroma and pleasant taste, as well as its stimulation from caffeine (Wang et al., 2022). Coffee is the main source of caffeine, an alkaloid antagonist of the adenosine receptors A2 and A1 involved in the stimulation of the central nervous system, yielding increased vigilance, capacity for work, and improved humour, as well as decreased motor reaction time and fatigue (Barroso et al., 2022). Coffee has also a wide range of biological activities, including refreshing, antidepressant, antioxidant, antibacterial, protecting DNA, and anticancer, which are closely associated with its chemical components such as caffeine, chlorogenic acids, trigonelline, diterpenes, phenolics, and volatile organic compounds (VOCs) (Wang et al., 2022).

Worldwide, there has been growing interest in specialty coffee products, and this is part of a broader trend in consumer behavior, in which individuals are highly concerned about product quality, origin, and economic and environmental sustainability of coffee (Guimarães, Leme, De Rezende, Pereira, & Dos Santos, 2019). Specialty coffees are made of the highest quality coffee beans to reveal their outstanding flavor potential; high level flavor is essential for determining the coffee quality (Córdoba et al., 2021). Coffee beverages, such as filter coffees and specialty coffees with peculiar sensory characteristics, have climbed in fashionability, with the different brewing techniques to obtain them. Also, scientific interest has increased in this field; in fact, this trend of increasing filtered coffee consumption is expected to continue in the coming years. Most coffee beverages are prepared by various hot brewing methods, depending on the geographic, cultural, and social context, as well as on personal preference (Cordoba, Pataquiva, Osorio, Moreno, & Ruiz, 2019).

Coffee brewing is regarded as a solid-liquid extraction, from an engineering perspective, that takes place between hot water and ground

Abbreviations: EY, extraction yields; PE, percentage of extraction; SCA, specialty coffee association; TDS, total dissolved solids.

* Corresponding author. Chemistry Interdisciplinary Project (Chip), School of Pharmacy, University of Camerino, via Madonna delle Carceri, 62032, Camerino, Italy.

E-mail address: giovanni.caprioli@unicam.it (G. Caprioli).

https://doi.org/10.1016/j.lwt.2023.114471
Received 26 August 2022; Received in revised form 5 January 2023; Accepted 12 January 2023
Available online 13 January 2023

coffee beans when the water passes through a bed of coffee grounds (Sano et al., 2019). The most important parameters, to keep under control during brewing, are coffee mass to water ratio, grind size and distribution, brewing time, water temperature, and agitation (Barroso et al., 2022). Coffee extraction is the final step in coffee production and has a great influence on the final form and properties of the beverage (Stanek et al., 2021). Among the different brewing methods used for specialty and filter coffee applications, drip methods (using a coffee cone and paper filter) such as immersion methods (ground coffee is immersed in water) have been proposed (Córdoba, Moreno, Osorio, Velásquez, & Ruiz, 2021). Recently, V60, French Press (FP) and AeroPress, have been the most common extraction methods for the development of filter coffee or long coffee. In fact, V60 is the traditional pour-over system, in which hot water is poured through coffee grounds in a filter paper; FP is the classical full immersion system, easily replicable, with a mechanical filtration; while AeroPress uses pressure, it's appropriate for strong extractions, uses a paper filter (Stanek et al., 2021). To give a comprehensive overview of the filter coffee world, it was chosen to compare Pure Brew to these three extraction methods. However, the development of filter coffee in a bar needs to use the appropriate tools for preparation, in addition to the coffee machine, and a long extraction time for coffee extraction is needed, which often takes a barista 4–5 min just to prepare one long coffee; for this reason, nowadays filter coffee is not common in the bar.

In this regard, the advantages of Pure Brew, in comparison with the other methods, are: a) No need for other equipment once the Coffee Shop has an espresso machine ready for Pure Brew extraction. b) Lowest time from order to coffee, with positive impressions by the customer (lower waiting time) and lowest working time for the barista. c) Highest reproducibility of coffee quality, regarding the variables studied until now; this improves the dependability of the coffee shop for the customer.

Therefore, this study aimed to investigate the differences between the newly developed filter coffee extraction method, Pure Brew, with traditional ones (V60, French Press, AeroPress), in terms of particle size of the powders, physicochemical characteristics, extraction yields, volatile profile and bioactive compounds. To the best of our knowledge, this is the first paper where these parameters for filter coffee produced by the novel Pure Brew technique are studied. All analyses were carried out on three differently roasted coffees (i.e., light, medium and dark), to choose the most suitable coffee for each specific roast, to bring the study as close as possible to the consumers. In this way, it has been realizable to explore at full the world of coffee, and for this reason the selection was made among three different coffees with distinct roastings and origins. It is impossible include a very high number of coffees in a scientific study, but here were taken representatives among light, medium, dark; among natural, washed and blended coffees; and between micro-lots and mainstream.

2. Materials and methods

2.1. Coffee material and samples

For all extractions, three different types of coffee, with different degrees of roasting, were used: specialty Don Cayito, white honey (Coffea arabica from Gardelli Specialty Coffee) for light roasting, specialty Kakindu, natural (Coffea arabica from Gardelli Specialty Coffee) for medium roasting and specialty 100% Arabica blonde roasted coffee (Coffea arabica from Starbucks) for dark roasting. Different coffees were chosen to give as more as possible realistic picture of the "filter" and "specialty" coffee worlds. Indeed, the consumers do not select a green coffee that has been roasted at different degrees of roast; but, as reported in our study, it chooses the coffee that better enhance the proper degree of roast. To avoid oxidative damage, each packet of coffee beans (250 g) was opened immediately before brewing. Beans were ground using a professional grinder (Atom Brew Pro - Eureka). After coffee, water is the second essential ingredient for coffee brewing, and its ionic content is crucial in coffee brewing (Cordoba, Fernandez-Alduenda, Moreno, & Ruiz, 2020). All samples were fitted using the same commercial water brand, Nerea water, chosen for its mineral salt content, i.e., 161 mg/L of dry residue, associated with its salt balance.

2.2. Particle size analysis

After the grinding process, coffee powder was studied with Mastersizer 3000 Aero Series dry dispersion units (Malvern PANalytical Ltd., UK), which operate by laser diffraction to measure the particle size (from 0.01 to 3500 μm). The device works with a non-stop air flow, generated by a mechanical compressor at 6.5 bar. It transfers the particles at 2–3 bar to the ray diffraction. In this way, the particles move in laminar flow and the vacuum extraction unit (KARCHER Professional NT 45/1 Tact, Germany) removes the samples from the aero dry. Ground coffee powders with various particle sizes were collected: one-fifth for Mastersizer 3000 and the rest for the extraction of filter coffees. The particle size distribution for each sample was checked five times and the mean value was applied for comparison.

2.3. Coffee brew preparation methods

A specific routine was used for each of the four brewing methods, maintaining around 250 ml of the final volume in the cup. Three replicates were prepared for each brewing method.

2.3.1. V60

This coffee maker comprises three parts: a cone-shaped top dripper with ribs along the inner edges and a single large hole in the bottom, a paper filter (Hario V60 Paper Filter), and a glass container (Hario V60 Range Server 600 ml) (Angeloni et al., 2019). Initially, a small amount of water at 93 °C was poured to wet the filter, then the coffee was placed until a flat surface was obtained. Subsequently, 60 ml of water at 93 °C, was poured over the coffee, which was left pre-infusing for 15 s; water was always poured in concentric circles, starting from the center, and then widening, trying to maintain a constant flow, at 30 s an additional 100 ml of water was poured. Finally, 130 ml of water was added at 1 min 20 s. To conclude was made the spin (to take up all the coffee), then the upper piece of the instrument was shaken manually 3 times. The coffee water ratio was 1:15.

2.3.2. French Press

The French Press (Lacor French Press wood) was composed of a cylindrical jug crossed by a plunger, forming a knob, and ends with a metal mesh filter. Then, the lid closes the coffee maker. Initially, the coffee was ground and placed in the instrument. Subsequently, it was calibrated, and water was added. During this last operation, strong turbulence was created from above at 1 min, 2 min, and 3 min, then the cap was removed and turned with the dedicated spatula 4 times. At 4 min it was filtered, the cap was inserted, and the filter was slowly pushed into the coffee. The coffee water ratio was 1:15.

2.3.3. AeroPress

The AeroPress was invented in 2005 by Aerobie (Alan Adler); the device consists of two nested cylinders. One has a flexible hermetic seal, and "stays" inside the larger cylinder (Angeloni et al., 2019). First, the paper filter (AeroPress® Micro Filter) resting on the syringe base of the AeroPress was wetted, then the instrument was placed on a scale and a tare was made; coffee was poured, and the tare was redone. Afterward, the blooming (phase in which all the ground coffee was covered with water) was done three times, 60 ml of water was poured to wet all the coffee; 15 s after that, the remaining water was poured all at once; then, the slurry was mixed with the spatula, for optimal extraction. Finally, the upper part of the AeroPress was forced by applying pressure for about 30 s. The coffee water ratio was 1:15.

2.3.4. Pure brew

The Pure brew was obtained with the VA388 Black Eagle Maverick machine (Simonelli Group, Victoria Arduino). Pure Brew technology was an extraction method that uses pulsating frequencies using low-pressure water (less than 0,15 bar). The Pure Brew coffee filter consists of a micro-thin double mesh conical basket that can contain up to 20 g of coffee. Combining Pure Brew technology with the patented filter basket made it possible to obtain filtered coffee by pressing a button. The water temperature was 93 °C. The coffee water ratio was 1:15.

2.4. Brewing characteristics (extraction yields, TDS, and pH)

Before the selected parameters were analyzed and evaluated, all samples were brought to 20 °C. A digital pH meter (Mettler Toledo, Columbus, UK) was used to determine pH. To calculate extraction yields, total dissolved solids (TDS) were measured using a refractometer (VST LAB Coffee III Refractometer, USA). TDS is considered the brew strength, which is the mass fraction of soluble solids in the brew, while PE (percentage of extraction) is expressed by the "extraction yield", which is the mass fraction of soluble solids removed from the coffee grounds (Frost, Ristenpart, & Guinard, 2020). These amounts were incorporated by Lockhart in the classic "Coffee Brewing Control Chart" (Fig. 1). This chart serves as the foundation of vocational training in the coffee industry and is the basis of strict requirements for home brewer certification. The chart is divided into 9 regions, with vertical separation versus TDS, labeled as "strong" or "weak", and horizontal separation versus PE-labeled as "bitter" or "underdeveloped". The chart's central region is associated with the Specialty Coffee Association's "Golden Cup Standard", which spans TDS values of 1.15–1.35% and PE values of 18–22%, which is denoted as "ideal" (Batali, Ristenpart, & Guinard, 2020). For the construction of this, it was used VST App. The diagonal lines in the chart represent the brew ratio (i.e., the mass of water per mass of coffee grounds). Note that the physical properties presented in the chart can be manipulated during brewing via a wide variety of parameters including grind size, brew ratio, water mineral content, extraction time, brewing method, and temperature (Cotter, Batali, Ristenpart, & Guinard, 2021).

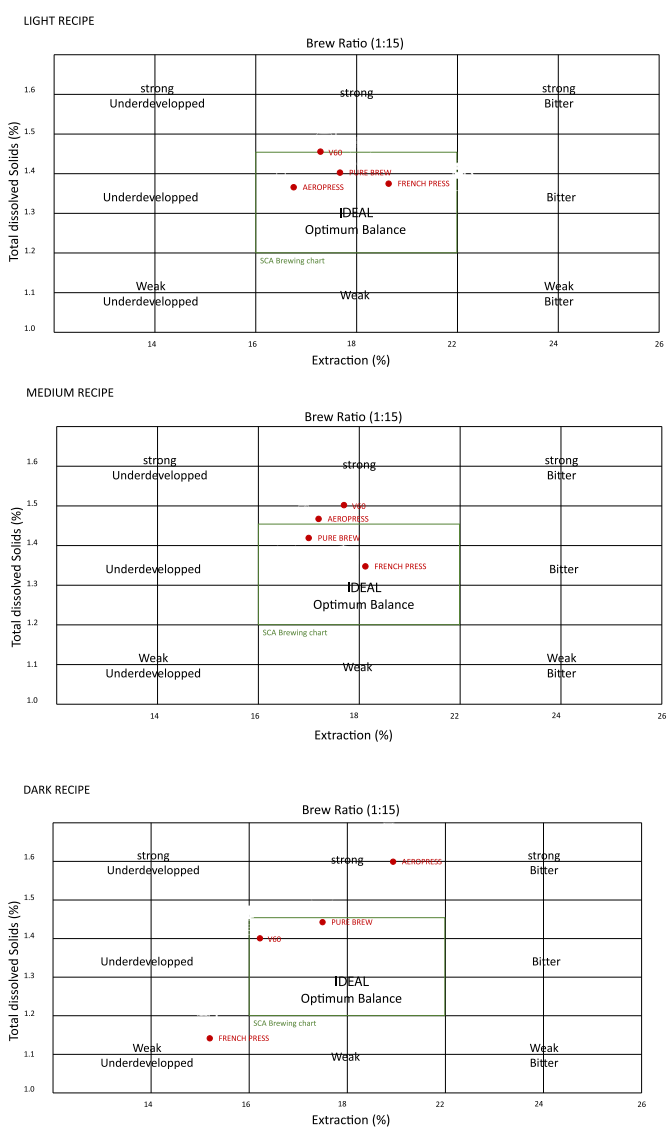

Fig. 1. Filter coffee extraction yields, in classic "Coffee Brewing Control Chart" at three different roasting degrees (light, medium and dark) ($n = 3$).

2.5. Analyses of bioactive compounds by UHPLC-MS/MS

Liquid coffee samples were centrifuged at 15000 rpm for 5 min and filtered before UHPLC-MS/MS analysis. UHPLC-MS/MS investigations were achieved using an Agilent 1290 Infinity series and a Triple Quadrupole 6420 from Agilent Technology (Santa Clara, CA), equipped with an electrospray ionization (ESI) source operating in negative and positive ionization mode, following a previously published method (Angeloni, Nzekoue, et al., 2020). MS/MS parameters of each analyte were used in flow injection analysis (FIA) (1 μl of a 10 mg L^{-1} standard solution) by Optimizer Software (Agilent). The column used was a Kinetex PFP analytical column (100 × 2.1 mm i.d., 2.6 μm) from Phenomenex (Torrance, CA, USA). The mobile phase was a mixture of (a) water and (b) methanol, both with formic acid 0.1%, at a flow rate of 0.2 ml min^{-1} in gradient elution mode. The composition of the mobile phase varied as follows: 0–2 min, 20% B; 2–15 min, 80% B; 15–18 min, 80% B; 18–23 min, 100% B; 23–35 min, 20% B. Through a 0.2 μm polyamide filter from Sartorius Stedim (Goettingen, Germany), all solvents and solutions were filtered. The injection volume was 2 μl. The column temperature was 30 °C, while the drying gas temperature in the ionization source was 350 °C. The gas flow was 10 L/min, the nebulizer pressure was 25 psi, and the capillary voltage was 4000 V. Detection was completed in the dynamic-MRM mode, and the dynamic-MRM peak areas were integrated for quantification. The selected ion transitions and the mass spectrometer parameters including the specific time window for each compound (retention time) are described in Table 1S.

2.6. Analysis of volatile organic compounds

A gas chromatography/mass selective detector (GC/MSD with PAL3) (Agilent, Santa Clara, CA, USA, Agilent 7890B GC Hardware with Agilent 5977 Series MSD and MassHunter GC/MSD Data Acquisition, PAL3 -Auto Sampler System) was used. The column used for separation was DB-WAX (0.25 mm × 60 m, 0.25 μm) (Agilent 122–7062, CA, USA). The workstation in the GC-MS system was AgilentChem. The flow rate (He) was 1.2 ml min^{-1} under spitless mode. The temperature of the injector was 260 °C. The temperature for the column was programmed as follows: from 35 °C (4 min) to 120 °C (2.5 °C per min), from 120 °C to 250 °C (15 °C per min), then 250 °C for 3.33 min; total run time was 50 min. Through the electron impact (EI) mode and the SCAN mode, data were acquired. Sample injection techniques with SPME were implemented through the PAL3 autosampler system. Fiber assembly was from Supelco (Bellefonte, PA, USA) and had a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) coating with 1 cm length stationary phase SPME. For analysis, 3 ml of each filter coffee sample were placed in a screw-top vial. The vial was tightly screwed on a magnetic cap with a septum and the system was set for automatic functioning mode. The sample was placed into an agitator where the sample was incubated at 60 °C and agitated at 250 rpm for 20 min. Then, SPME was automatically inserted in the sample and remained for 20 min for

adsorption. Following the processes SPME, after adsorption, was automatically injected into the gas-chromatographic system. A desorption time of 5 min was sufficient to desorb analytes from the fiber. Cleaning was automatically performed with the PAL system by inserting the fiber in the conditioning port at 230 °C for 20 min after each process. Linear chain alkanes (C6–C26) were used to calculate retention indices. Thus, the detected VOCs were identified by comparing their retention indices and mass spectra with those of standards from the US National Institute of Standards and Technology database (NIST-USA, http://webbook.nist.gov).

2.7. Statistical analysis

All the analyses were performed at least in triplicate ($n \geq 3$) and data are presented as mean ± standard deviation. Statistical analysis was performed with one way ANOVA and $p < 0.05$ was considered statistically significant. Finally, data on all compounds were examined by Principal Component Analysis (PCA), operating in correlation, using Minitab V18.1 (Minitab INC., USA). The PCA was applied to display the information of the various types of coffee, at different degrees of roasting, which were used for the four different methods of extraction of the filter coffees.

3. Results and discussion

3.1. Particle size analysis

Due to the laser diffraction, the particle size distribution analysis was performed using the Mastersizer 3000 instrument. Measures were replicated five times for each sample and the average was used to produce the Gaussian graph. The graph (Fig. 1S and Table 2S) provides particle size information through the volume density percentage. The volume density percentage comes through scattered light, because large particles scatter light at small angles with the laser beam, while small particles scatter light at large angles. This angular scattering intensity data is used to calculate the particle size (Khamitova et al., 2020). Fig. 1S and Table 2S underline that size of particles was distinguishable among coffee samples. This analysis was performed to confirm that the grinding process obeyed the ideal one, according to each specific type of extraction. For V60, the grind used was usually medium; a grind was measured ranging from 876 ± 1.92 μm for light, to 945 ± 2.81 μm for medium, up to 1070 ± 3.41 μm for dark coffee degree. On the other side, a different trend was measured for the AeroPress, for which the grind used was usually medium, 901 ± 1.12 μm for light, 800 ± 3.21 μm for medium, and 786 ± 2.05 μm for dark. For the French Press, the grind was coarser: 1250 ± 1.18 μm in the light, 1390 ± 3.81 μm in the medium, and 1230 ± 2.40 μm in the dark. Finally, for Pure Brew, the grinding was 1250 ± 1.18 μm for the light, 1130 ± 2.13 μm for the medium, and 1050 ± 2.86 μm for the dark.

3.2. Brewing characteristics (extraction yields, TDS, and pH)

The chemical composition of total dissolved solids (TDS) can count on green coffee quality, roasting process, and brewing method. Because of varying waterless solubility, the chemical composites in roasted coffee are extracted at different rates, therefore EY will determine the flavor properties of the brew (Córdoba et al., 2021). With the analysis of EY for different methods, values of TDS (Table 1) for Pure Brew's different extractions are very similar to each other. This is evident from the graphics (Fig. 1) since values of PE (percentage of extraction) for Pure Brew extraction with light, medium, and dark fall into an ideal situation and in the graphic area of ideal optimum balance referred to as the Coffee Brewing Control Chart (Fig. 1). Besides, in the Pure Brew extraction, the final volume in the cup, in ml (Table 1) is higher compared to V60, AeroPress, and French Press. V60 medium extraction led to a coffee with strong characteristics as shown in Fig. 1; it was observed that brewing time for this extraction is the highest among V60 ones. In most cases, low brewing time falls in the graphic area of ideal optimum balance (Cotter et al., 2021), referring to Fig. 1. On the other hand, the French Press method led to two ideal situations in the case of light and medium roasted coffees, while for dark it falls in the graphic area of weak and under-developed coffee. AeroPress method falls in the ideal area of Fig. 1 for light, while it falls in the strong area for medium and dark. Measurements of pH (Table 1) quantify the aqueous hydrogen ion concentration and provide a measure of deprotonated acid molecule levels (Rao & Fuller, 2018). The acidity of the coffee bean peaks during the first crack and decreases as roasting continues. The pH value of green coffee is about 5.8, it decreases during roasting until the first crack reaching values of about 4.8, before constantly increasing with further roasting (Tsiafitsa, Oikonomopoulou, Stramarkou, Krokida, & Papassiopi, 2022).

3.3. Time factor

In Coffee world, for brew preparation, time is essential in the daily life of a barista (Table 3S) and plays an important role in this study. In fact, the brewing time was measured, but to this, the preparation time of the different extraction methods, shown in Table 3S, must be added. In the case of V60, French Press and AeroPress, the preparation time referred to the time in which the equipment was prepared, the water heated, the coffee was ground, and finally, the filter coffee was made. The innovation is intended to show that Pure Brew makes coffee with a brewing time comparable to the other methods, with no constant attention required, but also with a shorter preparation time; for Pure

Table 1
Extraction parameters: extraction methods, grind, amount of ground coffee in grams, the volume of the final cup in **millilitres**, brew ratio (coffee to water ratio), TDS % (total dissolved solids), pH and PE % ($n = 3$).

Extraction method	Grinding level	**Coffee powder (g)**	Final volume in the cup (ml)	Brew Ratio	TDS %	pH	PE %
V60 LIGHT	medium	20 g	253 ± 2.08 [a]	1:15	1.45 ± 0.01 [a]	4.97 ± 0.07 [a]	19.25
FRENCH PRESS LIGHT	coarse	20 g	251 ± 1.53 [a]	1:15	1.37 ± 0.01 [b]	4.96 ± 0.01 [a]	20.65
AEROPRESS LIGHT	medium	20 g	264 ± 1.53 [b]	1:15	1.37 ± 0.02 [b]	4.77 ± 0.01 [b]	18.87
PURE BREW LIGHT	coarse	20 g	267 ± 1.52 [b]	1:15	1.41 ± 0.01 [c]	4.91 ± 0.02 [c]	19.44
V60 MEDIUM	medium	20 g	251 ± 1.53 [a]	1:15	1.51 ± 0.01 [d]	4.73 ± 0.07 [d]	19.74
FRENCH PRESS MEDIUM	coarse	20 g	249 ± 3.06 [a]	1:15	1.35 ± 0.03 [b]	4.73 ± 0.07 [d]	20.21
AEROPRESS MEDIUM	medium	20 g	251 ± 2.00 [a]	1:15	1.47 ± 0.03 [a]	4.65 ± 0.07 [e]	19.24
PURE BREW MEDIUM	coarse	20 g	256 ± 2.06 [c]	1:15	1.42 ± 0.02 [e]	4.85 ± 0.02 [f]	19.93
V60 DARK	medium	20 g	252 ± 4.16 [a]	1:15	1.41 ± 0.02 [e]	5.12 ± 0.01 [g]	18.37
FRENCH PRESS DARK	coarse	20 g	248 ± 4.58 [a]	1:15	1.15 ± 0.02 [f]	5.18 ± 0.02 [h]	17.15
AEROPRESS DARK	medium	20 g	252 ± 2.08 [a]	1:15	1.61 ± 0.02 [g]	5.15 ± 0.01 [h]	20.97
PURE BREW DARK	coarse	20 g	257 ± 2.65 [c]	1:15	1.44 ± 0.01 [e]	5.13 ± 0.01 [h]	19.28

n.d.*: not detected (peak area value below 5E + 04).
Results are mean ± standard deviation from triplicate extractions.
Values within the same column are significantly different ($p < 0.05$) for the parameter considered if their values do not show uppercase letters in common.

Brew there is just no need to prepare the equipment or to heat the water once you have the filter coffee machine.

3.4. Validation of the UHPLC-MS/MS method for bioactive compounds

The analytical method was validated by considering the linearity, reproducibility, and sensitivity of the method for all the checked bioactive compounds in dynamic MRM mode (Table 4S). By injecting standard solutions at different concentration ranges (from 0.001 μg/mL to 5 μg mL^{-1}) was assessed linearity of the analytical method to build 8 points curves for each analyte. The coefficients of correlation ranged from 0.993 to 1, confirming the high linearity of the method (Table 4S). After three replicated injections of mixed standard solution (0.5 μg/mL) on the same day (intraday precision) and three consecutive days (interday precision), the relative standard deviations (% RSDs) for determining the reproducibility of the HPLC-MS/MS method were evaluated. The intraday precision ranged from 0.4% to 6.2%, while the interday precision was between 4.0% and 15.2% for all the targeted compounds. Assessing the limits of detection (LODs) and the limits of quantification (LOQs) for each monitored bioactive compound the sensitivity of the analytical method was validated. After the injections of standard solutions of known concentrations, the signal-to-noise ratios (S/N) were calculated. LODs and LOQs were estimated as the concentrations of analytes giving the S/N of 3:1 and 10:1 respectively. The LODs ranged from 0.0003 μg/mL to 0.03 μg/mL, while the LOQs were between 0.001 μg/mL and 0.1 μg/mL (Table 4S).

3.5. Analyses of bioactive compounds

In the present work, UHPLC-MS/MS was used to analyze 30 bioactive compounds in filter coffee samples, and 13 compounds were detected and quantified (Table 2). Some studies have assessed the influence of contact time and brew ratio on bioactive compound extraction (Cordoba et al., 2019). It is noteworthy that the roasting process has a huge impact on the coffee bean's physical structure, especially the so-called "first crack" that increases the overall volume, inside porosity, and pore volume of the coffee bean, enlarging the surface area for the caffeine extraction (Cortés-Macías, López, Gentile, Girón-Hernández, & López, 2022). PB filter coffee showed the highest levels of caffeine in medium (598.28 ± 8.84 μg/mL) and dark (556.13 ± 1.22 μg/mL) coffee compared to the other brewing methods, while for a light degree, the highest level of caffeine was detected in FP method (734.72 ± 7.07 μg/mL). PB filter coffee at medium (1726.8 ± 22.4 μg/mL) and dark (1407.89 ± 9.53 μg/mL) roasting degrees exhibited also a more abundant total content of bioactive compounds. Concerning CGAs, 5-CQA (953.76 ± 7.06–577.45 ± 8.36 μg/mL) was the most abundant compound, followed by 3-CQA (278.39 ± 7.07–136.88 ± 2.56 μg/mL), and 3,5-diCQA (85.58 ± 3.41–20.23 ± 0.69 μg/mL), followed by caffeic acid (3.35 ± 0.21–1.30 ± 0.16 μg/mL), vanillic acid (1.09 ± 0.01–0.68 ± 0.02 μg/mL), ferulic acid (0.44 ± 0.02–0.27 ± 0.02 μg/mL) and other phenolic acids. The Pure Brew exhibited the highest levels of 5-CQA in the medium (849.45 ± 7.24 μg/mL) and dark (656.64 ± 2.86 μg/mL) roast, while in the light roast it was drawn most by the FP (953.76 ± 7.06 μg/mL). The 3,5-CQA showed the same trend in the medium (66.44 ± 2.68 μg/mL) and dark (29.13 ± 3.15 μg/mL) roast for the Pure Brew, while in the light roast it was extracted more from the V60 (85.58 ± 3.41 μg/mL). Even at a medium roast, vanillic acid (1.09 ± 0.01 μg/mL), caffeic acid (2.70 ± 1.42 μg/mL), and p-cumaric acid (0.22 ± 0.01 μg/mL) were extracted more from Pure Brew, compared to other methods. The CGAs contribute a lot to the acidity and bitterness of coffee, as well as to a mildly stimulating effect. Thus, it was possible to state that, at the light roast, caffeine, CQAs, and other bioactive molecules were more extracted with FP, while at medium and dark roasts, the method extracting more bioactive molecules and antioxidants was always the PB. The fact that the FP reported higher values of caffeine and CQAs at light roasting was connected to the high PE% (20.65%), then in the other two roasting degrees, the values were lower, but still higher PE % (Table 1), which in the dark roasting also resulted in it being weak extracted (Fig. 1). These results were expected because FP was considered a full immersion technique where the ground coffee and water are well mixed for a long extraction time (±4:25 min:second) (Table 3S) (Frost et al., 2020), it wasn't a pour-over system (V60) where the water flowed, but it remains inside the instrument. However, PB reported higher caffeine and CQAs values and it can be related to the reason that it is an automatic system using pulsated pressures, compared to the others using manually applied pressures, but unlike the FP it was always in the optimal extraction range at all three roasting degrees (Fig. 1). So, it was assessed that FP and PB share with each other the mechanical filter, while the paper filter present in V60 and AP will give us a smaller extraction of these compounds and will not allow us to always be within the optimal extraction range (Fig. 1). The preparation of a pulsated pressure PB (automatic coffee machine) extracted the components quickly and at the same time the higher amount of water led to a higher extraction efficiency (Gloess et al., 2013). In filter coffee, the extraction was slower and most efficient in the beginning and at the end of the extraction process, according to Ludwig et al., 2012.

3.6. VOCs

Volatile profiles of the four different extraction methods of coffee, at three roasting degrees, were assessed by HS-SPME-GC-MS. The analyses of VOCs (volatile organic compounds) were acquired in full scan mode, using a method previously described (2.6). The scanned ions of each sample were calculated through their percentage of relative peak area (RPA) (Khamitova et al., 2020). A total of 71 volatile compounds were identified representing 77.09–96.88% of the total headspace composition (Table 3). The chemical classes detected were furans (15), pyrazines (15), ketones (9), aldehydes (13), pyrroles (3), acids (3), phenolic compounds (4), pyridines (4), terpene alcohols (3) and esters (1), which represent more than 75% of the volatile compounds in filter coffee beverages. Most of them are reported as common VOCs detected in coffee (Caporaso, Genovese, Canela, Civitella, & Sacchi, 2014; Wang et al., 2022). The fifteen selected furans exhibited malty and sweated roasted aromas (Cordoba et al., 2019). 2-Furanmethanol (8.30 ± 0.12–9.65 ± 0.4%) (candy, burnt, and smoky) (Galarza & Figueroa, 2022) was found at the highest level in PB (9.48 ± 0.4%) at light roasting, while was maximum in V60 at medium (9.55 ± 0.03%) and dark (9.65 ± 0.4%) roasting. Another important furan derivative is 2-Furanmethanol acetate (5.38 ± 0.2–9.38 ± 0.7%) (floral, herbal, and fruity) (Zhao et al., 2020), found in the highest quantities in AP among light roast (5.74 ± 0.5%), in V60 among medium roast (7.93 ± 0.01%) and in PB among dark roasts (9.28 ± 0.7%). Many aldehydes were identified and quantified in filter coffee as key odorants and are reported in literature to be formed as Strecker degradation products of the branched-chain amino acids (BCAA), responsible for cocoa, malty and fermented flavors in coffee (Angeloni et al., 2021). 2-Methylpropanal (0.25 ± 0.02–0.55 ± 0.04%), 2-Methylbutanal (0.35 ± 0.8–1.79 ± 0.4%), and 3-Methylbutanal (0.32 ± 0.2–2.09 ± 0.4%), have been associated with a high impact on the flavor of coffee and they were present in light roasted coffees in greater quantities in AP, while in medium and dark roasted coffees in PB. Moreover, 5-Methyl 2-furancarboxaldehyde, a furan derivative associated with high olfactometric activity (Zapata Ochoa et al., 2018), and with almond, caramel, sweet and cooked attributes, was found at the highest level in PB (9.38 ± 1.2%) in case of lightly roasted coffee; on the other hand, V60 brews prepared from medium (10.89 ± 1.1%) and dark (8.61 ± 1.4%) roasted coffees showed the highest levels of this compound. The most concentrated compound of this class is furfural (9.03 ± 1.1–19.13 ± 1.5%), in light roasted coffees it can be found at maximum level in PB (17.47 ± 1.3%), while at medium (19.13 ± 1.5%) and dark (11.51 ± 1.2%) degree was found mostly in V60. Furfural derivatives can be formed by the reaction between monosaccharides and an amino acid at high

Table 2
Quantitative determination of 13 bioactive compounds (μg/mL) detected in different filter coffee by UHPLC-MS/MS, relative standards deviations (RSDs%) was in a range from 1,3 to 8,5% (n = 3).

Roasting degree	Light			Medium				Dark				
Compound/sample	V60	FRPRESS	AEROPRESS	PUREBREW	V60	FRPRESS	AEROPRESS	PURE BREW	V60	FRPRESS	AEROPRESS	PURE BREW
Gallic acid	0.06 ± 0.01[a]	0.06 ± 0.01[a]	0.03 ± 0.01[b]	0.03 ± 0.01[b]	0.04 ± 0.01[b]	0.03 ± 0.01[b]	0.04 ± 0.01[b]	0.04 ± 0.01[b]	0.06 ± 0.01[a]	0.01 ± 0.01[c]	0.03 ± 0.01[c]	0.03 ± 0.01[c]
3-Caffeoylquinic acid	206.85 ± 1.41[a]	278.39 ± 7.07 [b]	194.35 ± 2.25 [c]	198.52 ± 2.12 [c]	215.29 ± 2.15 [d]	189.84 ± 1.32 [c,e]	193.79 ± 4.24 [c]	207.89 ± 2.14 [a]	206.85 ± 0.85 [a]	136.88 ± 2.56 [f]	154.83 ± 4.14 [g]	162.95 ± 1.73 [h]
(+) -Catechin	0.04 ± 0.02 [a]	0.45 ± 0.03 [b]	0.03 ± 0.04 [a]	0.02 ± 0.01 [a]	0.02 ± 0.01 [a]	0.04 ± 0.03 [a]	0.02 ± 0.02 [a]	0.04 ± 0.01 [a]	0.04 ± 0.01 [a]	0.08 ± 0.02 [a]	0.03 ± 0.02 [a]	0.04 ± 0.01 [a]
5-Caffeoylquinic acid	923.95 ± 1.41 [a]	953.76 ± 7.06 [b]	879.62 ± 2.45 [c]	892.84 ± 1.35 [c,d]	831.33 ± 6.52 [e]	788.89 ± 6.83 [f]	808.27 ± 2.42 [g]	849.45 ± 7.24 [h]	611.29 ± 4.42 [i]	577.45 ± 8.36 [l]	631.93 ± 2.92 [i,m]	656.64 ± 2.86 [n]
Vanillic acid	0.79 ± 0.02 [a]	1.01 ± 0.03 [b]	0.89 ± 0.04 [c]	0.84 ± 0.02 [a,c]	1.04 ± 0.01 [b]	0.68 ± 0.02 [a]	0.77 ± 0.02 [a]	1.09 ± 0.01 [b]	0.77 ± 0.01 [a]	0.78 ± 0.02 [a]	1.04 ± 0.03 [b]	0.94 ± 0.01 [c]
Caffeic acid	2.67 ± 0.85 [a]	3.15 ± 0.71 [b]	2.69 ± 0.04 [a]	3.35 ± 0.21[b]	2.05 ± 0.12 [a]	2.01 ± 1.41 [a]	2.59 ± 0.31 [a]	2.70 ± 1.42 [a]	1.29 ± 1.08 [c]	2.02 ± 1.01 [a]	1.30 ± 0.16 [c]	1.37 ± 0.42 [c]
(−) -Epicatechin	0.07 ± 0.01 [a]	0.08 ± 0.01 [a]	0.07 ± 0.01 [a]	0.08 ± 0.02 [a]	0.08 ± 0.01 [a]	0.06 ± 0.01 [b]	0.07 ± 0.01 [a]	0.07 ± 0.01 [a]	0.02 ± 0.01 [c]	0.04 ± 0.01 [d]	0.05 ± 0.01 [b]	0.05 ± 0.01 [b]
Syringic acid	0.01 ± 0.01 [a]	n.d.*	0.01 ± 0.01 [a]	0.03 ± 0.01 [a]	0.02 ± 0.01 [a]	0.02 ± 0.01 [a]	0.02 ± 0.01 [a]	n.d.*	0.02 ± 0.01 [a]	0.02 ± 0.01 [a]	0.01 ± 0.01 [a]	0.02 ± 0.01 [a]
p-Coumaric acid	0.28 ± 0.02 [a]	0.31 ± 0.01 [a]	0.26 ± 0.03 [a]	0.28 ± 0.07 [a]	0.19 ± 0.04 [b]	0.19 ± 0.02 [b]	0.19 ± 0.07 [b]	0.22 ± 0.01 [c]	0.13 ± 0.01 [d]	0.09 ± 0.01 [e]	0.09 ± 0.02 [f]	0.07 ± 0.03 [f]
Ferulic acid	0.39 ± 0.01[a]	0.44 ± 0.02 [b]	0.37 ± 0.01 [a]	0.39 ± 0.01 [a]	0.44 ± 0.02 [b]	0.36 ± 0.01 [a]	0.37 ± 0.02 [a]	0.40 ± 0.02 [b]	0.28 ± 0.01 [c]	0.27 ± 0.02 [c]	0.32 ± 0.07 [d]	0.35 ± 0.05 [a]
3,5-Dicaffeoylquinic acid	85.58 ± 3.41[a]	75.94 ± 1.52[b]	77.66 ± 2.14[b]	78.37 ± 2.11[b]	62.75 ± 1.34 [c]	48.42 ± 1.26 [d]	59.44 ± 1.39 [c]	66.44 ± 2.68 [e]	24.00 ± 2.37 [f]	20.23 ± 0.69 [g]	26.47 ± 2.18 [f]	29.13 ± 3.15 [h]
Caffeine	648.78 ± 8.73[a]	734.72 ± 7.07 [b]	607.69 ± 1.68 [c]	597.76 ± 1.41 [d]	573.51 ± 6.36 [e]	555.96 ± 1.26 [f]	566.75 ± 7.32 [f]	598.28 ± 8.84 [d]	548.89 ± 2.03 [f]	526.62 ± 8.05 [g]	520.45 ± 2.31 [g]	556.13 ± 1.22 [f]
Trans-cinnamic acid	0.18 ± 0.01[a]	0.21 ± 0.02 [b]	0.19 ± 0.01 [a]	0.21 ± 0.02 [b]	0.19 ± 0.01 [a]	0.19 ± 0.01 [a]	0.19 ± 0.01 [a]	0.21 ± 0.01 [b]	0.01 ± 0.01 [c]	0.17 ± 0.01 [d]	0.19 ± 0.01 [a]	0.20 ± 0.02 [a,b]
Total content	1869.67 ± 15.92 [a]	2048.46 ± 23.57 [b]	1736.86 ± 8.72 [c]	1772.74 ± 7.37 [d]	1686.95 ± 16.61[e]	1586.70 ± 12.2 [f]	1632.53 ± 15.85 [e,g]	1726.8 ± 22.4 [c,h]	1393.62 ± 10.83 [i]	1264.68 ± 20.78 [l]	1336.71 ± 11.89 [i,m]	1407.89 ± 9.53 [i,n]

n.d.*: not detected (peak area value below 5E + 04).
Results are mean ± standard deviation from triplicate extractions.
Values within the same row are significantly different ($p < 0.05$) for the parameter considered if their values do not show uppercase letters in common.

Table 3
Volatile compounds obtained by HS-SPME-GC-MS, retention time (RT), linear retention index (LRI) and mean relative peak area (RPA), percentage of volatiles was in a range from 1,6–9% ($n = 3$).

RT	(lit) LRI1	(exptl) LRI2	*COMPOUND NAME AND CLASS*	Light Roast coffee				Medium Roast coffee				Dark Roast coffee			
				V60	**FRPRESS**	**AEROPRESS**	**PUREBREW LIGHT**	**V60**	**FRPRESS**	**AEROPRESS**	**PUREBREW MEDIUM**	**V60**	**AEROPRESS**	**FRPRESS**	**PUREBREW DARK**
Aldehydes															
6.05	552	554	2-Methylpropanal	0.48 ± 0.02 [a]	0.39 ± 0.01 [b]	0.39 ± 0.05 [b]	0.55 ± 0.04 [c]	n.d.*	0.26 ± 0.03 [d]	n.d.*	0.28 ± 0.04 [d]	n.d.*	n.d.*	n.d.*	0.25 ± 0.02 [d]
8.55	662	660	2-Methylbutanal	1.69 ± 0.7 [a]	1.42 ± 0.6 [b]	1.79 ± 0.4 [a]	1.36 ± 0.5 [c]	0.66 ± 0.9[d]	1.09 ± 0.6 [e]	0.74 ± 0.8 [d]	1.09 ± 0.8 [e]	0.35 ± 0.8 [f]	0.39 ± 0.3 [f]	0.71 ± 0.5 [d]	0.79 ± 0.6 [d]
8.75	652	650	3-Methylbutanal	1.86 ± 0.1 [a]	1.71 ± 0.2 [b]	2.09 ± 0.4 [c]	1.56 ± 0.8 [d]	0.54 ± 0.4 [e]	1.12 ± 0.1 [f]	0.52 ± 0.1 [e]	1.12 ± 0.2 [f]	0.42 ± 0.1 [e]	0.32 ± 0.2 [e]	0.76 ± 0.1 [g]	0.74 ± 0.2 [g]
32.6	1104	1102	Nonanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.34 ± 0.03[a]	n.d.	0.26 ± 0.04 [a]	n.d.	0.1[a]	n.d.
36.64	833	830	Furfural	15.91 ± 1.1 [a]	16.07 ± 1.3 [a]	16.01 ± 1.4 [a]	17.47 ± 1.3 [b]	19.13 ± 1.5 [c]	16.79 ± 1.5 [d]	18.67 ± 1.9 [e]	18.21 ± 1.1 [e]	11.51 ± 1.2 [f]	9.03 ± 1.1 [g]	10.15 ± 0.02[h]	10.04 ± 0.02[h]
39.36	962	960	Benzaldehyde	0.50 ± 0.01 [a]	0.42 ± 0.02 [a]	0.67 ± 0.02 [b]	0.58 ± 0.02 [a]	0.71 ± 0.02[b]	0.66 ± 0.03 [b]	0.62 ± 0.02 [b]	0.68 ± 0.04 [b]	0.52 ± 0.06[a]	0.79 ± 0.04 [b]	0.86 ± 0.02 [b]	0.95 ± 0.02[b]
40.95	965	961	5-Methyl-2-furancarboxaldehyde	8.17 ± 1.3 [a]	8.32 ± 1.4 [a]	8.21 ± 1.1 [a]	9.38 ± 1.2 [b]	10.89 ± 1.1 [c]	9.02 ± 1.5 [b]	10.07 ± 1.2 [c]	9.79 ± 1.1 [c]	8.61 ± 1.4 [d]	8.15 ± 1.5 [d]	8.32 ± 1.1 [d]	8.1 ± 1.1 [d]
41.64	1046	1045	1H-Pyrrole-2-carboxaldehyde, 1-ethyl-	0.30 ± 0.01 [a]	0.32 ± 0.07 [a]	0.24 ± 0.01 [b]	0.26 ± 0.04 [b]	0.2 ± 0.01 [b]	0.33 ± 0.04 [a]	n.d.	0.27 ± 0.03 [b]	n.d.	0.44 ± 0.01 [c]	n.d.	0.33 ± 0.01 [a]
41.98	1016	1015	1H-Pyrrole-2-carboxaldehyde, 1-methyl-	1.29 ± 0.8 [a]	1.41 ± 0.4 [b]	1.13 ± 0.3 [c]	1.26 ± 0.8 [a]	1.2 ± 0.9 [a]	1.52 ± 0.5 [c]	1.24 ± 0.3 [a]	1.6 ± 0.5 [d]	1.67 ± 0.7 [d]	2.13 ± 0.8 [e]	2.15 ± 0.9 [e]	2.33 ± 0.8 [e]
42.32	1029	1020	5-Ethylfurfural	n.d.	n.d.	0.68 ± 0.07 [a]	n.d.	0.45 ± 0.01 [b]	0.36 ± 0.02 [c]	0.62 ± 0.04 [a]	0.98 ± 0.06 [d]	n.d.	n.d.	0.15 ± 0.03 [e]	0.16 ± 0.02 [e]
44.5	1008	1005	2-Thiophenecarboxaldehyde	0.73 ± 0.02 [a]	0.71 ± 0.01 [a]	0.74 ± 0.03 [a]	0.52 ± 0.07 [b]	0.37 ± 0.02 [c]	0.34 ± 0.04 [c]	0.58 ± 0.02 [b]	0.76 ± 0.07 [a]	n.d.	n.d.	0.84	0.42 ± 0.08 [b]
46.96	1015	1013	1H-Pyrrole-2 carboxaldehyde	1.28 ± 1.6 [a]	1.40 ± 1.2 [b]	1.41 ± 1.5 [b]	1.21 ± 1.7 [a]	1.34 ± 1.2 [c]	1.17 ± 1.8 [d]	1.52 ± 1.9 [b]	1.16 ± 1.2 [a]	2.42 ± 1.2 [d]	n.d.	0.28 ± 0.9 [e]	0.22 ± 0.7 [e]
51.117	1233	1235	5-Hydroxymethylfurfural	0.39 ± 0.01[a]	0.85 ± 0.05 [b]	0.21 ± 0.08 [c]	0.48 ± 0.09 [a]	1.46 ± 0.02 [d]	0.19 ± 0.05 [c]	0.42 ± 0.04 [a]	0.37 ± 0.01 [a]	n.d.	n.d.	n.d.	n.d.
			Total Aldehydes	**32.06[a]**	**33.02[b]**	**33.57[b]**	**34.63[c]**	**36.95[d]**	**32.85[a]**	**35.84[c]**	**36.31[d]**	**25.76[e]**	**21.25[f]**	**24.32[e]**	**24.33**
Ketones															
11	595	590	2,3-Butanedione	0.28 ± 0.02 [a]	0.26 ± 0.03 [a]	0.24 ± 0.01 [a]	0.26 ± 0.03 [a]	0.24 ± 0.02 [a]	0.28 ± 0.01 [a]	0.2 ± 0.01 [a]	0.29 ± 0.04 [a]	0.14 ± 0.01 [b]	0.2 ± 0.03 [a]	0.2 ± 0.06 [a]	0.21 ± 0.05 [a]
14.8	698	690	2,3-Pentanedione	1.08 ± 0.1 [a]	1.01 ± 0.2 [a]	0.92 ± 0.1 [a]	0.93 ± 0.5 [a]	0.85 ± 0.1 [b]	0.76 ± 0.7 [b]	0.67 ± 0.1 [b]	0.94 ± 0.5 [c]	0.24 ± 0.1 [d]	0.22 ± 0.8 [d]	0.36 ± 0.1 [d]	0.36 ± 0.9 [d]
18.44	786	780	2,3-Hexanedione	0.21 ± 0.05 [a]	0.24 ± 0.06 [a]	n.d.	0.22 ± 0.03 [a]	n.d.	0.23 ± 0.04 [a]	n.d.	0.23 ± 0.08 [a]	n.d.	0.24 ± 0.02 [a]	n.d.	n.d.
28.65	665	660	1-Hydroxy-2-propanone	0.46 ± 0.06 [a]	0.55 ± 0.06 [b]	0.83 ± 0.03 [c]	0.62 ± 0.01 [b]	0.68 ± 0.02 [b]	0.69 ± 0.06 [b]	1.5 ± 0.02 [c]	0.62 ± 0.06 [b]	0.68 ± 0.06 [b]	0.49 ± 0.06 [b]	0.24 ± 0.05 [d]	0.24 ± 0.03 [d]
39.7	967	960	1-(Acetyloxy)-2-butanone	0.31 ± 0.06 [a]	0.35 ± 0.05 [a]	0.4 ± 0.06 [a]	0.39 ± 0.08 [a]	n.d.	0.49 ± 0.04 [a]	0.4 ± 0.03 [a]	0.55 ± 0.03 [a]	n.d.	0.48 ± 0.04 [a]	0.48 ± 0.06 [a]	0.54 ± 0.05 [a]
40.95	1011	1010	1-(2-Furanyl) -1-propanone	0.72 ± 0.05 [a]	0.77 ± 0.05 [a]	0.68 ± 0.06 [a]	0.72 ± 0.06 [a]	0.93 ± 0.3 [a]	1.07 ± 0.4 [b]	0.88 ± 0.06 [a]	1.06 ± 0.8 [b]	0.86 ± 0.7 [a]	0.7 ± 0.03 [a]	1.37 ± 0.06 [c]	1.44 ± 0.06 [c]
41.13	881	880	4-Cyclopentene-1,3-dione	0.55 ± 0.09 [a]	0.61 ± 0.05 [a]	0.4 ± 0.01 [a]	0.63 ± 0.06 [a]	0.56 ± 0.01 [a]	0.8 ± 0.02 [a]	0.66 ± 0.03 [a]	n.d.	n.d.	n.d.	n.d.	n.d.
43.08	1106	1100	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.78 ± 0.05 [a]	0.82 ± 0.06 [a]	0.91 ± 0.06 [a]	n.d.	1.29 ± 0.06 [b]	1.51 ± 0.06 [b]	n.d.	1.24 ± 0.06 [b]	0.19 ± 0.06 [a]	n.d.	n.d.	n.d.
46.624	n.d.	n.d.	Maltol	0.44 ± 0.04 [a]	0.47 ± 0.08 [a]	0.38 ± 0.08 [a]	0.25 ± 0.06 [b]	0.33 ± 0.03 [b]	0.25 ± 0.06 [b]	n.d.	0.51 ± 0.07 [a]	n.d.	n.d.	n.d.	n.d.
			Total Ketones	**4.83[a]**	**5.08[b]**	**4.76[a]**	**4.02[a]**	**4.88[a]**	**6.08[c]**	**4.31[a]**	**5.44[b]**	**2.11[d]**	**2.33[d]**	**2.65[d]**	**2.79[d]**
Furans															
7.4	606	600	2-Methylfuran.	0.35 ± 0.05 [a]	0.41 ± 0.01 [a]	0.55 ± 0.03 [b]	n.d.	n.d.	0.35 ± 0.08 [a]	0.5 ± 0.05 [b]	n.d.	0.51 ± 0.03 [b]	0.82 ± 0.01 [c]	0.37 ± 0.04 [a]	0.42 ± 0.08 [a]
22.749	856	850	2-(2-Propenyl) furan	0.19 ± 0.06 [a]	0.26 ± 0.05 [a]	0.31 ± 0.03 [a]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.16 ± 0.01 [a]	0.24 ± 0.09 [a]
24.531	845	830	2-(Methoxymethyl)furan	n.d.	n.d.	0.2 ± 0.02 [a]	n.d.	n.d.	n.d.	0.2 ± 0.03 [a]	n.d.	0.23 ± 0.04 [a]	n.d.	0.34 ± 0.02 [a]	0.33 ± 0.02 [a]
26.18	809	800	Dihydro-2-methyl-3(2H) furanone.	0.43 ± 0.08 [a]	0.45 ± 0.09 [a]	0.42 ± 0.01 [a]	0.48 ± 0.05 [a]	0.53 ± 0.03 [b]	0.55 ± 0.03 [b]	0.36 ± 0.01 [a]	0.65 ± 0.01[c]	0.22 ± 0.05 [d]	0.41 ± 0.01[a]	0.47 ± 0.05 [a]	0.51 ± 0.08 [a]
39.2	893	890	2-n-Butyl furan	0.49 ± 0.06 [a]	0.45 ± 0.05 [a]	0.51 ± 0.03 [a]	0.46 ± 0.01 [a]	0.65 ± 0.01[b]	0.55 ± 0.06 [a]	0.54 ± 0.2 [a]	0.54 ± 0.05 [a]	0.92 ± 0.01[c]	0.72 ± 0.05 [c]	0.73 ± 0.04 [c]	0.86 ± 0.2 [c]
39.77	995	990	2-Furanmethanol acetate	5.65 ± 0.7 [a]	5.58 ± 0.9 [a]	5.74 ± 0.5 [a]	5.38 ± 0.2 [a]	7.93 ± 0.01[b]	6.61 ± 0.9 [c]	6.44 ± 0.2 [c]	6.63 ± 0.9 [c]	8.96 ± 0.2 [d]	8.13 ± 0.8 [d]	8.56 ± 0.5 [d]	9.28 ± 0.7 [e]
41.4	1096	1090	2-Furanmethanol propanoate	0.43 ± 0.01 [a]	n.d.	0.26 ± 0.05 [b]	0.6 ± 0.01[c]	0.29 ± 0.06[b]	0.74 ± 0.05 [c]	0.4 ± 0.03 [b]	0.69 ± 0.1[c]	0.56 ± 0.4 [c]	n.d.	1.98 ± 0.5 [d]	2.07 ± 1.8 [d]
41.65	1088	1080	2,2′-Methylenebisfuran	0.59 ± 0.03 [a]	0.67 ± 0.06 [b]	0.52 ± 0.01 [a]	0.41 ± 0.02 [c]	0.53 ± 0.09 [a]	0.96 ± 0.07 [d]	0.92 ± 0.08 [d]	0.86 ± 0.05 [d]	1.34 ± 0.14 [e]	2.39 ± 0.12 [f]	2.18 ± 0.09 [f]	2.12 ± 0.11 [f]
42.69	859	850	2-Furanmethanol	8.30 ± 0.12 [a]	8.77 ± 0.03 [a]	8.46 ± 0.03 [a]	9.48 ± 0.4 [b]	9.55 ± 0.03 [b]	9.36 ± 0.03 [b]	9.19 ± 0.5 [b]	9.02 ± 0.03 [b]	9.65 ± 0.4 [b]	9.04 ± 0.03 [b]	8.79 ± 0.5 [b]	8.78 ± 0.03 [b]
41.86	1039	1020	2-Acetyl-5-methylfuran	n.d.	0.18 ± 0.03 [a]	n.d.	0.1 ± 0.06 [a]	n.d.	0.38 ± 0.01 [a]	n.d.	0.28 ± 0.03 [a]	n.d.	0.44 ± 0.01 [a]	n.d.	0.51 ± 0.01 [a]
42.9	1190	1189	2-(2-furanylmethyl) -5-methylfuran	0.40 ± 0.06 [a]	0.41 ± 0.05 [a]	0.35 ± 0.03 [a]	n.d.	0.39 ± 0.01 [a]	0.4 ± 0.05 [a]	0.74 ± 0.03 [b]	0.46 ± 0.06 [a]	0.92 ± 0.06 [c]	0.93 ± 0.03 [c]	1.34 ± 0.2 [d]	0.85 ± 0.08 [c]
38.7	911	910	2-Acetylfuran	2.41 ± 0.1 [a]	2.40 ± 0.1 [a]	2.42 ± 0.5 [a]	2.6 ± 0.7 [a]	3.5 ± 0.6 [b]	2.93 ± 0.5 [a]	2.98 ± 0.1 [a]	3.24 ± 0.1 [b]	2.59 ± 0.1 [a]	2.89 ± 0.1 [a]	3.13 ± 0.1 [b]	3.22 ± 0.15 [b]
43.215	1232	1230	2-Furanmethanol pentanoate	n.d.	n.d.	0.23 ± 0.04 [a]	n.d.	n.d.	n.d.	0.48 ± 0.05 [b]	n.d.	n.d.	n.d.	0.67 ± 0.07 [c]	n.d.
48.935	n.d.	n.d.	α-Furfuryliden-α-furylmethylamine	0.38 ± 0.03 [a]	0.37[a]±0.02	0.42 ± 0.03 [a]	0.31 ± 0.05 [a]	0.46 ± 0.08 [a]	0.4 ± 0.03 [a]	0.5 ± 0.02 [a]	0.3 ± 0.01 [b]	0.92 ± 0.03 [c]	0.8[c]	0.88 ± 0.08 [c]	0.87 ± 0.1 [c]
49.9	1224	1223	Dihydrobenzofuran	n.d.	n.d.	0.16 ± 0.05 [a]	0.24 ± 0.06 [a]	n.d.	n.d.	n.d.	n.d.	0.14 ± 0.03 [a]	0.14 ± 0.03 [a]	n.d.	0.15 ± 0.03 [a]
			Total Furans	**19.62[a]**	**19.95[a]**	**20.55[b]**	**20.06[b]**	**23.83[c]**	**23.23[c]**	**23.34[c]**	**22.67[d]**	**26.96[e]**	**26.71[e]**	**29.61[f]**	**30.21[f]**
Phenolic compounds															
45.406	1090	1085	Guaiacol	0.85 ± 0.01 [a]	0.19 ± 0.03 [b]	n.d.	0.19 ± 0.06 [b]	n.d.	0.29 ± 0.02 [b]	n.d.	0.35 ± 0.08 [b]	1.27 ± 0.13 [c]	1.3 ± 0.09 [c]	1.17 ± 0.07 [c]	1.7 ± 0.15 [d]
46.672	980	970	Phenol	0.47 ± 0.05 [a]	0.32[a]	n.d.	n.d.	0.2 ± 0.05 [a]	0.54 ± 0.03 [a]	0.8 ± 0.08 [b]	0.51 ± 0.09 [a]	1.13 ± 0.03 [c]	0.2 ± 0.05 [a]	0.85 ± 0.02 [b]	0.53 ± 0.01 [a]
47.35	1075	1060	M-cresol	0.46 ± 0.03 [a]	0.18 ± 0.04 [b]	n.d.	0.23 ± 0.02 [b]	0.1 ± 0.03 [c]	0.32 ± 0.01 [d]	0.36 ± 0.04 d	0.2 ± 0.03 [b]	0.43 ± 0.02 [a]	0.36 ± 0.03 [d]	0.45 ± 0.01 [a]	0.29 ± 0.01 [d]
48.309	1317	1315	4-Vinylguaiacol	2.07 ± 0.1 [a]	2.24 ± 0.3 [a]	1.82 ± 0.5 [b]	1.74 ± 0.2 [b]	1.53 ± 0.03 [b]	1.69 ± 0.4 [b]	2.06 ± 0.6 [a]	1.78 ± 0.2 [b]	1.26 ± 0.4 [b]	0.89 ± 0.5 [c]	1.12 ± 0.2 [b]	1.22 ± 0.8 [b]
			Total Phenolic compounds	**3.85[a]**	**2.93[b]**	**1.82[c]**	**2.16[b]**	**1.83[c]**	**2.84[b]**	**3.22[a]**	**2.84[b]**	**4.09[c]**	**2.75[b]**	**3.59[a]**	**3.74[a]**

(*continued on next page*)

Table 3 (*continued*)

RT	(lit) LRI1	(exptl) LRI2	*COMPOUND NAME AND CLASS*	Light Roast coffee				Medium Roast coffee				Dark Roast coffee			
				V60	FRPRESS	AEROPRESS	PUREBREW LIGHT	V60	FRPRESS	AEROPRESS	PUREBREW MEDIUM	V60	AEROPRESS	FRPRESS	PUREBREW DARK
Pyridine															
22.099	746	740	Pyridine	1.35 ± 0.4 ^{a}	0.94 ± 0.07 ^{b}	0.79 ± 0.03 ^{b}	1.5 ± 0.9 ^{a}	0.93 ± 0.3 ^{b}	0.85 ± 0.5 ^{b}	0.47 ± 0.4 ^{c}	1.54 ± 0.6 ^{a}	2.55 ± 0.2 ^{d}	2.4 ± 0.5 ^{d}	2.83 ± 0.9 ^{d}	3.26 ± 0.7 ^{d,e}
41.61	1035	1030	N-acetyl-4(H)-Pyridine	0.57 ± 0.06^{a}	0.56 ± 0.02 ^{a}	0.49 ± 0.09 ^{a}	0.35 ± 0.03 ^{a}	0.28 ± 0.04 ^{a,b}	0.6 ± 0.5 ^{a}	0.44 ± 0.5 ^{a}	0.7 ± 0.03 ^{a}	0.4 ± 0.5 ^{a}	0.27 ± 0.03 ^{a}	0.48 ± 0.02 ^{a}	0.42 ± 0.07 ^{a}
43.605	1038	1030	2-Acetylpyridine	0.17 ± 0.02^{a}	0.22 ± 0.05^{a}	n.d.	n.d.	0.1 ± 0.03^{b}	0.33 ± 0.03^{c}	n.d.	0.26 ± 0.03^{c}	n.d.	n.d.	0.32 ± 0.04 ^{c}	0.35 ± 0.04 ^{c}
50.28	1145	1140	3-Pyridinol	0.25 ± 0.01^{a}	0.54 ± 0.07 ^{b}	n.d.	0.26 ± 0.03^{a}	0.64 ± 0.03 ^{c}	n.d.	n.d.	0.21 ± 0.09 ^{a}	n.d.	0.1 ± 0.07 ^{d}	0.17 ± 0.05 ^{d}	n.d.
			Total Pyridine	**2.34^{a}**	**2.26^{a}**	**1.28^{b}**	**2.11^{a}**	**1.95^{a}**	**1.78^{b}**	**0.91^{c}**	**2.50^{a}**	**2.71^{a}**	**2.95^{d}**	**2.77^{a,d}**	**3.80^{a,d}**
Pyrazine															
23.2	736	740	Pyrazine	0.30 ± 0.01 ^{a}	0.27 ± 0.04^{a}	0.17 ± 0.01^{b}	0.35 ± 0.05 ^{a}	n.d.	n.d.	n.d.	0.28 ± 0.07 ^{a}	0.13 ± 0.08 ^{b}	n.d.	0.18 ± 0.02^{b}	0.26 ± 0.01^{a}
26.419	831	820	Methylpyrazine	3.82 ± 0.9 ^{a}	4.05 ± 0.2 ^{a}	3.78 ± 0.5 ^{a}	4.53 ± 0.9 ^{b}	2.76 ± 0.2 ^{c}	2.21 ± 0.1^{c}	2.48 ± 0.7 ^{c}	2.89 ± 0.1^{c}	3.43 ± 0.3^{a}	2.54 ± 0.9 ^{c}	3.05 ± 0.4 ^{a}	3.25 ± 0.9 ^{a}
29.4	917	910	2,5-Dimethylpyrazine	3.54 ± 0.7 ^{a}	3.35 ± 0.1 ^{a}	3.37 ± 0.4 ^{a}	3.81 ± 0.5 ^{a}	2.36 ± 0.6 ^{b}	2.1 ± 0.8 ^{b}	2.1 ± 0.8 ^{b}	2.74 ± 0.5 ^{b}	2.81 ± 0.7 ^{b}	2.4 ± 0.6 ^{b}	2.67 ± 0.8 ^{b}	2.96 ± 0.9 ^{a,b}
29.7	917	910	2,6-Dimethylpyrazine	2.77 ± 0.1 ^{a}	2.69 ± 0.2 ^{a}	2.61 ± 0.4 ^{a}	3.06 ± 0.5 ^{b}	n.d.	2.02 ± 0.4 ^{a}	n.d.	2.14 ± 0.3 ^{a}	1.65 ± 0.2 ^{c}	n.d.	2.31 ± 0.1 ^{a}	2.53 ± 0.7 ^{a}
30.7	926	920	2,3-Dimethylpyrazine	0.52 ± 0.01 ^{a}	0.48 ± 0.04 ^{a}	0.49 ± 0.01 ^{a}	0.56 ± 0.01 ^{a}	0.43 ± 0.05 ^{a}	0.37 ± 0.02 ^{a}	0.37 ± 0.01 ^{a}	0.38 ± 0.03 ^{a}	0.39 ± 0.02^{a}	0.37 ± 0.02 ^{a}	0.41 ± 0.08 ^{a}	0.45 ± 0.09 ^{a}
32.8	1393	1390	2-Ethyl-6-methylpyrazine	2.60 ± 0.9 ^{a}	2.48 ± 0.6 ^{a}	2.8 ± 0.5 ^{a}	2.71 ± 0.4 ^{a}	1.86 ± 0.5 ^{b}	1.77 ± 0.3 ^{b}	1.67 ± 0.8 ^{b}	1.74 ± 0.4 ^{b}	2.47 ± 0.90 ^{a}	2.03 ± 0.4 ^{a,b}	2.22 ± 0.3 ^{b}	1.98 ± 0.2 ^{b}
33.18	1005	1000	2-Ethyl-5-methylpyrazine	n.d.	n.d.	1.94 ± 0.5 ^{a}	2.24 ± 0.9 ^{b}	1.5 ± 0.3 ^{a}	1.69 ± 0.2 ^{a}	1.4 ± 0.5 ^{a}	n.d.	1.68 ± 0.6 ^{a}	1.21 ± 0.5 ^{a}	1.66 ± 0.8 ^{a}	n.d.
33.8	1004	1002	2-Ethyl-3-methylpyrazine	2.45 ± 0.5 ^{a}	2.32 ± 0.2 ^{a}	1.4 ± 0.3 ^{b}	2.52 ± 0.4 ^{a}	1.67 ± 0.6 ^{b}	1.68 ± 0.3 ^{b}	0.6 ± 0.4 ^{c}	1.73 ± 0.6 ^{b}	1.77 ± 0.2 ^{b}	1.66 ± 0.9 ^{b}	1.84 ± 0.8 ^{b}	2.04 ± 0.9 ^{a}
35.39	1084	1080	2,6-Diethylpyrazine	0.73 ± 0.01 ^{a}	0.72 ± 0.06 ^{a}	0.74 ± 0.01 ^{a}	0.72 ± 0.04 ^{a}	0.36 ± 0.02 ^{b}	0.57 ± 0.07 ^{c}	0.36 ± 0.01 ^{c}	0.6 ± 0.05 ^{c}	0.45 ± 0.01 ^{c}	0.42 ± 0.04 ^{c}	0.72 ± 0.01 ^{a}	0.96 ± 0.09 ^{a}
35.9	1082	1080	3-Ethyl-2,5-dimethylpyrazine	2.25 ± 0.01 ^{a}	2.02 ± 0.4 ^{a}	2.15 ± 0.7 ^{a}	2.36 ± 0.5 ^{a}	1.58 ± 0.4 ^{b}	1.51 ± 0.9^{b}	1.52 ± 0.7 ^{b}	1.52 ± 0.4 ^{b}	1.99 ± 0.4 ^{a,b}	1.68 ± 0.01 ^{b}	1.76 ± 0.2 ^{b}	2.26 ± 0.01 ^{a}
36.9	1084	1080	2-Ethyl-3,5-dimethylpyrazine	0.84 ± 0.09^{a}	n.d.	0.71 ± 0.08^{a}	1.07 ± 0.3 ^{b}	1.54 ± 0.2 ^{c}	0.51 ± 0.01^{a}	1.97 ± 0.2 ^{d}	0.85 ± 0.01^{a}	3.41 ± 0.9 ^{e}	2.54 ± 0.3 ^{f}	0.63 ± 0.01 ^{a}	n.d.
37	1090	1090	2-Methyl-6-propylpyrazine	0.16 ± 0.02 ^{a}	0.25 ± 0.01^{a}	n.d.	0.32 ± 0.06 ^{a}	n.d.	0.001 ± 0.07 ^{b}	n.d	0.27 ± 0.01^{a}	n.d.	0.001 ± 0.08 ^{b}	0.17 ± 0.09 ^{a}	0.27 ± 0.01 ^{a}
38.125	1031	1030	2-Ethenyl-6-methylpyrazine	0.47 ± 0.01^{a}	0.42 ± 0.01^{a}	0.42 ± 0.01^{a}	0.42 ± 0.04 ^{a}	n.d.	0.3 ± 0.01^{a}	0.37 ± 0.07^{a}	n.d.	0.48 ± 0.09 ^{a}	0.39 ± 0.05^{a}	0.43 ± 0.45 ^{a}	0.48 ± 0.01 ^{a}
38.447	1162	1160	3,5-Diethyl-2-methylpyrazine	1.12 ± 0.7 ^{a}	0.99 ± 0.01 ^{b}	1.1 ± 0.2 ^{a}	0.96 ± 0.7 ^{b}	0.71 ± 0.01^{b}	0.73 ± 0.01^{b}	0.56 ± 0.01^{c}	0.61 ± 0.01^{c}	0.64 ± 0.01^{c}	0.69 ± 0.01^{c}	0.87 ± 0.01 ^{d}	1.03 ± 0.2 ^{a}
39.9			2-Methyl-6-(1-propenyl) pyrazine	0.22 ± 0.05 ^{a}	0.23 ± 0.01^{a}	0.19 ± 0.01^{a}	0.2 ± 0.01^{a}	0.23 ± 0.01^{a}	0.27 ± 0.09^{a}	0.35 ± 0.0^{a}	0.25 ± 0.01^{a}	n.d.	0.4 ± 0.01^{b}	0.21 ± 0.01 ^{a}	0.26 ± 0.01 ^{a}
			Total Pyrazine	**21.79^{a}**	**20.27^{b}**	**21.87^{c}**	**25.83^{d}**	**15.00^{e}**	**15.73^{e}**	**13.75^{f}**	**16.00^{e,g}**	**21.30^{a}**	**16.33^{e}**	**19.13^{b}**	**18.73^{b}**
Acids															
36.4	610	600	Acetic acid	1.09 ± 0.5 ^{a}	0.61 ± 0.08 ^{b}	1.52 ± 0.11 ^{c}	0.75 ± 0.04 ^{b}	0.1 ± 0.01 ^{d}	1.1 ± 0.4 ^{a}	1.99 ± 0.8 ^{c}	0.5 ± 0.09 ^{d}	n.d.	n.d.	n.d.	n.d.
43.02	863	855	Isovaleric acid	0.54 ± 0.06 ^{a}	0.72 ± 0.03 ^{a}	1.22 ± 0.5 ^{b}	1.22 ± 0.5 ^{b}	0.29 ± 0.07 ^{c}	0.36 ± 0.02 ^{c}	n.d.	0.53 ± 0.09 ^{a}	n.d.	n.d.	n.d.	n.d.
48	1273	1271	Nonanoic acid	0.24 ± 0.07 ^{a}	0.37 ± 0.02 ^{b}	0.27 ± 0.09 ^{a}	1.78 ± 0.01 ^{c}	0.28 ± 0.08 ^{a}	0.21 ± 0.07 ^{a}	n.d.	n.d.	0.14 ± 0.04 ^{d}	0.11 ± 0.05 ^{d}	0.48 ± 0.03 ^{b}	n.d.
			Total Acids	**1.87^{a}**	**1.70^{a}**	**3.01^{b}**	**3.75^{b}**	**1.24^{a}**	**1.67^{a}**	**2.33^{c}**	**1.03^{a}**	**0.40^{d}**	**0.11^{d}**	**0.58^{d}**	**0.00^{d}**
Terpene Alcohols															
	1074	1071	cis-Linalooloxide (furan)	0.48 ± 0.09 ^{a}	0.41 ± 0.04 ^{a}	0.47 ± 0.02 ^{a}	0.48 ± 0.01 ^{a}	0.5 ± 0.02 ^{a}	0.49 ± 0.01 ^{a}	0.44 ± 0.05 ^{a}	0.47 ± 0.03 ^{a}	0.33 ± 0.07 ^{b}	0.29 ± 0.04 ^{b}	0.25 ± 0.09 ^{b}	0.35 ± 0.06 ^{b}
37	1086	1086	trans-Linalooloxide (furanoid)	0.27 ± 0.05 ^{a}	0.37 ± 0.08 ^{b}	0.32 ± 0.01 ^{b}	0.39 ± 0.04 ^{b}	0.3 ± 0.06 ^{b}	0.33 ± 0.05 ^{b}	0.25 ± 0.02 ^{a}	0.36 ± 0.03 ^{a}	0.41 ± 0.01 ^{a}	0.23 ± 0.05 ^{c}	0.22 ± 0.03 ^{c}	0.23 ± 0.08 ^{c}
40.215	1099	1091	Linalool	0.70 ± 0.01 ^{a}	0.80 ± 0.09 ^{a}	0.65 ± 0.09 ^{a}	0.62 ± 0.02 ^{a}	0.69 ± 0.03 ^{a}	0.73 ± 0.03 ^{a}	0.8 ± 0.05 ^{a}	0.72 ± 0.03 ^{a}	0.17 ± 0.01 ^{b}	0.47 ± 0.03 ^{c}	0.37 ± 0.07 ^{c}	0.38 ± 0.01 ^{c}
			Total Terpene Alcohols	**1.45^{a}**	**1.58^{a}**	**1.44^{a}**	**1.49^{a}**	**1.49^{a}**	**1.55^{a}**	**1.49^{a}**	**1.55^{a}**	**0.91^{b}**	**0.99^{b}**	**0.84^{c}**	**0.96^{b}**
Pyrroles															
39.14	755	745	Pyrrole	0.22 ± 0.03 ^{a}	0.18 ± 0.04 ^{a}	0.17 ± 0.02 ^{a}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
45.049	1187	1185	1-Furfurylpyrrole	2.10 ± 0.9 ^{a}	1.92 ± 0.5 ^{a}	1.98 ± 0.03 ^{a}	0.18 ± 0.01 ^{b}	1.57 ± 0.6 ^{c}	0.3 ± 0.07 ^{d}	1.97 ± 1.2 ^{a}	1.76 ± 0.8 ^{a}	n.d.	2.28 ± 1.6 ^{e}	2.76 ± 1.5 ^{e}	2.29 ± 1.3 ^{e}
46.479	1064	1062	2-Acetylpyrrole	0.62 ± 0.04 ^{a}	0.57 ± 0.05 ^{a}	0.76 ± 0.02 ^{a}	0.57 ± 0.03 ^{a}	0.96 ± 0.9 ^{b}	0.59 ± 0.01 ^{b}	1.17 ± 0.3 ^{c}	1.76 ± 0.4 ^{c}	1.37 ± 0.9 ^{c}	1.24 ± 0.2 ^{c}	1.18 ± 0.1 ^{c}	0.99 ± 0.5 ^{b}
			Total Pyrroles	**2.94^{a}**	**2.67^{a}**	**2.91^{a}**	**0.75^{b}**	**2.53^{a}**	**0.89^{b}**	**3.14^{c}**	**3.52^{c}**	**1.37^{d}**	**3.52^{c}**	**3.94^{c}**	**3.28^{c}**

(*continued on next page*)

Table 3 (*continued*)

RT	(lit) LRI1	(exptl) LRI2	*COMPOUND NAME AND CLASS*	Light Roast coffee				Medium Roast coffee				Dark Roast coffee			
				V60	FRPRESS	AEROPRESS	PUREBREW LIGHT	V60	FRPRESS	AEROPRESS	PUREBREW MEDIUM	V60	AEROPRESS	FRPRESS	PUREBREW DARK
Esters															
25.32	918	910	3-methyl 2-buten-1-yl acetate	0.23 ± 0.02 [a]	0.21 ± 0.01 [a]	0.21 ± 0.07 [a]	0.1 ± 0.02 [a]	n.d.	0.21 ± 0.01 [a]	0.21 ± 0.04 [a]	0.22 ± 0.09 [a]	0.12 ± 0.02 [a]	0.16 ± 0.01 [a]	0.26 ± 0.02 [a]	0.22 ± 0.02 [a]
Others															
42.15	n.d.	n.d.	Butyrolactone	n.d.	n.d.	0.49 ± 0.01 [a]	n.d.	0.3 ± 0.01 [a]	n.d.	0.33 ± 0.01 [a]	n.d.	0.42 ± 0.02 [a]	0.68 ± 0.01 [b]	0.11 ± 0.03 [a]	n.d.
			TOTAL VALUE	**96,88[a]**	**93,4[b]**	**93,99[b]**	**97,61[a]**	**93,31[b]**	**85,05[c]**	**90,57[d]**	**93,62[b]**	**90,35[d]**	**77,09[e]**	**90,06d**	**89,11f**

n.d.*: not detected (peak area value below 5E + 04).
Results are mean ± standard deviation from triplicate extractions.
Values within the same row are significantly different ($p < 0.05$) for the parameter considered if their values do not show uppercase letters in common.
1Linear retention indices reported in literature.
2Experimental linear retention index.

temperatures (Gong et al., 2021). The important presence of furfural in samples contributed to cereal and bread-like flavour (Angeloni, Scortichini, et al., 2020). Among pyrazines, the most abundant is Methylpyrazine (2.21 ± 0.1–4.53 ± 0.9%) (chocolate, corn-like, nutty), found at the highest percentage in Pure Brew at light roast (4.53 ± 0.9%), then in medium (2.89 ± 0.1%) and dark (3.43 ± 0.1%) roasted samples (Caporaso, Whitworth, & Fisk, 2022). Other molecules showing a similar trend are 2,5-Dimethylpyrazine (2.1 ± 0.8–3.81 ± 0.5%), (nutty, roasted, fruity, and grassy) and 2,6-Dimethylpyrazine (1.65 ± 0.2–3.06 ± 0.5%) (cocoa, toast nuts, roasted meat, and solvent) which are found at maximum in PB in light, medium, and dark roasted samples (Kalschne, Viegas, De Conti, Corso, & de Toledo Benassi, 2018). A similar trend is also showed by 2-Ethyl-6-methyl pyrazine (1.67 ± 0.8–2.8 ± 0.5%) (earthy and moldy), elevated in AP (2.8 ± 0.5%) in light, and in V60 in a dark (2.47 ± 0.90%) and medium (1.86 ± 0.5%) roast. In general, the formation of pyrazines was related to the process of heating food, where amino acids react with sugars in Maillard reactions (Spada et al., 2021). Among ketones, represented mainly by 2,3-Butanedione (0.29 ± 0.04–0.14 ± 0.01%) and 2,3-Pentanedione (0.22 ± 0.8–1.08 ± 0.1%) that are key odorants; it is possible to assert that they are associated with buttery and creamy flavour (Seninde & Chambers, 2020). In our findings, for light roasting, they are maximum in V60, while for medium and dark they are at the highest level in PB. Higher concentrations of ketones are detected in filtered coffee brew rather than in espresso (Angeloni et al., 2021). Pyrroles (0.75–3.94%) were usually related to nutty, hay-like, and herb aroma (Heo, Adhikari, Choi, & Lee, 2020); they are present with the highest area in dark roasts in PB (2.29 ± 1.3%), followed by a medium in AP (1.97 ± 1.2%) and light V60 (2.10 ± 0.9%) roasted samples. Among phenolic compounds, guaiacol and 4-vinyl guaiacol were the most abundant volatiles identified (Abdelwareth, Zayed, & Farag, 2021). The one present at the highest level is 4-vinyl guaiacol (0.89 ± 0.5–2.24 ± 0.3%), known to be associated with spice and clove flavours; it is present at its highest in FP in the light (2.24 ± 0.3%) and AP (2.06 ± 0.6%) in medium roasted products, then in V60 (1.26 ± 0.4%) for the dark ones. Instead, guaiacol (0.19 ± 0.02–1.7 ± 0.15%) is very evident in dark roasts, mostly in PB dark (1.7 ± 0.15%). Guaiacol is related to smoke, sweet, and medicinal flavours, and it evokes a burning sensation even at very low concentrations (Cserháti & Forgács, 2020). For short-chain fatty acids (SCFAs) (n.d. - 3.75%) a unique profile appears: they practically disappear in dark roasting. In fact, during the roasting process, carbohydrates, like sucrose, begin to break down, leading to the formation of SCFAs, such as acetic acid (Angeloni et al., 2019). Depending on roasting conditions, acetic acid concentration can become 25 times higher than its initial green bean concentration. Overall, acetic acid reaches its maximum level in light (1.52 ± 0.11%) or medium roasts (1.99 ± 0.8%) roasted samples highest in AP, then quickly dissipates as roasting progresses due to its high volatility (Angeloni, Scortichini, et al., 2020). Pyridine (0.9–4.03%) was known to have fishy, roasted, and astringent characteristics, and it can give a sharp burnt taste at concentrations as low as ppm scale. Pyridine was produced by trigonelline degradation and Maillard reactions (Heo et al., 2020), especially in coffee that is subjected to high temperatures or strong roasting processes. The highest area was in the dark (3.80%) and medium roast (2.50%) in PB and decreases in light roasting were maximum in V60 (2.34%). Among the terpene alcohols, cis-Linalooloxide (furan) (sweet-fruity) is present at the highest level in PB at light (0.48 ± 0.01%) and dark roasting (0.35 ± 0.06%), while at medium in V60 (0.5 ± 0.02%) (De Melo Pereira et al., 2019). Previous studies in brewed coffee have shown that the extraction method influences the intensity of sweet flavour and related attributes (caramel, malty, fruity, and floral flavour) (Angeloni et al., 2019; Cordoba et al., 2019). Likewise, we observed that hot immersion (AP and FP) was characterized mainly by the sweetness and hot dripping (V60 and PB) with a higher bitter intensity. These dissimilarities could be related to the caffeine content, which is, in general, higher in hot dripping than immersion. Like previous findings, our results showed

that FP and AP showed a lower total content of non-volatile compounds and TDS (Table 1) (Table 2), which could explain the higher sweetness molecules perceived in the resulting beverages. Overall, hot dripping coffees achieved a better balance of molecules and demonstrated more balanced coffees.

3.7. Principal Component Analysis (PCA)

Principal component analysis was applied to evaluate the relationship between the different coffee extraction methods and the four-coffee preparation method at the three different degrees of coffee roasting. The first two components of the PCA accounted for variances of 33.5% and 17.7%, respectively, for a total of 51.02%. The score plot (Fig. 2) separates the preparation methods, with the different coffees used at three different roasting degrees; particularly the clustering of coffees according to the degree of roasting (light, medium, and dark) was clear while a defined trend cannot be found for the different types of extraction used (V60, FP, AP, and PB). The first two components of the PCA for light roasting accounted for variances of 39.1% and 41.8%, respectively, for a total of 80.9%. The first two components of the PCA for medium roasting accounted for variances of 34.7% and 44.0%, respectively, for a total of 78.7%. The first two components of the PCA for dark roasting accounted for variances of 35.5% and 47.7%, respectively, for a total of 83.2%. In this way, the three score plots clearly demonstrated the clustering of the four filter coffee extraction methods, in fact AP and V60 were found to be significantly different from Pure Brew in all three coffee roasts. As regards FP, a significant clustering have been found in the light roast, while in medium and dark FP was quite similar to PB. The similarity between the two coffees was due to the mechanical filter, whereas V60 and AP utilized a paper filter. FP showed a good extraction of non-volatile compounds, especially in the light roast, however, their extraction was lower than in PB. In conclusion, PB surely is closer to FP than to the other extraction methods, but PB displayed some differences with FP as it fit into the optimal extraction range at all three roasting levels, its preparation requires half time and it results in a more balanced cup in terms of aroma/volatile molecules.

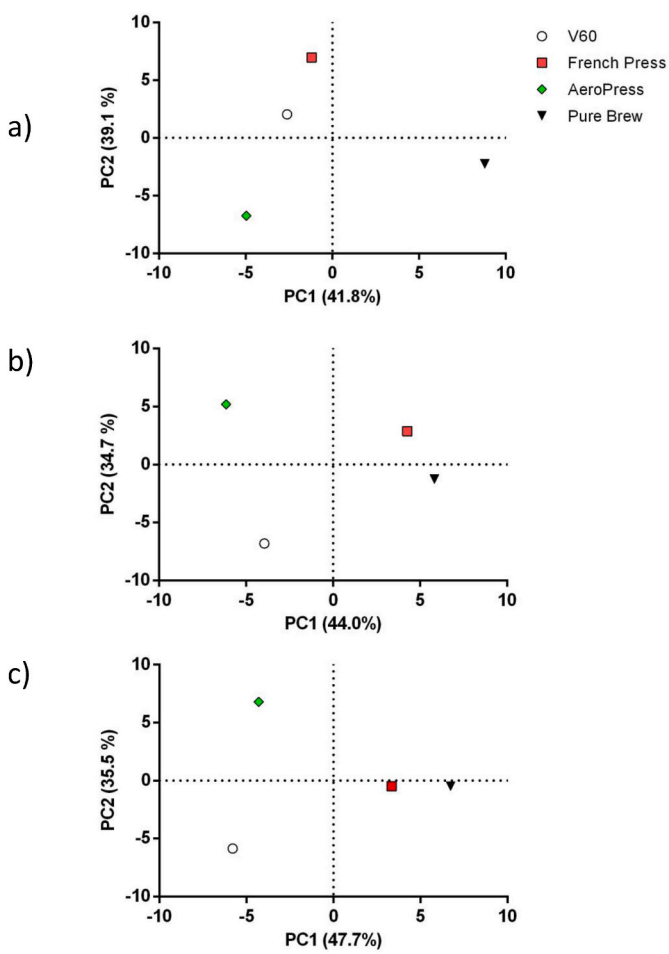

Fig. 2. *Score* plot, PCA of the four extraction methods at the three different degrees of roasting, i.e. a) light, b) medium, c) dark.

4. Conclusion

Feature evaluation of an espresso machine that can make filter coffee (Pure Brew) was not reported in any study and in the current work we compared these new technique with the most known filter coffee methods (V60, French Press, and AeroPress) studying variables not evaluated before. From the obtained results, the new extraction method, Pure Brew, has shown performances similar to the known filter coffee preparation methods already on the market (i.e. V60, French Press, and AeroPress) or, in some cases, better; this is the case for the extraction yields (in fact, it fell into the ideal extraction percentage (18–22%) at three degrees of roasting), and bioactive compounds content (for a medium and dark roast). The evaluation of these analyses could contribute to the commercial development of this new and innovative way of obtaining filter coffee (Pure Brew), which today is prepared mainly with the traditional techniques considered in our study. Moreover, Pure Brew has the advantage, concerning other methods, of being faster; more, with a single coffee machine, it is possible to prepare espresso and filter coffee, yielding a saving in cost and space occupied by equipment.

CRediT authorship contribution statement

Agnese Santanatoglia: Conceptualization, Methodology, Writing – original draft. **Giovanni Caprioli:** Data curation, Supervision, Writing – review & editing. **Marco Cespi:** Supervision. **Dario Ciarlantini:** Supervision, Methodology, Validation. **Luca Cognigni:** Validation, Investigation. **Lauro Fioretti:** Conceptualization, Data curation, Supervision. **Filippo Maggi:** Software, Validation. **Ahmed M. Mustafa:** Methodology, Validation. **Franks Nzekoue:** Methodology. **Sauro Vittori:** Resources, Supervision.

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.

Data availability

No data was used for the research described in the article.

Acknowledgment

The authors are grateful to Simonelli Group SpA (Belforte del Chienti, Macerata, Italy) for partially funding this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2023.114471.

References

Abdelwareth, A., Zayed, A., & Farag, M. A. (2021). Chemometrics-based aroma profiling for revealing origin, roasting indices, and brewing method in coffee seeds and their commercial blends in the Middle East. *Food Chemistry, 349*, Article 129162. https://doi.org/10.1016/j.foodchem.2021.129162

Angeloni, G., Guerrini, L., Masella, P., Bellumori, M., Daluiso, S., Parenti, A., et al. (2019). What kind of coffee do you drink? An investigation of the effects of eight different extraction methods. *Food Research International, 116*, 1327–1335. https://doi.org/10.1016/j.foodres.2018.10.022

Angeloni, S., Mustafa, A. M., Abouelenein, D., Alessandroni, L., Acquaticci, L., Nzekoue, F. K., … Caprioli, G. (2021). Characterization of the aroma profile and main key odorants of espresso coffee. *Molecules, 26*(13), 3856. https://doi.org/10.3390/molecules26133856

Angeloni, S., Nzekoue, F. K., Navarini, L., Sagratini, G., Torregiani, E., Vittori, S., et al. (2020). An analytical method for the simultaneous quantification of 30 bioactive compounds in the spent coffee ground by HPLC-MS/MS. *Journal of Mass Spectrometry, 55*(11), e4519. https://doi.org/10.1002/jms.4519

Angeloni, S., Scortichini, S., Fiorini, D., Sagratini, G., Vittori, S., Neiens, S. D., … Caprioli, G. (2020). Characterization of odour-active compounds, polyphenols, and fatty acids in coffee silverskin. *Molecules, 25*(13), 2993. https://doi.org/10.3390/molecules25132993

Barroso, L. A., Macedo, A. S., Lemos, I. L., de Andrade Neves, N., Schmiele, M., da Silveira, J. V. W., … Fonte, P. (2022). Optimization of the brewing parameters on coffee extraction using a central composite rotatable design. *JSFA Reports, 2*(3), 107–115. https://doi.org/10.1002/jsf2.33

Batali, M. E., Ristenpart, W. D., & Guinard, J. X. (2020). Brew temperature, at fixed brew strength and extraction, has little impact on the sensory profile of drip brew coffee. *Scientific reports, 10*(1), 1–14. https://doi.org/10.1038/s41598-020-73341-4

Caporaso, N., Genovese, A., Canela, M. D., Civitella, A., & Sacchi, R. (2014). Neapolitan coffee brew chemical analysis in comparison to espresso, Moka and American brews. *Food Research International, 61*, 152–160. https://doi.org/10.1016/j.foodres.2014.01.020

Caporaso, N., Whitworth, M. B., & Fisk, I. D. (2022). Prediction of coffee aroma from single roasted coffee beans by hyperspectral imaging. *Food Chemistry, 371*, Article 131159. https://doi.org/10.1016/j.foodchem.2021.131159

Cordoba, N., Fernandez-Alduenda, M., Moreno, F. L., & Ruiz, Y. (2020). Coffee extraction: A review of parameters and their influence on the physicochemical characteristics and flavour of coffee brews. *Trends in Food Science & Technology, 96*, 45–60. https://doi.org/10.1016/j.tifs.2019.12.004

Córdoba, N., Moreno, F. L., Osorio, C., Velásquez, S., & Ruiz, Y. (2021). Chemical and sensory evaluation of cold brew coffees using different roasting profiles and brewing methods. *Food Research International, 141*, Article 110141. https://doi.org/10.1016/j.foodres.2021.110141

Cordoba, N., Pataquiva, L., Osorio, C., Moreno, F. L. M., & Ruiz, Y. (2019). Effect of grinding, extraction time, and type of coffee on the physicochemical and flavor characteristics of cold brew coffee. *Scientific Reports, 9*(1), 1–12. https://doi.org/10.1038/s41598-019-44886-w

Cortés-Macías, E. T., López, C. F., Gentile, P., Girón-Hernández, J., & López, A. F. (2022). Impact of post-harvest treatments on physicochemical and sensory characteristics of coffee beans in Huila, Colombia. *Postharvest Biology and Technology, 187*, Article 111852. https://doi.org/10.1016/j.postharvbio.2022.111852

Cotter, A. R., Batali, M. E., Ristenpart, W. D., & Guinard, J. X. (2021). Consumer preferences for black coffee are spread over a wide range of brew strengths and extraction yields. *Journal of Food Science, 86*(1), 194–205. https://doi.org/10.1111/1750-3841.15561

Cserháti, T., & Forgács, E. (2020). *Chromatography in food science and technology*. CRC Press. https://doi.org/10.1201/9781003075929

De Melo Pereira, G. V., de Carvalho Neto, D. P., Júnior, A. I. M., Vásquez, Z. S., Medeiros, A. B., Vandenberghe, L. P., et al. (2019). Exploring the impacts of postharvest processing on the aroma formation of coffee beans–A review. *Food Chemistry, 272*, 441–452. https://doi.org/10.1016/j.foodchem.2018.08.061

Frost, S. C., Ristenpart, W. D., & Guinard, J. X. (2020). Effects of brew strength, brew yield, and roast on the sensory quality of drip-brewed drip-brewed coffee. *Journal of Food Science, 85*(8), 2530–2543. https://doi.org/10.1111/1750-3841.15326

Galarza, G., & Figueroa, J. G. (2022). Volatile compound characterization of coffee (coffea arabica) processed at different fermentation times using SPME–GC–MS. *Molecules, 27*(6), 2004. https://doi.org/10.3390/molecules27062004

Gloess, A. N., Schönbächler, B., Klopprogge, B., Dambrosio, L., Chatelain, K., Bongartz, A., … Yeretzian, C. (2013). Comparison of nine common coffee extraction methods: Instrumental and sensory analysis. *European Food Research and Technology, 236*(4), 607–627. https://doi.org/10.1007/s00217-013-1917-x, 607–627 (2013).

Gong, M., Zhou, Z., Liu, S., Zhu, S., Li, G., Zhong, F., et al. (2021). Formation pathways and precursors of furfural during Zhenjiang aromatic vinegar production. *Food Chemistry, 354*, Article 129503. https://doi.org/10.1016/j.foodchem.2021.129503

Guimarães, E. R., Leme, P. H. M. V., De Rezende, D. C., Pereira, S. P., & Dos Santos, A. C. (2019). The brand-new Brazilian specialty coffee market. *Journal of Food Products Marketing, 25*(1), 49–71. https://doi.org/10.1080/10454446.2018.1478757

Heo, J., Adhikari, K., Choi, K. S., & Lee, J. (2020). Analysis of caffeine, chlorogenic acid, trigonelline, and volatile compounds in cold brew coffee using high-performance liquid chromatography and solid-phase microextraction—gas chromatography-mass spectrometry. *Foods, 9*(12), 1746. https://doi.org/10.3390/foods9121746

Kalschne, D. L., Viegas, M. C., De Conti, A. J., Corso, M. P., & de Toledo Benassi, M. (2018). Steam pressure treatment of defective Coffea canephora beans improves the volatile profile and sensory acceptance of roasted coffee blends. *Food Research International, 105*, 393–402. https://doi.org/10.1016/j.foodres.2017.11.017

Khamitova, G., Angeloni, S., Borsetta, G., Xiao, J., Maggi, F., Sagratini, G., … Caprioli, G. (2020). Optimization of espresso coffee extraction through variation of particle sizes, perforated disk height, and filter basket aimed at lowering the amount of ground coffee used. *Food Chemistry, 314*, Article 126220. https://doi.org/10.1016/j.foodchem.2020.126220

Ludwig, I. A., Sanchez, L., Caemmerer, B., Kroh, L. W., De Peña, M. P., & Cid, C. (2012). Extraction of coffee antioxidants: Impact of brewing time and method. *Food Research International, 48*(1), 57–64. https://doi.org/10.1016/j.foodres.2012.02.023

Rao, N. Z., & Fuller, M. (2018). Acidity and antioxidant activity of cold brew coffee. *Scientific Reports, 8*(1), 1–9. https://doi.org/10.1038/s41598-018-34392-w

Sano, Y., Kubota, S., Kawarazaki, A., Kawamura, K., Kashiwai, H., & Kuwahara, F. (2019). A mathematical model for coffee extraction based on the volume averaging theory. *Journal of Food Engineering, 263*, 1–12. https://doi.org/10.1016/j.jfoodeng.2019.05.025

Seninde, D. R., & Chambers, E. (2020). Coffee flavour: A review. *Beverages, 6*(3), 44. https://doi.org/10.3390/beverages6030044

Spada, F. P., Balagiannis, D. P., Purgatto, E., do Alencar, S. M., Canniatti-Brazaca, S. G., & Parker, J. K. (2021). Characterization of the chocolate aroma in roast jackfruit seeds. *Food Chemistry, 354*, Article 129537. https://doi.org/10.1016/j.foodchem.2021.129537

Stanek, N., Zarębska, M., Biłos, Ł., Barabosz, K., Nowakowska-Bogdan, E., Semeniuk, I., … Szkutnik, K. (2021). Influence of coffee brewing methods on the chromatographic and spectroscopic profiles, antioxidant and sensory properties. *Scientific Reports, 11*(1), 1–13. https://doi.org/10.1038/s41598-021-01001-2

Tsiafitsa, A., Oikonomopoulou, V., Stramarkou, M., Krokida, M., & Papassiopi, N. (2022). Effect of heat treatment on physicochemical and sensory properties of selected coffee varieties. *European Food Research and Technology*, 1–12. https://doi.org/10.1007/s00217-022-04025-8

Wang, X., Wang, Y., Hu, G., Hong, D., Guo, T., Li, J., … Qiu, M. (2022). Review on factors affecting coffee volatiles: From seed to cup. *Journal of the Science of Food and Agriculture, 102*(4), 1341–1352. https://doi.org/10.1002/jsfa.11647

Zapata Ochoa, J. A., Londoño Zapata, V., Naranjo Cano, M., Osorio Monsalve, J. J., López Córdoba, C. A., & Quintero Ortíz, M. M. (2018). *Characterization of aroma compounds present in an industrial recovery concentrate of coffee flavour*. https://doi.org/10.1080/19476337.2017.1406995

Zhao, G., Ding, L. L., Hadiatullah, H., Li, S., Wang, X., Yao, Y., … Jiang, S. (2020). Characterization of the typical fragrant compounds in traditional Chinese-type soy sauce. *Food Chemistry, 312*, Article 126054. https://doi.org/10.1016/j.foodchem.2019.126054