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Impact of the human factor on the reproducibility of different coffee brewing methods

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ABSTRACT

Filter coffee can be prepared using various methods, most of which are time-consuming and dependent on the skill of the operator/barista. In this regard, a medium-roasted specialty coffee has been selected to test four different filter extraction methods (Pure Brew, V60, AeroPress and French Press). Each method was performed by six different expert baristas to understand the influence of the human factor on the preparation. Pure Brew and V60 reported excellent reproducibility concerning the total dissolved solids, brewing time and amounts of bioactive compounds by HPLC–MS/MS and volatile compounds by GC–MS; while for viscosities analysis, Pure Brew and French Press were detected as the more reproducible. The pressure and turbulence applied by baristas for pouring water during preparation proved to be key variables from the point of view of reproducibility in filter coffee extraction.

1. Introduction

Coffee is one of the most widely consumed beverages in the world and one of the most traded commodities. Nowadays, the largest producing and exporting countries, are Brazil (USD 4.6 billion), Vietnam (USD 3.5 billion) and Colombia (USD 2.58 billion), while the largest importing countries in 2017 were the United States (USD 6.3 billion), Germany (USD 3.5 billion) and France (USD 2.8 billion) (Voora et al., 2019). Coffee is often consumed more than once a day, and in a variety of different contexts; consumers cite flavour and quality as major driving factors for coffee consumption (Samoggia and Riedel, 2019), resulting in the rise of "specialty" coffee and the expanding research about coffee flavour and brewing in the past decade (Mestdagh, Glabasnia and Giuliano, 2017). Specialty coffee as a segment has emerged in the last years as a response to the consumer's demand for equity between the producer and the processing side (Ponte, 2002). In this way, specialty coffees are made of the highest quality coffee beans to reveal their outstanding flavour potential. The flavour is considered an essential criterion in determining the coffee quality, and it is directly affected by the presence of defective coffee beans (Sittipod et al., 2019; Córdoba et al., 2021). Coffee represents a unique beverage, also due to the complexity of its chemical composition, with more than 1.500 chemical compounds (Farag et al., 2022). Coffee beans contain non-volatile compounds, such as caffeine, which has strong pharmacological and physiological effects, including cardiovascular, respiratory, renal, and smooth muscle effects, as well as effects on mood, memory, alertness, physical and cognitive performance (McLellan et al., 2016); it also contains water, carbohydrates, fibre, proteins, amino acids, lipids, carboxylic acids including organic and chlorgenic acids, and trigonelline. More than 1.000 volatile organic compounds (VOCs) have so far been identified in the gas phase of coffee, but only a fraction is odour-active, thus being relevant for a typical coffee aroma (Gloess et al., 2013). Typically, coffee preparation involves three main stages: first, the raw coffee beans are roasted; after that, the roasted beans are ground to facilitate a better extraction during the final brewing stage and finally the latter involves the extraction of coffee soluble fraction from the roasted and ground coffee grains with water. Coffee brewing is a solid–liquid extraction where some parameters have a significant impact on the extraction kinetics of the different

Abbreviations: HPLC–MS/MS, high-performance liquid chromatography-tandem mass spectrometry; GC–MS, gas chromatography-mass spectrometry; SCA, specialty coffee association; VA, Victoria Arduino; TDS, total dissolved solids; PCA, principal component analysis; PE, percentage of extraction; EY, extraction yields; SD, standard deviation; RSD, relative standard deviation; BT, brew time; CGA, chlorogenic acids.

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chemical compounds (Córdoba et al., 2021). Important parameters include the brew ratio (dry coffee mass to water volume used), grind size and distribution, brewing and extraction time, temperature of water, turbulence and pressure (Stanek et al., 2021). Additionally, there are a wide variety of techniques used in the brewing stage; these methods fall into three broad categories: pour-over methods, infusion methods and pressure methods (Moroney et al., 2016). More recently, V60, French Press and AeroPress, have become the most commercially used extraction methods for the preparation of filter coffee or long coffee. In fact, V60, the traditional pour-over and infusion system, is about pouring hot water through coffee grounds on a filter paper; French Press is the classical full immersion system with a mechanical filtration; AeroPress, using pressure, is appropriate for more complete extractions, and uses a paper filter (Santanatoglia et al., 2023a). In this study, it was chosen to compare the reproducibility of the newly set Pure Brew (VA) in comparison to the other filter coffee extraction methods. The fundamental aim of this study was to assess how to consistently brew coffee of the highest possible quality, being affected as little as possible by the barista, hence by the human factor. Specifically, the study describes how consistent the results in terms of TDS (total dissolved solids), extraction yields, bioactive compounds (by HPLC–MS/MS), VOCs (by GC–MS) and rheological properties were obtained for filter coffees from different extraction methods (Pure Brew, V60, AeroPress, and French Press). Moreover, it was assessed how these characteristics of filter coffee were affected by the operation of six different professional baristas. To date, no study in the literature has conducted such an investigation, so the results are certainly a novelty.

2. Material and methods

2.1. Chemicals and reagents

The analytical standards for the bioactive compounds analysis by HPLC–MS/MS were supplied by Sigma-Aldrich (Milan, Italy). Individual stock solutions of each analyte at a concentration of 1000 mg/L were prepared by dissolving pure standard compounds in HPLC methanol and stored in glass-capped bottles at 4 °C. Moreover, standard working solutions were prepared daily at different concentrations by appropriate dilution of the stock solution with methanol. HPLC-grade formic acid 99–100% was purchased from Merck (Darmstadt, Germany). HPLC-grade acetonitrile and methanol were supplied by Sigma Aldrich (Milan, Italy). Deionised water was obtained from a Milli-Q Reagent Water System (Millipore, Bedford, MA). All other solvents and chemicals were of analytical grade. All solvents and solutions were filtered through a 0.2 μm polyamide filter from Sartorius Stedim (Goettingen, Germany).

2.2. Coffee sample preparation

For all analyses, one type of coffee was used: *Coffea arabica* from Gardelli Specialty Coffee, Kakindu natural, Kenya, associated with medium roasting, terroir Kiambu (Kenya). The pack of coffee beans (250 g) was opened immediately before dispensing, to avoid oxidative damage. Beans were always ground with a professional grinder (Mythos one, Victoria Arduino). The grinding was measured by Mastersizer 3000 Aero Series dry dispersion units (Malvern PANalytical Ltd., Great Malvern, UK): for Pure Brew the grind was 1030 ± 2.13 μm, while for the French Press, the grind was coarser: 1290 ± 3.81 μm. On the other side, a different trend was measured for the AeroPress, for which the grind used was 800 ± 3.21 μm and for V60, the grind used was usually at 945 ± 2.81 μm. The grain size was analysed to understand that the optimal grain size for each extraction method was observed. All samples were prepared with commercial natural water (Nerea). This water was chosen for its mineral salt content, i.e., 161 mg/L of dry residue, associated with its salt balance. Indeed, the chemical composition of water was suitable to be an effective extractor; according to the SCA parameters, water must have a dry residue in the range of 125–175 mg/L (SCA, 2021). A specific procedure was used for each of the four brewing methods (Fig. 1), maintaining a starting quantity of coffee at 15 g for all preparations.

2.2.1. Pure brew

Pure brew coffee was obtained with the Black Eagle Maverick machine (Simonelli Group, Victoria Arduino). Pure Brew technology is an extraction method that uses pulsating frequencies with low-pressure water (less than 0.15 bar with respect to atmospheric pressure). Pure Brew filter consists of a micro-thin double mesh conical basket, which can contain up to 20 g of coffee. By combining Pure Brew technology with the patented filter basket, it was possible to obtain a filtered coffee simply by pressing a button. The water temperature was 93 °C. The coffee: water ratio was 1:16.6, the Pure Brew recipe of 60 g/L.

2.2.2. V60

Hario V60 is a patented system from Japanese company Hario, consisting of a coffee percolator "V-shaped" (with an angle of 60 °C, from which it takes its name). It consists of three parts: a carafe or glass base (Hario V60 Range Server, 600 mL), a ceramic drip coffee decanter reverse cone-shaped, and a paper filter (Hario V60 Paper Filter). Initially, a little amount of water at 93 °C is poured to wet the filter, then the coffee was placed until a flat surface was obtained. Subsequently, 60 mL of water at 93 °C were poured over the coffee, which was left to pre-infuse for 15 s (water was always spilt in concentric circles, starting from the centre, and then widening, trying to maintain a constant flow). At 30 s an additional 100 mL of water were poured; finally, 130 mL of water were added at 1'20". To conclude, the spin was made to take up all the coffee, and the upper piece of the instrument was shaken manually three times. The final coffee: water ratio was 1:15, 290 mL were added because some of the water was held back by the coffee cake.

2.2.3. AeroPress

AeroPress is a system invented in 2005 by Alan Adler, a manual coffee extractor using hand generated pressure in the brewing process. The device consists of two nested cylinders, a chamber, and a plunger with a hermetic seal. First, the paper filter (AeroPress® Micro Filter) was wetted resting in a plastic filter holder attached to the syringe base, then, the coffee was placed onto the filter paper. Afterwards, during the "blooming" phase, 60 mL of water were poured over the bed of coffee to fully saturate all the grounds. After 60 mL of water were poured, grounds were given 15 s to fully saturate and release carbon dioxide. Water was topped up to a total of 290 mL, then it was stirred with a spatula. Finally, after a further 20 s, the upper part of the AeroPress with the hermetic seal, was pressed down, applying pressure for approximately 30 s. The final coffee: water ratio was 1:15; 290 mL were added because some of the water was held back by the coffee cake.

2.2.4. French press

French Press (Lacor French Press wood) consists of a glass jug surrounded by a support structure, with a handle and a plunger that passes through the lid, to terminate with a metal filter, consisting of a fine mesh filter held between spiral and cross plate. Initially, the coffee was ground and inserted into the glass jug. Water at 93 °C was added up to 290 mL. During this operation, turbulence was created from above by stirring, at 1 min, 2 min and 3 min; the cap of the instrument was then removed and turned with a spatula 4 times. At 4 min the filter was slowly depressed into the coffee liquid to its full length. The coffee: water ratio was 1:14.

2.3. Coffee physicochemical characteristics

TDS is considered an index of brew strength and it is the mass fraction of soluble solids in the brew, while PE (percentage of extraction) is expressed by the "extraction yield", i.e., the mass fraction of soluble solids extracted from ground coffee (Batali et al., 2020). These physicochemical characteristics of filter coffee were measured using a

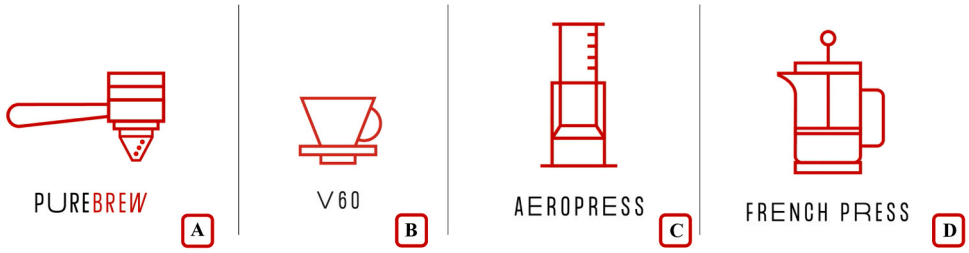

Fig. 1. Filter coffee extraction methods: Pure Brew (**A**), V60 (**B**), AeroPress (**C**) and French Press (**D**).

refractometer (VST LAB Coffee III Refractometer; USA) at room temperature. These parameters were incorporated by Lockhart in the classic "Coffee Brewing Control Chart". 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, labelled as "strong" or "weak", and horizontal separation versus PE, labelled as "bitter" or "underdeveloped". The chart's central region is associated with the Specialty Coffee Association's "Golden Cup Standard", in which TDS values span from 1.15% to 1.35%, with PE values in the range 18–22%, which is denoted as "ideal" (Batali et al., 2020) (Figure 1S). The chart also indicates that a high PE coffee is "bitter", and a low PE is "underdeveloped", whereas low TDS coffee is "weak", and high TDS coffee is "strong" (Cotter et al., 2021). For the construction of this, VST App (VST Coffee Tools) was used and the diagonal lines in the chart represent the brew ratio (i.e., mass of water per mass of coffee grounds).

2.4. Bioactive compounds quantitation by LC–MS

The coffee samples were diluted 10 times, centrifuged at 15000 rpm for 5 min and filtered with Phenex RC 4-mm 0.2-μm filter, from Phenomenex (Castel Maggiore, Italy), prior to HPLC–MS/MS analysis. The HPLC–MS/MS investigations were carried out using an Agilent 1290 Infinity series high-performance liquid chromatograph and a 6420 triple quadrupole mass spectrometer from Agilent Technologies (Santa Clara, CA) equipped with an electrospray ionisation source (ESI) operating in negative and positive ionization modes, according to the previously published method (Angeloni et al., 2020b; Santanatoglia et al., 2023a). Briefly, the column used was a Kinetex PFP analytical column (100 × 2.1 mm i.d., 2.6 μm). The mobile phase was composed of (A) water and (B) methanol, both with 0.1% formic acid, at a flow rate of 0.2 mL/min, in gradient elution mode. The injection volume was 2 μL and the column temperature was kept at 30 °C. The drying gas temperature in the ionisation source was 35 °C. The gas flow was 10 L/min, the atomizer pressure was 25 psi, and the capillary voltage was 4.000 V. Detection was executed in dynamic-MRM mode by comparison with authentic standards according to a previously published method (Angeloni et al., 2020b, Santanatoglia et al., 2023a). 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 1S).

2.5. Analysis of volatile organic compounds

A gas chromatography/mass selective detector (GC/MSD with PAL3) was used (Agilent, Santa Clara, CA, Agilent 7890B GC hardware with Agilent 5977 Series MSD and MassHunter GC/MSD data acquisition software, PAL3-Auto Sampler System). The column used for separation was DB-WAX (0.25 mm × 60 m, 0.25 μm; Agilent). The flow rate (He) was 1.2 mL/min in spitless mode. The injector temperature was 260 °C. The column temperature 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

Table 1
The analysis of different data for the coffee, amount of ground coffee (g), volume of final cup (mL), brew time (min: sec). Mean and standard deviation (SD) of brew time about six samples by six different baristas. Total dissolved solids (TDS), mean and standard deviation (SD) of TDS about six samples by six different baristas. Percentage of extraction (PE), mean and standard deviation (SD) of PE about six samples by six different baristas.

	Coffee powder (g)	Final volume in the cup (mL)	Brew Time (min:sec)	Mean	SD	TDS	Mean	SD	PE	Mean	SD
PURE BREW 1	15	250	1:42	1:41	± 00:01	1.65	1.71	± 0.03	21.2		
PURE BREW 2	15	257	1:42			1.72			21.4		
PURE BREW 3	15	248	1:41			1.70			21.6	21.7	± 0.28
PURE BREW 4	15	243	1:41			1.73			21.9		
PURE BREW 5	15	245	1:40			1.72			21.9		
PURE BREW 6	15	244	1:43			1.73			22.0		
V60 1	15	224	2:09	2:31	± 00:12	1.35	1.27	± 0.05	18.5		
V60 2	15	227	2:45			1.26			20.5		
V60 3	15	223	2:37			1.26			19.8	19.6	± 0.76
V60 4	15	218	2:39			1.19			20.4		
V60 5	15	222	2:28			1.30			19.4		
V60 6	15	220	2:29			1.28			19.2		
AEROPRESS 1	15	228	1:21	1:14	± 00:04	1.36	1.33	± 0.04	21.5		
AEROPRESS 2	15	228	1:19			1.38			21.9		
AEROPRESS 3	15	224	1:12			1.35			21.0	20.8	± 0.71
AEROPRESS 4	15	225	1:12			1.30			20.3		
AEROPRESS 5	15	227	1:11			1.29			20.3		
AEROPRESS 6	15	227	1:12			1.28			20.2		
FRENCH PRESS 1	15	210	3:27	3:21	± 00:05	0.92	1.02	± 0.09	15.3		
FRENCH PRESS 2	15	217	3:30			1.12			19.1	17.2	± 1.59
FRENCH PRESS 3	15	219	3:26			0.90			15.5		
FRENCH PRESS 4	15	216	3:15			1.08			18.4		
FRENCH PRESS 5	15	218	3:15			1.06			18.2		
FRENCH PRESS 6	15	202	3:18			1.06			17.0		

min), then 250 °C for 3.33 min; the total run time was 50 min. Data were acquired in electron impact (EI) mode and SCAN mode, according to the previously published method (Santanatoglia et al., 2023a). Briefly, sample injection techniques with SPME were implemented through the PAL3 autosampler system. The fibre assembly was from Supelco (Bellefonte, PA, USA) and had a 50/30 μm coating of divinylbenzene/Carboxen™/polydimethylsiloxane (DVB/CAR/PDMS). For the analysis, 3 mL of each filtered coffee sample were placed in a 20-mL screw-cap vial and the sample was incubated at 60 °C and shaken at 250 rpm for 20 min. Thereafter, the fibre was inserted into the vial and extraction was performed for 20 min. A desorption time of 10 min was sufficient to desorb the analytes from the fibre. Cleaning was performed automatically with the PAL system by inserting the fibre into the conditioning port at 230 °C for 20 min after each process. Analysis was performed in electron impact (EI) mode (ionisation source; 70 eV) with a scan range from *m/z* 29–400, after a solvent delay of 2.5 min. The compounds were identified by 2 approaches: (i) corresponding the RI reported in libraries (Adams, 2007; NIST 17, 2017; FFNSC 2, 2012) with the obtained RI, calculated from a mix of *n*-alkanes (C_8–C_{20} supplied by Supelco, Bellefonte, CA); (ii) comparing the obtained mass spectra with libraries (WILEY275, Adams, NIST 17 and FFNSC2) and available analytical standards.

2.6. Rheological analysis

Rheological analyses were performed using a rotational rheometer (Kinexus Lab+, Great Malvern, UK), equipped with a cone-plate (C 40/4) geometry (Chountoulesi et al., 2020). A viscosity test in the range of shear rate from 10 s^{-1} to 100 s^{-1} was performed at a constant temperature of 25 °C. The viscosity (Pa*s) of the systems was reported as the mean ± the standard deviation of the six replicates for each different extraction method, of the measured viscosity values in the analysed shear rate range.

2.7. Statistical analysis

A general overview of variability among the data determined using HPLC–MS/MS and GC–MS can be obtained by comparing the average values of RSD % of each brewing method (Fig. 4). Data on the analytes on HPLC–MS/MS and volatile compounds on GC–MS for the four types of coffee were examined by principal component analysis (PCA) using Minitab (V18.1, Minitab Inc., USA), using covariance.

3. Results and discussion

3.1. Coffee physicochemical characteristics

As reported in Table 1, it was observed that the Pure Brew method, among all four different extraction methods, led to the coffee preparation with the highest TDS value (1.73%), while French Press extraction method led to the lowest TDS value (0.90%). Pure Brew showed the highest mean value (1.71%) and the lowest standard deviation value (± 0.03%) among the four filter coffee extraction methods. On the contrary, French Press showed the lowest mean value (1.02%) and the highest standard deviation among all extraction methods (± 0.09%). TDS mean values for V60 and AeroPress were intermediate between Pure Brew and French Press (1.27% and 1.33%, respectively), with a standard deviation of ± 0.05% and ± 0.04%, respectively. The observed differences could be attributable to the fact that Pure Brew forms a compacted bed with an inflow at a lower pressure (0.15 bar) than that reached for espresso coffee (9 bar). It could at the same time promote higher concentrations of TDS, than for an instrument such as the French Press. However, TDS was particularly related to the body of the beverage (Angeloni et al., 2019). Also, in general, there was a correlation between TDS values and the particle size of the coffee powder (Frost et al., 2020). The trend related to the extraction methods (AeroPress, V60 and French Press), in fact, highlighted the lowest TDS with the French Press, which had the largest particle size, followed by V60 and AeroPress. On the contrary, for Pure Brew, a countertrend (high TDS, high particle size) was noted, which could be due to the low-pressure agitation through pulsing that is applied during extraction.

3.2. Time factor

The brewing time required was highly dependent on the brewing temperature and particle size to achieve an optimum extraction yield (Wang and Lim, 2021). Regarding the brew time (BT) (Table 1), the highest BT value was observed in French Press (BT between 3'15'' and 3'27''); meanwhile, the lowest one was observed in AeroPress (BT between 1'11'' and 1'21''). The brew time for Pure Brew (except for one value) ranged between 1'40'' and 1'43'', while for V60 it varied between 2'09'' and 2'45''. For all filter coffee extraction methods, mean and standard deviation were calculated. Pure Brew displayed the lowest value of standard deviation (± 00:01), followed by AeroPress (± 00:04), French Press (± 00:05) and V60 (± 00:12). The brewing time for Pure Brew, was an automated procedure highly reproducible (low standard deviation), in comparison to the brewing times from the other extraction methods, mainly dependent on the barista.

3.3. Extraction yield

The extraction yields of Pure Brew, V60, AeroPress and French Press are reported in Fig. 1S. The highest values of TDS were visible and confirmed from the graphics; in fact, values of PE for Pure Brew sit in the graphic area of "strong" coffee, according to the coffee brewing control chart (Figure 1SA). Instead, the value of PE for V60 falls in the "ideal" range of the chart, except for one result, which falls in the graphic area identified as "weak" (Figure 1SB). In AeroPress, values of PE fall always into "ideal", most of them being closer to "strong" values, than to "weak" ones (Figure 1SC). Finally, in French Press, three out of six values fall in the "weak" section of the chart and the remaining three values fall in the "weak – underdeveloped" graphic area (Figure 1SD). In this study, EY for Pure Brew accounted for very efficient extraction, compared to previous research (Santanatoglia et al., 2023a) where Pure Brew felt always "ideal". The changing of the TDS for Pure Brew in this study could be attributable to the change of grinder; indeed, in the previous study an Atom Brew Pro (Eureka) was used, whereas in this study the Mythos One (Victoria Arduino). In comparison to the previously mentioned study not only the grinder has changed but also the "coffee-to-water" brew ratio and the resulting final volume in the cup, which in this case led to stronger results. Furthermore, as already discussed in Section 3.1, the TDS of the French Press was the lowest and the one with the highest standard deviation; this finding agreed with the result of the extraction yields.

3.4. Bioactive compounds quantification

In this study 11 bioactive compounds were analysed through HPLC–MS/MS (Table 2). Quantitative data related to bioactive substances were expressed as concentrations (mg/ L of beverage). Our findings agree with previous studies (Angeloni et al., 2019; Santanatoglia et al., 2023a). In our study, the levels of bioactive compounds in coffee also depend on the method of preparation (Janda et al., 2020). Regarding caffeine content (Table 2), the RSDs % between the different values obtained from the six baristas were reported: for French Press 2.60%, for Pure Brew, RSD % was 4.30%, for V60 7.40% and for AeroPress 7.40%. Thus, caffeine was more consistently extracted with a low RSDs % using Pure Brew and French Press methods. Other important molecules analysed in the study were chlorogenic acids (CGA); they are known to display antioxidant and anti-inflammatory effects, with CGA being responsible for, at least to a certain extent, the association between coffee consumption and lower incidence of various

Table 2
Mean, standard deviation (SD), and RSD % of six samples were calculated by six different baristas for each filter coffee extraction method, of quantitative determination of 11 bioactive compounds expressed as mg/L detected in different filter coffee by HPLC–MS/MS.

	PUREBREW			V60			AEROPRESS			FRENCH PRESS		
Compounds	MEAN	SD	RSD%	MEAN	SD	RSD%	MEAN	SD	RSD%	MEAN	SD	RSD%
Gallic acid	0.100	± 0.000	16.3	0.100	± 0.100	54.8	0.100	± 0.000	33.4	0.100	± 0.000	32.4
Chlorogenic acid	606	± 81.0	13.3	437	± 21.7	5.10	417	± 112	27.0	399	± 104	26.0
Neochlorogenic acid	1037	± 526	50.7	993	± 111	11.2	1027	± 400	38.9	1065	± 150	14.0
Vanillic acid	2.70	± 0.400	15.1	2.30	± 0.400	18.6	1.70	± 0.700	39.2	2.00	± 0.700	32.2
Caffeic acid	5.50	± 2.80	50.2	5.10	± 0.400	7.00	5.50	± 1.60	29.2	5.40	± 1.70	31.0
(–) -Epicatechin	1.40	± 0.100	9.40	0.300	± 0.000	1.10	0.300	± 0.100	34.7	0.300	± 0.100	40.6
***p*-Coumaric acid**	0.500	± 0.100	24.0	0.400	± 0.000	4.40	0.400	± 0.200	36.3	0.400	± 0.100	30.6
Ferulic acid	1.40	± 0.000	0.700	1.00	± 0.100	10.5	1.10	± 0.400	0.500	1.00	± 0.300	28.8
3.5-Dicaffeoylquinic acid	198	± 3.50	1.80	126	± 20.8	16.5	150	± 46.9	31.2	102	± 54.5	53.4
Caffeine	1222	± 53.1	4.30	1114	± 82.6	7.40	982	± 72.9	7.40	966	± 25.4	2.60
***trans*-Cinnamic acid**	0.400	± 0.000	9.30	0.300	± 0.000	10.2	0.300	± 0.000	7.20	0.300	± 0.000	14.9
Mean RSD%			**14.4**			**11.5**			**28.8**			**27.8**

degenerative and non-degenerative diseases, in addition to high longevity (Farah and de Paula Lima, 2019). The main CGA in coffee is neochlorogenic acid (5-CQA) (Rojas-González et al., 2022), followed by chlorogenic acid (3-CQA) and 3,5-dicaffeoylquinic acid (3,5-diCQA) (Table 2). The RSD % of other phenolic and antioxidant compounds, like caffeic acid, vanillic acid and gallic acid (Erskine et al., 2022) was also reported in Table 2. Finally, for all 11 bioactive compounds, the mean, standard deviation, and RSD % were monitored. The lowest RSD % in total was found for V60 (11.5%), followed by Pure Brew (14.4%), French Press (27.8%) and AeroPress (28.8%) methods, thus showing that V60 and Pure Brew were the most reproducible filter coffee extraction methods from the point of view of bioactive compounds. The French Press system was expected to be the most reproducible, and not the V60 together with the Pure Brew, despite the latter being an automated system. French Press, being a full-immersion system (Cordoba et al., 2021), was expected to be the most reproducible as it eliminates the human factor to some extent, since the barista does not have to continuously pour the water; however, for this method of coffee preparation there was a lot of intervention at each minute which may have reduced the reproducibility (Section 2.2.4). However, the greater extraction of the bioactive compounds, other than for Pure Brew, was achieved using V60. It could also be related to the fact that French Press, being a total immersion system, requires an initial agitation operated by the barista. By assuming that the recipes of the six replicates of each extraction method for the baristas have been the same, as well as the temperature of the water, it could be assumed that the turbulence generated by baristas during the water pouring was a relevant variable affecting the coffee preparation. This study, therefore, showed that the turbulence factor in filter coffee preparation has an important impact on the reproducibility of the extraction of bioactive coffee compounds.

3.5. Volatile organic compounds quantification

The volatile profiles of the four different coffee brewing methods, each one prepared by six different baristas, were analysed. VOCs analysis was acquired in full scan mode, using a method previously described (Section 2.5). The scanned ions for each sample were calculated through their relative peak area percentage (RPA). A total of 49 volatile compounds were identified (Table 3), with a range of 68.95–87.85% of the total headspace composition. The chemical classes detected were aldehydes (8), ketones (5), furans (11), phenolic compounds (3), pyridines (3), pyrazines (11), acids (2), terpene alcohols (3) and pyrroles (3). Most of them are commonly found as VOCs in coffee (Wang et al., 2022). In this study, the means, standard deviation (SD) and RSD % of each compound between the different samples of the four different filter coffee extraction methods, prepared by six different baristas, were analysed in Table 3, and from these, a mean of total RSD % was calculated. Pure Brew showed the lowest RSD %, followed by V60, AeroPress and French Press. These results indicate that Pure Brew and V60 gave a more reproducible result in terms of the volatiles released from the coffee. In this study, some molecules were found to have a higher RPA, as already confirmed in previous studies (Santanatoglia et al., 2023a; Santanatoglia et al., 2023b). Among aldehydes, 5-methyl-2-furancarboxaldehyde was found to be present at a high concentration, with the highest mean value in AeroPress (10.7%), followed by V60 (10.4%), French Press (9.89%) and Pure Brew (9.74%) The presence of this molecule is associated with positive remarks related to sweet and almond flavours (Liu et al., 2021). 5-Methyl-2-furancarboxaldehyde showed the lowest value of RSD% in Pure Brew (3.99%), followed by French Press (8.46%), V60 (10.7%) and AeroPress (14.2%). Other important molecules were found in the aldehydes class. Furfural, which could also be included in furans, showed the highest RPA of all analytes considered in the study, contributes to the almond and burnt sugar aromas, and caramel flavour (Yu et al., 2020; Machado et al., 2022; Abouelenein et al., 2023). Furfural is the main degradation product of carbohydrates and is usually associated with nonenzymatic browning reactions, namely, the Maillard reaction, sugar degradation and caramelisation in acidic media (Pereira et al., 2011; Yu et al., 2020). Furfural was found with the highest mean value in V60 (19.5%), followed by AeroPress (18.8%), Pure Brew (17.8%) and French Press (16.5%), but it had the lowest value of RSD% in Pure Brew (4.52%), followed by AeroPress (5.51%), V60 (7.23%) and French Press (9.02%). The IARC (International Agency for Research on Cancer) has evaluated the carcinogenicity of furan and furan-containing compounds. Indeed, IARC considered furfural, a compound generated during heat-processes, such as during roasting process, as group 3 given that “the substance is not classifiable as to its carcinogenicity to humans” (Acquaticci et al., 2023; Liu et al., 2023). Two other molecules belonging to the furans class, 2-furanmethanol acetate (6.38–7.90%) and 2-furanmethanol (8.70–9.54%) had a positive RPA between analytes. These volatile compounds contribute to sweet-spicy, caramel, burnt, smokey, cherry, almond characteristics of coffee (Sarghini et al., 2019). 2-Furanmethanol acetate had the lowest RSD% in V60 (2.67%), while it was 2-furanmethanol in Pure Brew (2.98%). Pyrazines are formed in high amounts during roasting from the Maillard reaction between amino acids and sugars (Yu et al., 2021). Pyridine (0.430–1.49%) is known to have fishy and astringent characteristics; it is produced by trigonelline degradation and Maillard reactions (Heo et al., 2020; Santanatoglia et al., 2023a), being a Maillard reaction product, it is classified as group 2B (possible carcinogen) by IARC (IARC, 1995), but the levels present in coffee are mostly above the recommended levels established by Joint Expert Committee on Food Additives (JEFCA) (ADI of 0.002 mg/kg/day) (Claramunt et al., 2022). Methylpyrazine was determined to be the most abundant volatile compound from the pyrazine class in all filter coffee extraction methods. Methylpyrazine (2.16–2.91%), 2,5-dimethylpyrazine (1.81–2.77%) and 2,6-dimethylpyrazine (n.d.–2.23%) were the main volatiles of the pyrazine class, responsible for roasted, nutty, and earthy sensory characteristics of coffee (Dadalı, 2022); also, the

Table 3
Mean, standard deviation (SD), and RSD% of six samples by six different baristas for each filter coffee extraction method, of volatile compounds with their linear retention index (LRI) detected in different filter coffee extraction methods by GC–MS.

		PURE BREW			V60			AEROPRESS			FRENCH PRESS		
COMPOUNDS NAME AND CLASSES	LRI[1]	MEAN	SD	RSD%	MEAN	SD	RSD%	MEAN	SD	RSD%	MEAN	SD	RSD%
Aldehydes													
2-Methylpropanal	822	0.260	0.0200	9.44	0.420	0.120	29.1	n.d.*	n.d.*	n.d.*	0.210	0.0500	27.1
2-Methylbutanal	909	1.11	0.160	14.7	0.590	0.160	27.4	0.510	0.320	63.2	1.08	0.290	26.7
3-Methylbutanal	915	0.980	0.120	12.1	0.620	0.170	26.7	0.440	0.0900	21.4	1.32	0.270	20.5
Furfural	1449	17.7	0.800	4.52	19.5	1.41	7.23	18.7	1.03	5.51	16.5	1.48	9.02
Benzaldehyde	1502	0.650	0.170	26.3	0.610	0.110	15.6	0.690	0.140	20.6	0.790	0.310	38.3
5-Methyl, 2-furancarboxaldehyde	1531	9.74	0.390	4.00	10.4	1.11	10.7	10.7	1.52	14.2	9.89	0.840	8.46
1-Methyl-1 H-pyrrole-2-carboxaldehyde	1622	1.78	0.260	14.5	1.20	0.04	3.04	1.26	0.14	10.7	1.72	0.19	11.1
5-Ethylfurfural	1645	0.95	0.04	4.17	0.58	0.15	24.8	0.69	0.21	28.7	0.39	0.16	40.5
Ketones													
2,3-Butanedione	976	0.280	0.0500	16.3	0.200	0.0300	16.0	0.250	0.0900	38.2	0.310	0.150	47.8
2,3-Pentanedione	1055	0.940	0.0300	3.08	0.780	0.0700	9.59	0.620	0.220	35.2	0.590	0.370	62.2
1-(Acetyloxy)— 2-butanone,	1536	0.380	0.150	40.2	n.d.	n.d.	n.d.	0.640	0.160	25.4	0.340	0.120	36.8
1-(2-Furanyl)— 1-propanone,	1571	1.07	0.0100	1.15	0.830	0.0700	8.46	0.550	0.290	52.5	1.22	0.210	16.5
3-Ethyl-2-hydroxy-2-Cyclopenten-1-one	1820	1.22	0.130	11.0	1.44	0.170	11.7	n.d.	n.d.	n.d.	1.52	0.350	22.8
Furans													
2-Methylfuran	865	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.710	0.190	27.2	0.510	0.330	65.6
2-(Methoxymethyl) furan	1247	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.420	0.220	52.8	n.d.	n.d.	n.d.
Dihydro-2-methyl-3(2*H*)-furanone	1242	0.500	0.120	24.8	0.490	0.110	22.7	0.610	0.260	42.2	0.440	0.210	44.9
2-n-Butylfuran	1112	0.440	0.110	22.5	0.710	0.0800	11.4	0.700	0.200	29.0	0.560	0.310	53.4
2-Furanmethanol acetate	1529	6.84	0.580	8.42	7.90	0.210	2.67	6.38	0.860	13.5	6.54	0.240	3.66
2-Furanmethanol propanoate	1603	0.770	0.110	14.3	0.450	0.140	32.0	0.520	0.190	37.6	0.690	0.220	31.7
2,2'-Methylenebisfuran	1615	0.78	0.110	12.8	0.700	0.150	21.2	0.930	0.150	16.4	0.490	0.370	75.8
2-Furanmethanol	1619	8.71	0.260	2.98	9.54	0.450	4.71	9.24	1.19	12.9	9.28	1.63	17.6
2-(2-Furanylmethyl) — 5-methylfuran	1700	0.51	0.140	27.8	0.410	0.0500	12.0	0.810	0.110	13.5	0.720	0.280	40.6
2-Acetylfuran	1514	3.79	0.970	25.7	3.73	0.450	12.1	2.90	1.40	48.3	2.84	0.770	27.3
α-Furfuryliden-α-furylmethylamine	1210	0.320	0.140	47.1	0.430	0.0500	12.3	0.520	0.0800	14.7	0.450	0.180	39.3
Phenol													
Guaiacol	1840	0.440	0.130	30.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.240	0.0800	31.4
Phenol	1984	0.570	0.0900	15.6	0.380	0.310	82.0	0.840	0.330	39.5	0.510	0.0800	16.4
4-Vinylguaiacol	2182	1.80	0.110	6.17	1.58	0.170	10.8	2.76	0.770	27.8	1.62	0.290	17.7
Pyridine													
Pyridine	1185	1.49	0.110	7.64	0.890	0.0600	6.89	0.430	0.0900	20.9	0.770	0.170	22.3
N-Acetyl-4(H)-pyridine	1582	0.380	0.330	88.0	0.320	0.0700	20.1	0.370	0.0600	16.8	0.570	0.190	32.6
2-Acetylpyridine	1582	0.310	0.0900	30.3	0.0800	0.0800	88.4	n.d.	n.d.	n.d.	0.330	0.0800	23.1
Pyrazine													
Methylpyrazine	1269	2.91	0.0600	2.23	2.75	0.170	6.17	2.57	0.190	7.49	2.16	0.110	5.11
2,5-Dimethylpyrazine	1310	2.77	0.250	9.17	1.81	0.380	20.8	2.24	0.130	5.78	1.89	0.420	22.1
2,6-Dimethylpyrazine	1321	2.23	0.210	9.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.05	0.0200	1.01
2,3-Dimethylpyrazine	1343	0.320	0.0600	18.5	0.430	0.0800	17.3	0.330	0.130	40.4	0.360	0.0600	17.6
2-Ethyl-6-methylpyrazine	1320	1.55	0.170	11.2	1.81	0.180	9.74	1.61	0.160	10.0	1.80	0.100	5.40
2-Ethyl-5-methylpyrazine	1314	n.d.	n.d.	n.d.	1.57	0.190	12.1	1.42	0.0800	5.81	1.59	0.140	8.84
2-Ethyl-3-methylpyrazine	1363	1.62	0.0900	5.45	1.56	0.110	7.16	0.630	0.210	33.0	1.58	0.120	7.35
2,6-Diethylpyrazine	1436	0.510	0.210	40.2	0.390	0.0600	14.5	0.270	0.0600	20.7	0.510	0.120	23.1
3-Ethyl-2,5-dimethylpyrazine	1449	1.51	0.0400	2.31	1.47	0.0900	6.32	1.45	0.0600	4.32	1.56	0.180	11.8
2-Ethyl-3,5-dimethylpyrazine	1449	0.830	0.0100	1.70	1.62	0.180	10.9	1.79	0.190	10.8	0.550	0.0900	16.3
3,5-Diethyl-2-methylpyrazine	1500	0.630	0.0500	7.91	0.730	0.0500	7.37	0.480	0.0600	13.4	0.610	0.240	39.1
Acids													
Isovaleric acid	1665	0.700	0.200	24.2	0.320	0.0600	18.3	n.d.	n.d.	n.d.	0.290	0.100	34.4
Nonanoic acid	2147	n.d.	n.d.	n.d.	0.350	0.0700	20.3	n.d.	n.d.	n.d.	0.180	0.0600	34.8
Terpene Alchols													

(*continued on next page*)

Table 3 (*continued*)

COMPOUNDS NAME AND CLASSES	LRI[1]	PURE BREW MEAN	PURE BREW SD	PURE BREW RSD%	V60 MEAN	V60 SD	V60 RSD%	AEROPRESS MEAN	AEROPRESS SD	AEROPRESS RSD%	FRENCH PRESS MEAN	FRENCH PRESS SD	FRENCH PRESS RSD%
Linalool	1794	0.450	0.110	24.5	0.450	0.170	38.1	0.590	0.110	18.9	0.440	0.120	27.7
***cis*-Linalool oxide (furan)**	1723	0.380	0.210	54.3	0.310	0.0800	26.0	0.440	0.120	27.4	0.350	0.0900	26.8
***trans*-Linalool oxide (furanoid)**	1723	0.700	0.110	15.2	0.670	0.170	25.8	0.540	0.250	45.4	0.480	0.140	29.4
Pyrrole													
1-Furfurylpyrrole	1830	1.78	0.0400	2.51	1.63	0.250	15.18	1.85	0.290	15.9	0.310	0.110	35.5
2-Pyrrolealdehyde	2008	1.27	0.210	16.3	1.57	0.330	21.7	1.46	0.220	14.99	1.22	0.0700	5.54
2-Acetylpyrrole	1949	1.79	0.0600	3.57	0.760	0.350	46.2	1.27	0.110	9.00	0.660	0.0600	9.43
Mean RSD%				**17.2**			**19.4**			**24.1**			**26.5**

n.d.* : not detected (peak area value below 5E + 04).
[1] Experimental linear retention index.

pyrazines showed the lowest RSD% in Pure Brew filter coffee extraction methods. Finally, pyrroles were formed through the thermal process and pyrolysis of trigonelline. Those compounds have aromas of burnt-like, sweet and smoky (Lee et al., 2017; Dadalı, 2022). Overall, it was possible to confirm that the molecules most found in this type of coffee were associated with notes of sweetness. Moreover, the most reproducible extraction method with the lowest calculated RSD%, was Pure Brew (17.2%), followed by V60 (19.4%), AeroPress (24.1%) and French Press (26.5%). On the other hand, considering the aromatic notes associated with the VOCs, the V60 samples were connected to sweet, earthy and buttery oil notes, results being quite similar to AeroPress, which was associated with flowery and spicy notes, while Pure Brew samples VOCs were mostly associated with caramel, nutty and chocolate notes, quite similar to French Press. The obtained results led us to formulate the hypothesis that the filter material and shape can influence the volatile profile of filter coffee samples.

3.6. Rheological analysis

Rheology is a technique commonly employed for the characterisation of the consistency of several liquids (Tabilo-Munizaga and Barbosa-Cánovas, 2005). Indeed, rheological analyses have often been used for analysing the texture of foods as well as the consistency of different types of beverages as foam coffee (Angeloni et al., 2020a) or wine (Feng et al., 2019). Studies reporting the viscosity of espresso coffee can be found in the literature (Salamanca et al., 2017), mostly focusing on the foam (Angeloni et al., 2020a), but the viscosity of filter coffee has not been sufficiently investigated. In Fig. 2A, each column represents the average viscosity values calculated for six filter coffee samples obtained from the different extraction methods. The average viscosity values of coffee samples prepared using the analysed brewing methods are similar, ranging from 0.0011 (Pa*s) to 0.0013 (Pa*s). It was possible to observe differences in the RSD% of the samples (Fig. 2B), which can be related to the variability due to the coffee preparation from the different baristas, despite, these low viscosity values being irrelevant from a practical point of view. In terms of viscosity, Pure Brew possessed a similar viscosity to the French Press, since they were both obtained with mechanical filtration without a paper filter unlike the other two preparation methods (V60 and AeroPress). By comparing the methods using mechanical filtration, Pure Brew provides a more taste-pleasant and less dusted coffee than French Press. This can be ascribed to differences in the mechanical filtration processes. For French Press, a single mechanical filtration through a filter with a larger mesh is applied, leading to coffee with a higher sediment level than Pure Brew. On the other side, in order to minimize the presence of "fines" (solid particles) and have a cleaner coffee cup, the technology has been implemented for Pure Brew with a double mesh with double filtration.

3.7. Statistical analysis of variance

A general overview concerning how the different brewing methodologies affect the reproducibility of the prepared coffees is provided by comparing the average variability (expressed as RSD %) of all the analytes determined both with HPLC–MS/MS and GC–MS analysis (Fig. 3A and B, respectively). Fig. 3 indicates that the variability derived from the UHPLC–MS/MS analysis was higher (between around 10% and 30%) than that obtained for volatile compounds (between around 5% and 8%). However, independently of the instrumental analyses considered, the average variability for Pure Brew and V60 was lower than the other brewing methods, AeroPress and French Press, although such differences were statistically significant only for the bioactive compounds determined by UHPLC analysis (Kruskal-Wallis test). A more detailed

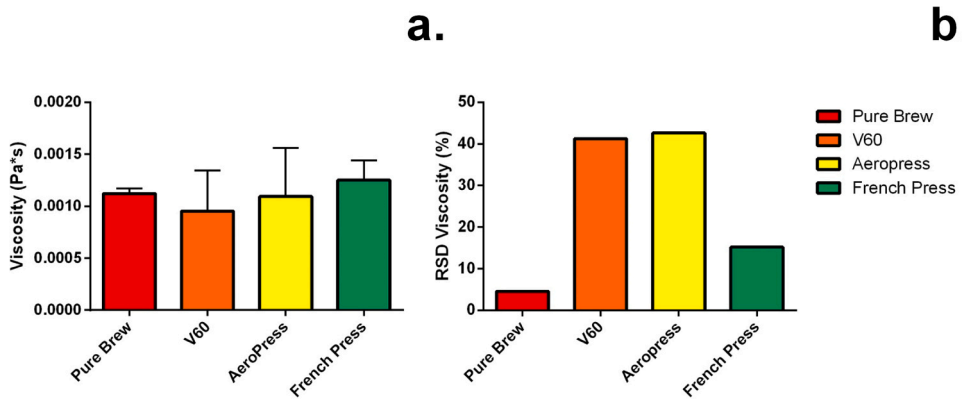

Fig. 2. Fig. 2A Viscosity (Pa*s) of coffee samples from different extraction methods. Each column represents the mean ± standard deviation of six independent samples. Fig. 2B RSD% of viscosity (Pa*s) of coffee samples from different extraction methods.

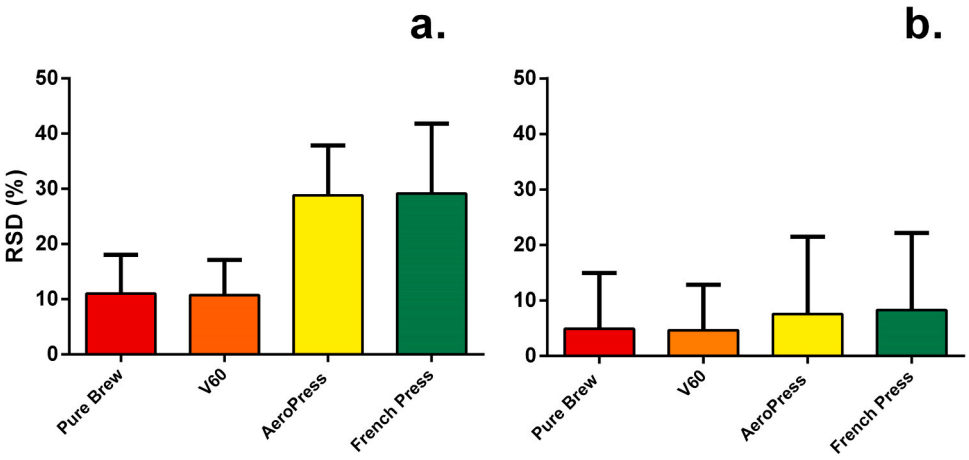

Fig. 3. The histogram created with the RSD% data, among the six preparations made by different baristas for each of the four extraction methods considered. Fig. 3A shows the histogram generated with the HPLC-MS/MS data. Fig. 3B presents the ones created with the GC-MS data. The variability of GC-MS data was lower than that of HPLC-MS/MS.

evaluation of the main sources of variabilities can be obtained from the PCA analysis (Fig. 4A and B) of the RSD % values determined for all the analytes. The score plot of the variability for the compounds determined with UHPLC is reported in Fig. 4A. The methods providing less total variability, Pure Brew and V60, are both characterized by low PC1 values (PC1 explained 83% of the variability). The differences in terms of single compounds variabilities can be observed from the loading plot (Fig. 4B). Specifically, it can be observed that the concentrations of 3,5-diCQA, 3-CQA, 5-CQA and *p*-coumaric acid are more consistent for the Pure Brew and V60 in comparison with the samples obtained with the other two brewing methods. Pure Brew and V60 differentiate in terms of PC2 (even if it describes only the 12% of the variability), with the first one having a higher variability than *p*-coumaric acid and the second one than 3,5-diCQA. Fig. 4C and D display the PCA results of volatile analytes determined using PCA GC–MS analysis. As already seen for the analytes determined from UHPLC and for those determined from GC–MS, the brewing methods Pure Brew and V60 assure higher consistency. Both these samples are located at low values of PC1 (58% of explained variability) and PC2 (32% of explained variability) in the score plot (Fig. 4C), meaning that they possess the lowest RSD values for most of the quantified analytes, and particularly for dihydro-2-methyl-3 (2*H*)-furanone, a-Furfurylden-a-fury methylamine and 2-(2-furanylmethyl)− 5-methylfuran.

4. Conclusion

In conclusion, it has emerged from this work that water pouring through the filter plays a very important role in the extraction of filter coffees. This has been confirmed by the greater reproducibility obtained from the V60 rather than the French Press, by chemical analysis. The results obtained are unexpected since both French Press and AeroPress involved applied pressure, respectively less and more, of the barista during the coffee preparation, in addition to the turbulence generated by pouring water on ground coffee, which is common to all extraction procedures. Therefore, it was possible to state that these two human factors, namely turbulence and the pressure generated by baristas, were able to alter the extraction of coffee and its consequent TDS, extraction yields and the amount of final compounds in the cup. There was no work in the literature dealing with the reproducibility of filter coffees produced by different baristas, especially considering all parameters

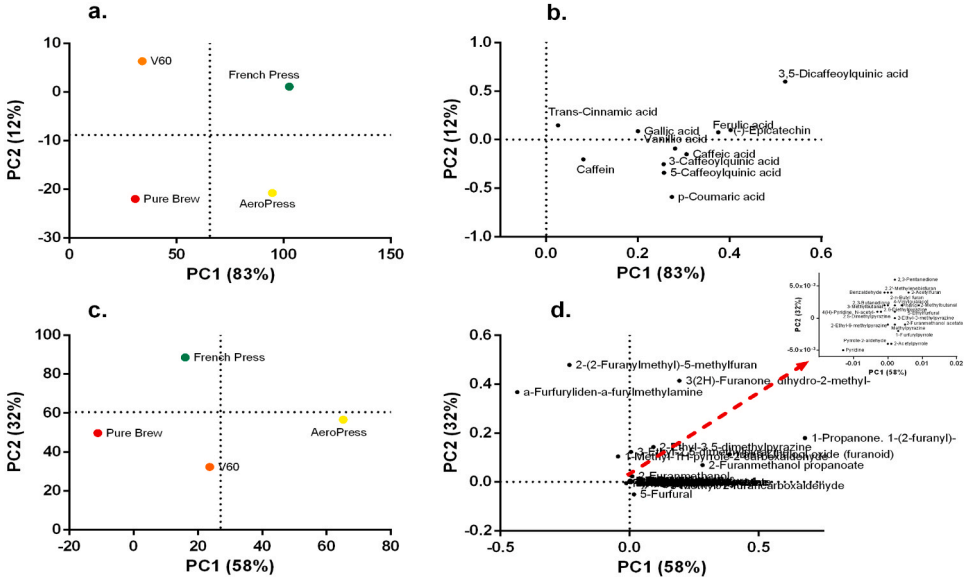

Fig. 4. The PCA was created with RSD% data, among the six preparations made by different baristas for each of the four extraction methods considered. Fig. 4A and B show the results generated with the HPLC-MS/MS data. Fig. 4C and D present the ones created with the GC-MS data.

analysed in this study: TDS, extraction yields, amount of bioactive and volatile compounds and rheological properties. The turbulence and the pressure applied by baristas during extraction proved to be key variables from the point of view of the reproducibility of filter coffee extraction. Therefore, this study provided useful information intended for baristas, who could learn from it which are the main factors to take into account during preparation to increase the reproducibility of their beverages. In summary, this work leaves open room for a yet unexplored field, which is the shape of the coffee filter. Indeed, the main similarity between two extraction technologies as Pure Brew and V60 was the shape of the filter which was cone-shaped in both systems, compared to the French press and AeroPress that employ a flat-shape coffee filter.

CRediT authorship contribution statement

Agnese Santanatoglia: Conceptualization, Methodology, Formal analysis, Writing – original draft. **Marco Cespi:** Data curation, Supervision. **Diego Romano Perinelli:** Data curation, Formal analysis, Validation. **Lauro Fioretti:** Conceptualization, Data curation, Supervision. **Gianni Sagratini:** Methodology. **Sauro Vittori:** Resources, Supervision. **Giovanni C**aprioli: Supervision, Writing – review & editing.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2023.105698.

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