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Chemical and Sensory Differences Among Coffee Beverages Brewed by Traditional Moka, Espresso, and Kamira, a Novel Italian Brewing Device

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Abstract

The chemical composition and sensory profile of coffee are influenced by brewing method, namely extraction pressure, temperature, contact time, and equipment. This study compared coffee prepared with a traditional moka pot, a conventional espresso machine, and a novel Italian device (Kamira). Volatile compounds were analyzed by headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography–mass spectrometry (GC–MS), leading to the determination of furan (34–42%), pyrrole (4–10%), and pyrazine (13–14%) derivatives. The most abundant fatty acids were palmitic (36–37%), linoleic (40%), and oleic (11%) acids. Physicochemical parameters (total solids, pH, and refractive index) were also measured. Caffeine and chlorogenic acids were quantified by liquid chromatography (HPLC). Differences in chlorogenic acids and volatile compounds were associated with variations in bitterness, acidity, astringency, and aroma intensity. Finally, a trained panel performed sensory evaluation to evaluate the olfactory and flavor attributes of the three types of coffee brews. Significant differences emerged among brewing systems. Espresso showed the highest caffeine content (55.3 $\pm$ 4.1 mg/100 g) and total solids (2.61 $\pm$ 0.11 g/100 g), together with a stable crema and intense sensory attributes. Moka coffee exhibited a rich aromatic profile but limited crema. The Kamira device produced an abundant crema and a chemical profile partially comparable to espresso. These findings confirm that brewing technology markedly affects coffee composition and sensory perception.

Keywords: coffee brewing; coffee maker; SPME; sensory; caffeine; Kamira

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Academic Editor: Javier Saurina

Received: 31 March 2026
Revised: 28 May 2026
Accepted: 30 May 2026
Published: 1 June 2026

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1. Introduction

Coffee is one of the most widely consumed beverages worldwide, and its sensory quality and chemical composition are strongly influenced by the coffee origin—variety, post-harvest processing, geographical site, and roasting degree—and by the brewing method. Differences in extraction pressure, temperature, contact time, and equipment design play a crucial role in determining the concentration of soluble compounds, the formation of crema, and the overall sensory profile of the final beverage. The mechanisms underlying the effect of the high extraction temperature and pressure on the resulting liquid have been deeply

investigated elsewhere with respect to substances of medicine and food homology [1]. Consequently, comparing brewing technologies is essential to better understand how process variables affect both chemical characteristics and consumer perception [2]. Among domestic coffee preparation methods, the traditional moka pot and the espresso machine represent two distinct extraction approaches. Moka coffee is typically obtained at moderate pressures and temperatures, producing a beverage with a rich aroma but limited crema formation, whereas espresso is extracted under high pressure, resulting in a concentrated drink characterized by a stable crema and intense sensory attributes. In recent years, alternative brewing systems have been developed, especially single-serve coffee systems, trying to find a compromise between these two methods, combining simplicity of use with espresso-like sensory features.

The brewing method is a fundamental parameter correlated to the chemical composition and the physical properties, hence, to the quality of a cup of coffee. Numerous are the brewing systems present in the market that can be categorized as traditional and modern. Generally, traditional coffee-making systems are linked to the habits of a geographical area, going from the most famous Italian moka and espresso to the Turkish or Americano brews, among others. In the modern systems, coffee powder is primarily contained within pods or capsules, designed for specific single-serve coffee machines. The popularity of these coffee machines is certainly linked to their greater convenience, which makes them suitable not only for home use but also for workplaces, as well as to the wide variety of coffee flavors available.

Coffee scientists have investigated to what extent the brewing technique affects the caffeine content [3], basically concluding that espresso and moka are those richest in caffeine. Recently, eighteen types of coffee differing in regard to species, roasting degree, and geographical origin were analyzed to determine the influence of coffee brewing on the contents of caffeine, phenolic compounds, and minerals [4]: the results showed that brewing method and coffee species significantly affect the chemical profile. Another study found that brewing methods significantly influence the levels of the coffee diterpenes cafestol and kahweol, with unfiltered methods producing much higher concentrations than paper-filtered methods, highlighting the key role of filtration, pressure, and grind size in determining their presence in the final cup [5]. Also, coffee-brewing methods influence the total phenolic content and antioxidant capacity of coffee, with capsule coffee providing higher phenolic levels and leading to greater antioxidant status in consumers compared to French-press coffee [6].

Among the phenolic constituents of coffee exerting antioxidant activity are chlorogenic acids, including caffeoylquinic acids (CQAs). Their presence, which confers the acidic, bitter, and astringent attributes to coffee flavor, has been correlated to pressurized brewing methods, particularly espresso and moka [7]. In this scenario, the Kamira coffee maker shows up as a novel device designed to operate through a brewing procedure similar to that of a traditional moka pot, while promoting the formation of a creamy coffee foam reminiscent of espresso [8]. However, there is no scientific information available regarding the chemical and sensory properties of coffee beverages produced using this system. Therefore, the aim of this study was to compare the chemical composition, and the chemico-physical and sensory characteristics of coffee beverages prepared using a traditional moka pot, a conventional espresso machine, and the Kamira coffee maker. In particular, by integrating analytical and sensory analyses, this work aims to evaluate the qualitative profile of the coffee brew produced with the Kamira coffee maker, finally drawing an estimate of the advantages and disadvantages derived from its use with respect to the espresso and moka coffee makers. Additionally, from a literature data overview, it emerges that most scientific works focused on the correlation between coffee quality and brewing

methods date back to a decade ago, therefore giving added value to this study in terms of updating and integrating the available data.

2. Materials and Methods

2.1. Samples and Reagents

2.1.1. Coffee Brews

For the preparation of coffee beverages, a mixture of roasted and ground coffee of the Arabica and Robusta varieties was used, which can be found commercially under the name of "Lavazza crema e gusto" (Lavazza, Turin, Italy). For all brewing methods, the same bottled water (Fontenoce, Cosenza, Italy) was used throughout the study. For moka coffee brew, a Moka Express 2 cups pot, 90 mL volume, aluminum made, produced by Bialetti (Brescia, Italy), was used. About 12 g of ground coffee was placed in the moka pot basket without pressing; an induction cooker was employed. Espresso coffee was prepared by using a semi-automatic machine called "Dedica" (De Longhi, Treviso, Italy). The nominal pressure of the pump was 15 bar. The weight of the coffee ground was about 7 g, and it was pressed before obtaining a volume of about 25 mL of beverage in about 10 s. The Kamira coffee was produced through the official coffee maker (Kamira S.r.l., Messina, Italy) that consists of a modified moka pot, as shown in Figure S1 of the Supplementary Materials [8]. This apparatus exploits a stovetop fed by either gas or induction. Amount of water and portafilter are similar to those of the espresso machine, while the procedure of extraction resembles that of the moka pot. The pathways of water and pressure are controlled by a lever. About 8 g of ground coffee was necessary to obtain 20 mL of coffee brew.

For each brewing method, multiple independent brew preparations were performed under identical operating conditions and pooled until a final volume of approximately 400 mL was obtained. The exact number of individual preparations depended on the beverage yield of each brewing system. This approach was adopted to reduce cup-to-cup variability and to obtain a representative composite sample for chemical analyses.

The aliquots intended for dry fraction analysis were frozen at −80 °C and then freeze-dried to constant weight using the Alpha 2-4 LD plus freeze-dryer (Christ, Osterode am Harz, Germany). The dried material was stored in airtight containers protected from light and humidity until analysis. To allow for a more meaningful comparison among beverages, selected analytes were also normalized on a beverage basis using the experimentally determined total solids of each brew. Because the three brewing systems differed in coffee dose and beverage yield per preparation, the chemical composition of the freeze-dried material was interpreted as representative of the extracted dry fraction of each brewing method. To allow for a more meaningful comparison among beverages, selected analytes were also normalized on a beverage basis using the experimentally determined total solids of each brew.

2.1.2. Reagents and Chemicals

All chemicals and solvents used were of analytical or chromatographic grade. Methanol, chloroform, n-hexane, acetonitrile, ethyl acetate, formic acid, diethyl ether, and heptane were purchased from Merck (Darmstadt, Germany). Potassium hydroxide (KOH), sodium chloride (NaCl), and sodium hydroxide (NaOH) were obtained from VWR International (Milan, Italy). Ultrapure water, standard solutions of fatty acid methyl esters (FAME mix), caffeine (99%), chlorogenic acid (≥95%), cafestol (≥98%), kahweol (≥90%), α-tocopherol (95%), γ-tocopherol (≥96%), and δ-tocopherol (≥90%) were purchased from Merck/Sigma-Aldrich (St. Louis, MO, USA). Nylon, PTFE, and PVDF membrane filters (0.22 µm) were obtained from VWR International. Calibration buffers (pH 4.00 and 7.00) used for pH-meter calibration were purchased from Carlo Erba Reagents (Milan, Italy). All

glassware and consumables used for sample preparation and chromatographic analysis were of analytical grade. The freeze dryer was an Alpha 2-4 LD plus by Christ (Osterode am Harz, Germany).

2.2. Chemico-Physical Parameters

2.2.1. pH and Total Titratable Acidity

The pH and total titratable acidity (TTA) of beverages made using a traditional moka pot, a home espresso machine, and a Kamira device were determined directly on the liquid matrix, immediately after preparation.

The pH was measured using a digital pH meter Eutech Instruments PC 700, supplied by ThermoFisher Scientific (Milan, Italy) and previously calibrated with standard buffer solutions at pH 4.00 and 7.00. Measurements were taken at room temperature (20–25 °C), and each sample was analyzed in triplicate.

The total titratable acidity was determined by potentiometric titration with a standardized 0.1 N NaOH solution, following a previously published method [9]. Briefly, a 40 mL aliquot of each sample was titrated with 0.1 N NaOH to a pH of 6.5 to determine the TTA of each coffee. The volume of NaOH consumed was recorded, and the acidity was expressed in milliequivalents of base used per liter (meq/L), according to the following equation:

$$\text{meq NaOH/L} = \frac{\text{mL NaOH} \times \text{N} \times 1000}{\text{mL sample}}$$

All determinations were performed in triplicate, and the results are reported as mean ± standard deviation.

2.2.2. Refractive Index

The refractive index was measured using a digital refractometer (Mettler Toledo, Greifensee, Switzerland, XS DBR 95) calibrated with distilled water. Measurements were performed at 20 °C, and the results were expressed as the mean of three independent determinations for each extraction method.

2.2.3. Total Dissolved Solids and Total Lipids

To determine total dissolved solids (TDS), 10 g of coffee extract was dried at 105 °C to constant weight (less than ±0.5 mg). Total lipids were extracted according to the Folch method [10]. Briefly, 4 g of lyophilized sample was transferred to 50 mL Falcon tubes and extracted with 40 mL of a chloroform/methanol mixture (2:1, v/v). The suspension was homogenized and then ultrasonicated (model LBS1, Falc Instruments S.r.l., Treviglio, Bergamo, Italy) for 30 min at 20 kHz and 0.4 W·mL^{-1} to promote complete extraction of the lipid fraction. At the end of the treatment, 5 mL of aqueous saline (0.73% NaCl, w/v) was added to promote phase separation. The system was shaken vigorously for 1 min and then centrifuged at 6000 rpm for 10 min. The lower chloroform phase, containing the lipids, was carefully recovered and transferred to a previously weighed flask. The solvent was removed by evaporation under pressure using a rotatory evaporator (Vacuum Controller V-855, Büchi Labortechnik AG, Flawil, Switzerland). The amount of total lipids was determined gravimetrically.

2.3. SPME-GC Analysis

The volatile composition of coffee beverages was determined by means of Headspace Solid-Phase Microextraction (HS-SPME) as the sampling technique, coupled with GC-MS and GC-FID for the separation of components. The fiber coating was a triple-phase 50/30 µm DVB/Car/PDMS provided by Supelco/Merck (Darmstadt, Germany). Imme-

diately after preparation, an aliquot of 5 mL of coffee beverage was placed in a 10 mL volume headspace vial, conditioned at 50 °C for 10 min, and extracted through fiber exposure for 15 min at 50 °C, under agitation (300 rpm). Separation and quantification of adsorbed analytes took place in a GC-2010 system (Shimadzu, Kyoto, Japan) equipped with an Omegawax-250 capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) supplied by Merck (Darmstadt, Germany). Injection temperature, 220 °C; mode, splitless with 1 min sampling time, then split ratio 1:50. Inlet pressure, 68.1 KPa; linear velocity, 20.8 cm·s^{-1}. Oven program was from 50 °C (held 1 min) to 250 °C (held 5 min) at 4 °C·min^{-1} to 270 °C (held 5 min) at 10 °C·min^{-1}. FID detector temperature, 280 °C; gases, H_2 (40 mL·min^{-1}); He (80 mL·min^{-1}); air (400 mL·min^{-1}). Data handling was by GCsolution software (version 2.0). Qualitative analysis was carried out by means of a GCMS-TQ8030 system (Shimadzu, Kyoto, Japan) under the same experimental conditions as reported above, with the exception of mass spectrometric parameters: ion source, 220 °C; interface temperature, 200 °C; electron multiplier voltage, 1.0 kV; mass range, 40–400 amu. Data handling was by GCMSsolution software (version 2.4). Mass spectral databases for qualitative analysis were FFNSC 2 (Wiley), Adams 4th edition (Allured), and NIST11, each provided with Retention Index parameters. Experimental Retention Indices were measured by extracting under optimized HS-SPME conditions a lab-made mixture of n-paraffins ranging from n-hexane to n-hexadecane (range of concentration, 2.5–10.0 ppm). Each sample was run in triplicate.

2.4. Fatty Acids

The fatty acid profile was determined from the lipid extracts according to the AOAC method 996.06. The dried lipid fraction was subjected to cold esterification by adding 2 mL of heptane and 200 µL of methanolic potassium hydroxide (KOH) solution. The mixture was stirred vigorously at room temperature until the fatty acid methyl esters (FAMEs) were completely formed. After phase separation, the upper heptane fraction containing the FAMEs was recovered for chromatographic analysis. Then, 1 µL of each extract was analyzed by means of a gas chromatograph (GC) (Dani Master GC1000, Milan, Italy) equipped with a split/splitless injector and a flame ionization detector (FID). A Supelco SLB-IL100 capillary column, 60 m × 0.25 mm i.d., 0.20 µm film thickness (Supelco-Merck, St. Louis, MO, USA), was used. The following chromatographic conditions were used: column oven temperature from 165 °C to 210 °C (10 min hold) at 2 °C·min^{-1}; injector and detector temperature, 250 °C; and helium at a linear velocity of 30 cm/s (constant). The injection volume was 1.0 µL, with a split ratio of 1:100. Data acquisition and management were performed using Clarity Chromatography v4.0.2 software. All samples were analyzed in triplicate. FAMEs of nutritional interest were identified by direct comparison with the reference retention times of the compounds present in the standard mixture. The relative percentage of each FAME was calculated based on the total peak area of the chromatogram. The precision of the method was evaluated in terms of RSD% by injecting five replicates of the sample [11].

2.5. HPLC Analysis

2.5.1. Cafestol and Kahweol

The diterpenes of freeze-dried coffee brew samples were determined as previously described [12]. Briefly, 200 mg of freeze-dried sample was weighed into screw-capped glass tubes and resuspended in 7.5 mL of a 2:1, *v*/*v* methanol/water solution. Then, 3.0 g of solid potassium hydroxide (KOH) was added to the suspension, and the mixture was subjected to direct saponification in a thermostatic bath at 80 °C for 60 min. The saponified solution was subjected to liquid–liquid extraction using diethyl ether (repeated 4 times) and

centrifugation (4000 rpm, 10 min). The organic phase was then collected and dried using a rotatory evaporator. The resulting residue was reconstituted in 2.5 mL of acetonitrile, filtered through 0.22 µm PTFE membranes, and transferred to vials for chromatographic analysis. The dried extracts were stored at −22 °C until analysis, and the diterpene content was expressed as mg/100 g of sample after applying the dilution factor.

Afterward, chromatographic determination was performed using an Agilent 1260 Infinity HPLC system (Santa Clara, CA, USA) equipped with a DAD detector and an RP-C18 column (250 × 4 mm, 5 µm). Elution occurred isocratically using a mobile phase consisting of acetonitrile and water (55:45, v/v) at a flow rate of 0.8 mL min^{-1}. The injection volume was 20 µL, and the detection wavelengths were 225 nm for cafestol and 290 nm for kahweol. Compound identification was performed by comparing retention times and UV spectra with those of pure analytical standards. Quantification was performed using external calibration constructed from standard solutions of the two diterpenes in the appropriate concentration range. Results were expressed as mg/100 g of sample, and all determinations were performed at least in triplicate.

2.5.2. Tocopherols

Tocopherol extraction was performed from previously freeze-dried coffee samples. Briefly, 2 g of freeze-dried sample was transferred to amber tubes and mixed with 4 mL of n-hexane to promote solubilization of the lipid fraction. After vigorous shaking, 2 mL of methanolic potassium hydroxide (KOH) solution was added to promote matrix saponification. The mixture was then shaken and centrifuged for 10 min at 4000× g at 4 °C. The resulting supernatant was filtered through a 0.2 µm nylon membrane and transferred to amber vials for chromatographic analysis [13].

Following this, tocopherols were determined by means of a Prominence UFLC system equipped with a fluorescence detector (RF-20A) provided by Shimadzu, Milan, Italy. Chromatographic separation was performed on a LiChrosorb Si 60 column (5 µm, 4.6 mm × 250 mm; Merck, Darmstadt, Germany) protected by a LiChroCART 4-4 guard column packed with the same stationary phase. The mobile phase consisted of a mixture of n-hexane/ethyl acetate (90:10, v/v), eluted isocratically at a flow rate of 0.8 mL min^{-1}. The injection volume was set at 20 µL, and the column temperature was maintained at 40 °C.

Detection was performed by fluorescence with excitation wavelengths at 295 nm and emission at 330 nm. Chromatographic data acquisition and processing were performed using LabSolutions software (version 5.10.153, Shimadzu, Kyoto, Japan). Compound identification was performed by comparing retention times with those of commercial α-, γ-, and δ-tocopherol standards analyzed under the same chromatographic conditions. Quantification was performed by external calibration, using six-point calibration curves for each analyte. Total tocopherol content was calculated as the sum of the individual isoforms determined. All determinations were performed in triplicate.

2.5.3. Chlorogenic Acids and Caffeine

For each sample, 10 mg of lyophilized product was weighed into a 15 mL tube and suspended in 10 mL of ultrapure water containing 0.1% (v/v) formic acid. The suspension was vortexed for 1 min, sonicated for 10 min at room temperature, and then centrifuged for 10 min at 6000 rpm. The supernatant was filtered through a 0.22 µm membrane (PVDF or PTFE) directly into HPLC vials. The determinations were performed in triplicate (three independent preparations). Chromatographic analysis was performed on an Agilent 1260 Infinity HPLC system (Santa Clara, CA, USA) equipped with a DAD detector and a Zorbax Eclipse Plus C18 column (100 mm × 2.1 mm internal diameter, 1.8 µm particle size) maintained at 20 °C. The separation was performed using the following:

- Mobile phase A: Water + 0.1% (*v*/*v*) formic acid.
- Mobile phase B: Acetonitrile.

Gradient elution was performed according to a previous report: 0–1 min, 5% B; 1–10 min, 25% B; and 10–20 min, 50% B [2]. The flow rate was set to 0.35 mL/min, and the injection volume was 3 µL. Detection wavelengths: 325 nm for chlorogenic acids and 272 nm for caffeine. Peak assignment occurred by comparing retention times and UV spectra with those of analytical standards. At the end of each run, the column was returned to the initial conditions (5% B) and re-equilibrated until the baseline stabilized before the next injection. Analyte concentrations were normalized on a beverage basis. This conversion was consistent with both the experimentally determined total solids of each brew and the actual freeze-dried yields obtained from the pooled 400 mL samples. For physicochemical and chromatographic determinations, the reported values derive from analytical triplicates performed on pooled brew samples representative of each brewing method.

2.6. Sensory Panel

2.6.1. Evaluation Form and Descriptors

The coffee sensory evaluation form was structured into four sections, each including predefined descriptors with operational definitions. Visual evaluation considered crema color, crema persistence, and crema texture. Olfactory evaluation was based on aroma intensity and aroma quality. Gustatory evaluation comprised sweetness, acidity, bitterness, body, and aftertaste. Harmony, clean cup, and repeatability were attributes of overall balance. Descriptor definitions are reported in Table 1.

Table 1. Sensory descriptors and operational definitions used for coffee evaluation.

Descriptor	Description
Crema color	Ranging from light hazelnut to dark brown; uniform and free of bubbles.
Crema persistence	Duration and stability/compactness of the crema over time.
Crema texture	Even appearance and texture; no spotting, streaks, or burnt patches.
Aroma intensity	Perceived strength on direct sniffing (orthonasal perception).
Aroma quality	Pleasantness and aromatic complexity.
Sweetness	Sweetness balance; absence of excessive bitter notes.
Acidity	Freshness and liveliness, typically associated with Arabica coffees.
Bitterness	Balanced bitterness, not harsh or unpleasant.
Body	Tactile mouthfeel and perceived viscosity.
Aftertaste	Duration and pleasantness of the lingering finish.
Harmony	Integration among sweetness, acidity, body, and aroma.
Clean cup	Absence of defects or unpleasant residual notes.
Repeatability	Consistency across repeated trials.

2.6.2. Panel Composition and Sample Serving

The sensory evaluation was performed by a panel of 10 assessors using a structured descriptive approach, in accordance with established sensory methodology for assessor training and sensory profiling [14,15]. The assessors had previous experience in sensory-evaluation activities and were familiarized with the descriptor list and the 0–10 intensity scale before sample assessment. Prior to data collection, a short calibration session was carried out to harmonize the interpretation of the descriptors, with particular attention paid to crema-related attributes, aroma descriptors, taste attributes, and overall balance

descriptors. The descriptor list was defined a priori to cover the main visual, olfactory, gustatory, and overall balance attributes expected to discriminate coffee beverages prepared using different brewing systems. The three brewing methods were evaluated in duplicate, resulting in six coded samples: 1A, 1B, 2A, 2B, 3A, and 3B. All six samples were evaluated within the same sensory session. Duplicate evaluations were presented as separate coded samples. Samples were served using coded identifiers, and assessors were not informed of the brewing method corresponding to each code during the evaluation. The serving order was randomized across assessors to reduce order and carry-over effects. Water and unsalted crackers were provided as palate cleansers between samples. Sensory scores were recorded on a structured 0–10 intensity scale, where 0 indicated "not perceptible" and 10 indicated the maximum perceived intensity for each descriptor. The use of 0 was retained because some attributes, particularly crema-related descriptors in moka coffee, could be absent or nearly absent.

2.6.3. Statistical Analysis

Sensory data were screened for completeness and plausibility by means of range checks and consistency across duplicate evaluations. To avoid treating technical duplicates as independent observations, replicate A and replicate B were aggregated within each assessor, method, and descriptor using the median value. Descriptor distributions were summarized using descriptive statistics, including mean, standard deviation (SD), median, interquartile range (IQR), minimum, and maximum. Agreement between duplicate evaluations was additionally examined through absolute differences between replicates and intraclass correlation coefficients (ICCs). Since the same assessors evaluated all brewing methods and the sensory scores were measured on a discrete 0–10 scale, global between-method differences for each descriptor were assessed using the Friedman test for repeated measures [16]. When the global test was significant, paired Wilcoxon signed-rank tests were used for post hoc comparisons, with Holm adjustment applied to control for multiple testing [17]. Multivariate relationships among brewing methods and sensory descriptors were explored by principal component analysis (PCA) on aggregated sensory profiles after variable standardization [18]. All sensory and volatile-profile statistical analyses and graphical visualizations were performed in R [19].

2.7. Statistical Handling of Volatiles

Volatile-profile data, expressed as mean ± standard deviation of three analytical replicates, were preprocessed before multivariate analysis. A logarithmic transformation (log10) was applied to reduce skewness, followed by autoscaling (z-score normalization) on a per-compound basis to ensure comparability across variables with different scales and variances. Exploratory data analysis included the evaluation of the coefficient of variation (CV) distribution to assess analytical repeatability across the different brewing methods. In addition, the relative composition of the main chemical classes was calculated and expressed as a percentage contribution to the total volatile fraction. Multivariate analysis was carried out using principal component analysis (PCA) on the standardized dataset to reduce dimensionality and identify the main sources of variance, in accordance with established chemometric approaches [18]. Both score plots (samples) and loading plots (variables) were examined, with particular emphasis on compounds showing the highest contribution within the PC1–PC2 subspace. To identify discriminant compounds among the different extraction techniques (espresso, moka, and Kamira), a discriminant score was calculated based on the relative differences in mean compound intensities across the three groups. Compounds were subsequently ranked according to their discriminant power and visualized using top-marker plots. Finally, hierarchical cluster analysis (HCA) was

applied to the normalized data using Euclidean distance and Ward's linkage method to identify similarity patterns among compounds and brewing techniques [20]. The results were visualized using heatmaps coupled with dendrograms.

3. Results and Discussion

For the chemical and physicochemical analyses, each brewing method was represented by a pooled composite sample obtained by combining multiple independent brew preparations under the same operating conditions until a final volume of approximately 400 mL was reached. This approach was adopted to reduce cup-to-cup variability and to obtain a representative average compositional profile for each brewing system. However, it should be acknowledged that pooling does not allow the variability among independent brew preparations to be assessed directly. Therefore, the results reported in Sections 3.1–3.3 should be interpreted as descriptive of the mean compositional profile of each brewing method rather than as a measure of the full variability inherent to the brewing process.

3.1. Chemical and Physical Characteristics of Coffee Beverages

The comparison between coffee samples obtained using a moka pot, a home espresso maker, and Kamira revealed clear differences in both the physicochemical parameters of beverages and the composition of the corresponding freeze-dried residue. Overall, the espresso sample showed the most concentrated profile, with the highest values for refractive index, total solids, caffeine, chlorogenic acids, and compounds associated with the lipid fraction. The Kamira sample, however, stood out for its higher pH, lower titratable acidity, and lower chlorogenic acid content in the freeze-dried product, as well as lower extraction of the lipid fraction. The results related to the physicochemical parameters of the samples are reported in Table 2.

Table 2. Physicochemical parameters of the beverages obtained with the different extraction methods (mean ± standard deviation, n = 3).

Parameter	Moka	Espresso	Kamira
pH	5.32 ± 0.04	5.14 ± 0.03	5.47 ± 0.05
TTA * (meq/L)	13.7 ± 0.5	15.9± 0.7	10.8 ± 0.4
Refractive index (20 °C)	1.36 ± 0.01	1.40 ± 0.01	1.28 ± 0.01
Total solids in the brew (g/100 g)	2.34 ± 0.08	2.61 ± 0.11	2.02 ± 0.09

* TTA, total titratable acidity.

The pH values obtained confirmed that all beverages were mildly acidic, in agreement with the general physicochemical profile of roasted coffee beverages. However, more pronounced differences were observed for total titratable acidity. Espresso showed the highest values, whereas the lowest were recorded for the beverage prepared with Kamira. The higher total solids observed in espresso are consistent with the concentrated nature of pressure-assisted extraction and agree with previous comparative studies showing that brewing technology markedly affects beverage concentration and soluble-matter recovery [21]. In contrast, the lower total solids and lower titratable acidity observed in Kamira suggest a lower transfer of acidic and dissolved constituents to the final beverage, despite its espresso-like visual appearance. Under the present experimental conditions, these compositional differences indicate that brewing method affects not only the sensory profile of the beverage but also the extent to which soluble material is transferred into the cup.

3.2. Lipid Content and FA Profile

The total lipid content in the freeze-dried samples was low for all brewing methods, ranging from 2.3 ± 0.2 g/100 g in Kamira to 3.4 ± 0.4 g/100 g in espresso, while moka showed an intermediate value of 2.6 ± 0.3 g/100 g. These findings are consistent with previous reports indicating that most coffee lipids do not pass into the aqueous beverage but remain in the spent grounds [22]. Among the tested systems, espresso showed the highest lipid content, as expected when considering the high extraction pressure.

The fatty acid profile (Table 3) of the lipid fraction was substantially comparable in the three samples, with linoleic acid and palmitic acid as the predominant components, followed by oleic, stearic, and small amounts of arachidic and other minor fatty acids. Since the three samples were derived from the same starting coffee, the preparation method would be expected to affect mainly the amount of lipid material transferred into the beverage rather than the relative fatty acid composition itself. In fact, the extraction method primarily influences the amount of the lipid fraction that passes into the beverage, while having a much lesser impact on the percentage distribution of individual fatty acids within that fraction. This interpretation is consistent with previous studies indicating that brewing method influences the recovery of the lipid fraction, whereas the relative distribution of the major fatty acids remains comparatively stable when the same starting coffee is used [22,23].

Table 3. Fatty acid profile in the coffee brews. Results are expressed as g/100 g of lipids (mean ± standard deviation, n = 3).

Fatty Acid	Moka	Espresso	Kamira
Palmitic acid (C16:0)	36.8 ± 0.5	37.1 ± 0.4	36.6 ± 0.4
Stearic acid (C18:0)	8.1 ± 0.2	8 ± 0.2	8.2 ± 0.2
Oleic acid (C18:1 *n*-9)	11.3 ± 0.3	11 ± 0.3	11.4 ± 0.3
Linoleic acid (C18:2 *n*-6)	40.3 ± 0.6	40 ± 0.5	40.6 ± 0.5
Arachidic acid (C20:0)	2.21 ± 0.12	2.12 ± 0.13	2.32 ± 0.11
Behenic acid + other minor fatty acids	1.32 ± 0.13	1.83 ± 0.14	0.92 ± 0.12

3.3. Cafestol, Kahweol, Tocopherols, Chlorogenic Acid and Caffeine

Analyses of freeze-dried samples highlighted quantitative differences in caffeine, total chlorogenic acids, diterpenes, and tocopherols. In particular, the espresso sample showed the highest content of caffeine (55.3 ± 4.1 mg/100 g) and total chlorogenic acids (34.2 ± 6.4 mg/100 g), followed by moka (41.7 ± 2.9 mg/100 g caffeine; 24.6 ± 4.8 mg/g chlorogenic acids) and Kamira (39.8 ± 2.7 mg/100 g caffeine; 19.4 ± 3.7 mg/100 g chlorogenic acids).

The caffeine results are consistent with previous reports showing that espresso-type brewing generally yields the most concentrated beverages, owing to higher extraction efficiency, pressure-assisted mass transfer, and lower final beverage volume [21]. More broadly, caffeine content in coffee brews is known to depend not only on coffee species and roast degree, but also on brewing-related variables such as water-to-coffee ratio, extraction time, temperature, pressure, and beverage yield [24]. Also in the present study, espresso showed the highest caffeine concentration, whereas Kamira and moka displayed slightly lower values.

Chlorogenic acids represent a major fraction of coffee phenolics and contribute to the acidic, bitter, and astringent character of the beverage. Their higher concentration in espresso is in line with the more efficient extraction of hydrophilic constituents under pressure-assisted conditions, whereas the lower values observed in Kamira suggest a re-

duced transfer of this phenolic fraction into the final drink. This interpretation agrees with previous comparative studies showing that brewing method markedly affects chlorogenic acid recovery and, more generally, the concentration of soluble bioactive compounds in coffee beverages [21,25]. The lower chlorogenic acid content observed in Kamira may therefore be considered analytically compatible with a chemically milder beverage, although no direct physiological or clinical assessment was performed in the present study.

Regarding the lipophilic fraction, cafestol and kahweol contents were relatively similar in moka and espresso, with slightly higher values in espresso (0.68 ± 0.13 and 0.60 ± 0.10 mg/100 g, respectively) than in moka (0.65 ± 0.07 and 0.56 ± 0.05 mg/100 g, respectively), while Kamira showed the lowest values for both diterpenes (0.42 ± 0.04 and 0.38 ± 0.04 mg/100 g, respectively). This pattern suggests that diterpene transfer depends not only on extraction intensity, but also on the extent to which oily material and fine suspended particles are incorporated into the beverage. Previous studies have shown that espresso diterpene content is influenced by preparation parameters such as water amount, coffee dose, particle size, percolation time, temperature, and pressure [12], whereas earlier work on coffee brews prepared by different methods highlighted that lipid recovery is strongly method-dependent [22]. In this context, the lower diterpene values found in Kamira may reflect a more limited transfer or emulsification of the lipid-associated fraction into the final beverage. Although cafestol and kahweol have been associated with potentially beneficial bioactivities, they are also known to contribute to the cholesterol-raising effect of unfiltered coffee beverages [26].

As can be seen in Table 4, total tocopherols, despite being present at very low concentrations, also showed a trend consistent with that of the lipophilic component, with the highest value in espresso intermediate in moka, and lowest in Kamira. Given the fat-soluble nature of these compounds, their lower presence in Kamira is likely to depend on the same variables mentioned above for diterpenes.

Table 4. Non-volatile compounds of coffee brews normalized on a beverage basis, and determined by LC techniques (mean ± propagated standard deviation, $n = 3$).

Analyte	Moka	Espresso	Kamira
	mg/100 g Beverage	mg/100 g Beverage	mg/100 g Beverage
Caffeine	41.7 ± 2.9	55.3 ± 4.1	39.8 ± 2.7
Total chlorogenic acids	24.6 ± 4.8	34.2± 6.4	19.4 ± 3.7
Cafestol	0.65 ± 0.07	0.68 ± 0.13	0.42 ± 0.04
Kahweol	0.56 ± 0.05	0.60 ± 0.10	0.38 ± 0.04
Total tocopherols	$5.9 \times 10^{-3} \pm 2.0 \times 10^{-3}$	$8.9 \times 10^{-3} \pm 5.0 \times 10^{-3}$	$4.0 \times 10^{-3} \pm 2.0 \times 10^{-3}$

The findings outline that espresso emerged as the most effective method for the extraction of the hydrophilic fraction, particularly caffeine and chlorogenic acids, which are strongly influenced by extraction intensity, contact time, beverage concentration, and, in the case of espresso-like systems, pressure-assisted mass transfer. Moka showed lower levels of these analytes, but a diterpene content broadly comparable to that of espresso, suggesting that the transfer of lipophilic material into the beverage is not necessarily concomitant with the extraction of hydrophilic constituents. From a mechanistic point of view, these differences may reflect the distinct extraction regimes of the three systems. The lipophilic fraction and its occurrence in the final beverage depend, to a greater extent, on the transfer of oily material and fine suspended particles into the cup. In this respect, the present findings suggest that Kamira does not simply reproduce either moka or espresso extraction, but rather occupies an intermediate position, with a partial similarity to espresso for some features and a reduced transfer of lipid-associated compounds.

It is worthwhile emphasizing that the results obtained for the freeze-dried sample do not describe the composition of the roasted coffee itself, but rather that of the fraction actually transferred into the beverage during extraction and subsequently concentrated through freeze-drying. Therefore, the values for caffeine, chlorogenic acids, lipids, diterpenes, and tocopherols should be interpreted as indicators of the selective extraction yield of the different preparation methods, rather than as absolute indicators of the composition of the starting coffee.

3.4. Sensory Panel

3.4.1. Duplicate Evaluations and Brewing Methods

Agreement between duplicate evaluations was examined before aggregation of replicate A and replicate B for each panelist. Duplicate scores varied across descriptors and brewing methods (Figure S2). Scatterplots for aroma intensity, aroma quality, and bitterness showed points distributed close to the identity line across methods. For example, aroma intensity showed an ICC of 0.966 in Method 1, whereas aroma quality showed an ICC of 0.862 in Method 1. Lower ICC values were observed for some crema-related descriptors in moka coffee, including 0.392 for crema color and 0.096 for crema persistence. The descriptive agreement analysis based on absolute differences showed the same trend. Replicate scores were then aggregated using the median for each panelist, method, and descriptor before inferential analysis.

Figure 1 shows the sensory scores related to the brewing methods for a subset of descriptors. Global repeated-measures analysis showed significant differences for crema color, crema persistence, crema texture, sweetness, harmony, and repeatability (Friedman test, $p < 0.05$), whereas aroma intensity, aroma quality, acidity, bitterness, body, aftertaste, and clean cup did not differ significantly across methods. As can be seen in Table 5, post hoc paired Wilcoxon tests with Holm correction showed that moka differed significantly from both espresso and Kamira in regard to crema color, crema persistence, and crema texture. Sweetness also differed significantly across brewing methods. For harmony, a significant pairwise difference was observed only between moka and espresso, with median values of 5.25 and 6.75, respectively. Also, agreement between replicate A and replicate B for each sensory descriptor and brewing method was explored and is reported in Figures S2 and S3.

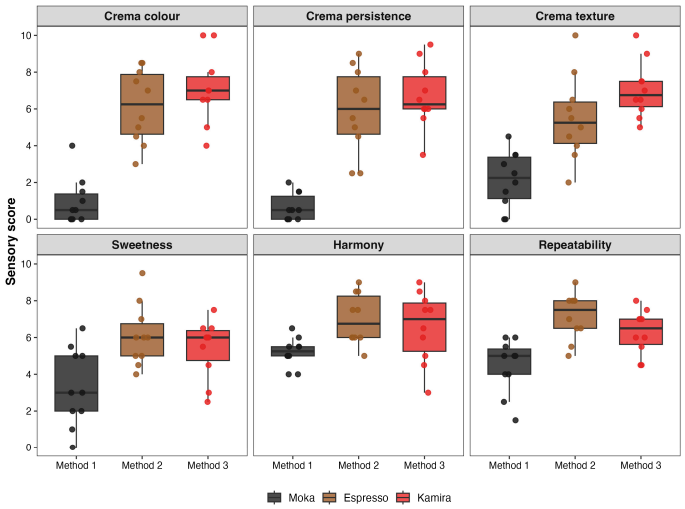


Figure 1. Boxplots of the sensory descriptors showing significant differences among brewing methods. Scores are based on panel-level values obtained by aggregating duplicate evaluations within each assessor. Significant global differences among brewing methods were identified by the Friedman test. Points represent individual assessors, boxes indicate the interquartile range, and the central line represents the median.

Table 5. Friedman test and Holm-adjusted post hoc Wilcoxon signed-rank tests for sensory descriptors across brewing methods.

Descriptor	Friedman χ^2	*p*-Value	Significant Holm-Adjusted Pairwise Comparisons
Crema color	15.436	0.000445	Moka vs. espresso (p.adj = 0.017); Moka vs. Kamira (p.adj = 0.017)
Crema persistence	15.436	0.000445	Moka vs. espresso (p.adj = 0.017); Moka vs. Kamira (p.adj = 0.017)
Crema texture	14.105	0.000865	Moka vs. espresso (p.adj = 0.025); moka vs. kamira (p.adj = 0.017)
Aroma intensity	1.000	0.606531	None
Aroma quality	4.108	0.128214	None
Sweetness	6.857	0.032258	Moka vs. espresso (p.adj = 0.039); moka vs. kamira (p.adj = 0.048)
Acidity	0.053	0.973684	None
Bitterness	0.722	0.696902	None
Body	3.077	0.214381	None
Aftertaste	1.632	0.442053	None
Harmony	8.909	0.011615	Moka vs. espresso (p.adj = 0.027)
Clean cup	3.324	0.189724	None
Repeatability	11.200	0.003698	Moka vs. espresso (p.adj = 0.027); moka vs. kamira (p.adj = 0.041)

All pairwise comparisons among brewing methods were performed when the global Friedman test was significant. Only statistically significant Holm-adjusted pairwise comparisons are reported in the table; non-significant comparisons, including espresso vs. Kamira, where applicable, are omitted for readability.

3.4.2. Exploratory PCA of Sensory Descriptors

As can be seen in Figure 2, espresso and Kamira showed markedly higher scores than moka for all crema-related descriptors, whereas no significant pairwise differences were found between espresso and Kamira. This finding suggests that the two pressure-oriented systems generated more similar visual and textural cues than moka, particularly in terms of foam development, crema persistence, and crema texture. This result is consistent with previous evidence showing that crema is not merely a visual attribute, but a complex multiphase structure that contributes to aroma release, in-mouth perception, and the overall sensory experience of espresso coffee [27,28]. More broadly, coffee foam formation and stability are influenced by gas release, emulsified lipids, suspended solids, melanoidins, and surface-active compounds, all of which may be affected by extraction pressure, flow dynamics, and the transfer of colloidal material into the beverage [29,30]. Therefore, the clear separation of moka from espresso and Kamira for crema-related attributes appears mechanistically consistent with the technological differences among the brewing systems.

Significant differences were also observed for sweetness, harmony, and repeatability. Moka showed lower sweetness scores than espresso and Kamira, while repeatability was also lowest for moka and highest for espresso. Harmony showed a more moderate pattern, with espresso differing significantly from moka, and Kamira occupying an intermediate position. These descriptors should be interpreted as integrative sensory attributes rather than as direct indicators of single chemical compounds. In coffee, perceived sweetness and harmony can be modulated by the balance among bitterness, acidity, body, aroma persistence, tactile perception, and visual cues such as crema. Accordingly, the lower sweetness and harmony scores observed for moka may reflect a less integrated sensory profile, mainly due to the limited crema development and lower perceived consistency across duplicate evaluations. The lower repeatability of moka may also be related to the greater sensitivity of stovetop extraction to small variations in heating rate, pressure build-up, and extraction end point. Comparative studies on coffee beverages have similarly shown that brewing method can affect selected sensory dimensions more strongly than others, rather than modifying the whole sensory profile uniformly [2,31,32].

By contrast, descriptors such as aroma intensity, aroma quality, acidity, bitterness, body, aftertaste, and clean cup did not differ significantly across methods. This does not necessarily indicate that the three beverages were identical for these attributes, but rather that, under the present experimental conditions and panel size, these descriptors

contributed less to statistical discrimination among brewing methods than crema-related and overall-balance descriptors. This result is plausible because aroma and taste perception are influenced not only by the concentration of volatile and non-volatile compounds, but also by matrix effects; foam-mediated aroma release; serving temperature; individual assessor sensitivity; and cross-modal interactions between visual, olfactory, gustatory, and tactile cues [27,28].

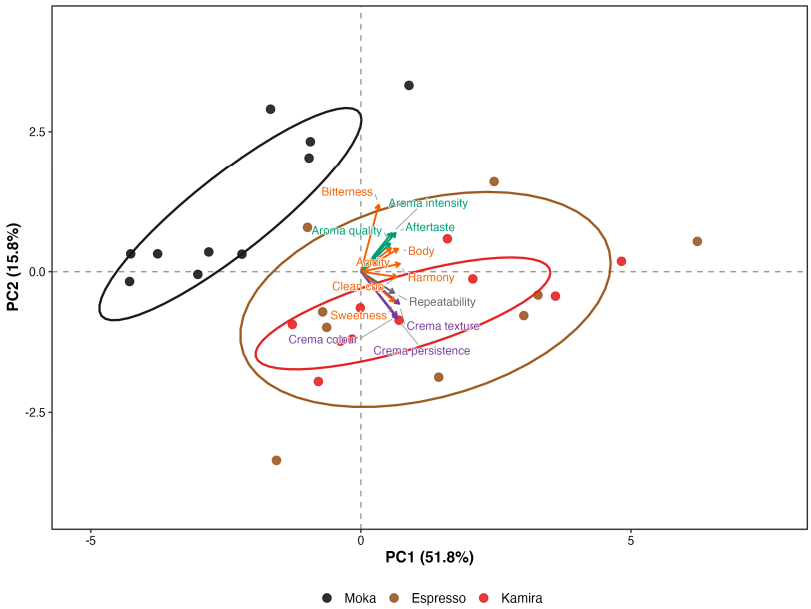


Figure 2. Exploratory principal component analysis (PCA) biplot of sensory profiles obtained for coffee beverages prepared by moka, espresso, and Kamira. Each point represents one assessor-level aggregated sensory profile for a given brewing method, obtained after aggregation of duplicate evaluations. Arrows indicate descriptor loadings. PC1 and PC2 explained 67.6% of the total variance. Ellipses are shown only as visual aids to summarize within-method dispersion and should not be interpreted as inferential confidence regions. Because PCA was used as an unsupervised exploratory method rather than as a predictive classification model, Q^2 or permutation-based validation was not applied.

The exploratory PCA complemented the univariate analysis by showing a clear separation of moka from espresso and Kamira along PC1, which accounted for most of the explained variance. Positive PC1 loadings were associated mainly with crema-related descriptors, harmony, and repeatability, whereas PC2 reflected a secondary gradient linked more closely to bitterness, aroma-related descriptors, and aftertaste. Espresso occupied a broader multivariate area, whereas Kamira formed a more compact cluster partially overlapping with espresso. Taken together, these results indicate that the sensory differentiation among brewing methods was mainly driven by crema-related attributes and by descriptors of overall profile coherence, rather than by a generalized shift in all aroma and taste descriptors.

The relationship between chemical composition and sensory perception was interpreted qualitatively and should be considered exploratory. No formal correlation analysis was performed because the chemical and sensory datasets had different experimental structures. Chemical data were summarized at the brewing-method level, whereas sensory data were obtained from assessor-level evaluations of the same three brewing methods. Therefore, a correlation based on mean chemical and sensory values would have relied essentially on only three experimental points, corresponding to moka, espresso, and Kamira, and would not have supported robust statistical inference. Accordingly, the observed correspondence between selected chemical features and sensory attributes should be regarded as hypothesis-generating rather than confirmatory.

3.5. Volatile Composition

3.5.1. SPME Method Development

Despite of previous works carried out on roasted coffee beans that required a long extraction period (50 min) and a temperature of 60 °C, in the present study, freshly brewed coffee beverages were subjected to fiber exposure for a considerably shorter time (15 min + 10 min of preconditioning) [33,34]. The triple-phase DVB/Car/PDMS, due to its multifaceted selectivity, proved itself to be the most suitable for the extraction of coffee volatiles that include compounds from a wide range of polarity. The choice of fiber coating was one of the numerous parameters investigated toward the definition of an optimized method. Sample volume, extraction duration and temperature, agitation, and preconditioning were tuned and tested; the obtained data, expressed as absolute peak areas, were plotted to define the optimal extraction conditions in terms of efficiency and yield. Supplementary Figure S4 shows the chromatographic separation of the three coffee brews. The volatile distribution across samples is detailed in Table 6, where the values of area percentages, along with retention indices, are reported. RSD values (0.01–1.05%) testify to the goodness of the SPME-GC method. Almost 70 compounds were identified that can be grouped under typical chemical classes: furan, pyrazine, pyrrole, pyridine, and sulfur-containing compounds. The three samples exhibited a similar qualitative composition in terms of components, whereas the quantitative relative abundances of these compounds differed among the samples. As expected, the chromatographic space was dominated by Maillard compounds that naturally form in coffee upon roasting because of the breakdown of sugars.

Table 6. HS-SPME-GC composition of the volatile fractions of coffee brews. Values are means of triplicate injections. RI_{exp} = experimental retention index; RI_{lit} = published retention index.

RI_{exp}	RI_{lit}	Compound	Espresso		Moka		Kamira	
			Area %	RSD	Area %	RSD	Area %	RSD
913	916	2-methylbutanal	0.43	0.06	0.32	0.05	0.46	0.11
915	920	3-methylbutanal	0.97	0.13	0.37	0.07	0.70	0.13
933	938	Ethyl alcohol	1.64	0.21	2.63	0.42	3.08	0.29
954	953	2,5-dimethylfuran	0.57	0.09	0.38	0.04	0.15	0.02
983	981	2,3-butanedione	2.66	0.32	1.04	0.15	2.08	0.31
990	987	3-methyl-2-butanone	0.25	0.02	0.36	0.06	0.33	0.14
1013	1011	Acetonitrile	0.40	0.06	0.18	0.02	0.28	0.09
1020	1018	Thiophene	0.11	0.01	0.18	0.06	0.18	0.03
1023	1025	(2E)-butenal	0.24	0.06	0.24	0.04	0.36	0.12
1065	1067	2,3-pentanedione	0.53	0.12	0.26	0.06	0.46	0.09
1089	1086	Dimethyl disulfide	0.27	0.04	0.45	0.13	0.59	0.06
1106	1102	β-pinene	0.17	0.02	0.23	0.02	0.25	0.06
1120	1118	Sabinene	0.19	0.03	0.18	0.03	0.24	0.02
1142	1138	2,3-hexanedione	0.31	0.08	0.12	0.01	0.34	0.06
1149	1143	Methyl-1H-pyrrole	0.22	0.06	0.12	0.04	0.24	0.04
1153	1147	3,4-hexanedione	0.27	0.04	0.19	0.05	0.28	0.07
1165	1158	2-vinyl-5-methylfuran	1.97	0.26	2.22	0.18	1.42	0.35
1172	1167	Myrcene	0.10	0.01	0.12	0.02	0.16	0.04
1182	1177	3,4-hexanedione	0.43	0.05	0.60	0.09	0.56	0.08
1185	1182	Pyridine	7.87	0.68	6.30	0.75	9.65	0.96

Table 6. *Cont.*

RI_{exp}	RI_{lit}	Compound	Espresso		Moka		Kamira	
			Area %	RSD	Area %	RSD	Area %	RSD
1196	1196	Limonene	0.73	0.12	0.52	0.06	0.12	0.02
1218	1215	Pyrazine	0.96	0.19	0.12	0.04	0.95	0.09
1260	1256	3-methyltetrahydrofuran	0.13	0.01	0.14	0.01	0.27	0.04
1269	1267	Methylpyrazine	5.72	0.29	3.31	0.42	4.96	0.33
1274	1271	4-methylthiazole	0.10	0.01	0.20	0.03	0.22	0.03
1277	1273	2,5-dimethylpyrrole	0.26	0.04	0.47	0.05	0.29	0.02
1295	1291	Acetoin	1.68	0.32	1.69	0.36	1.55	0.26
1327	1324	2,5-dimethylpyrazine	1.67	0.3	1.30	0.21	1.66	0.21
1335	1330	2,6-dimethylpyrazine	2.00	0.45	1.40	0.31	1.84	0.35
1339	1336	Ethylpyrazine	0.69	0.1	0.59	0.1	0.67	0.10
1369	1371	2-methyl-2-cyclopentenone	0.15	0.03	0.24	0.06	0.21	0.02
1384	1381	3-ethylpyridine	0.28	0.07	0.27	0.04	0.23	0.02
1391	1388	2-ethyl-6-methylpyrazine	1.54	0.18	2.16	0.24	1.54	0.23
1397	1394	2-ethyl-5-methylpyrazine	0.78	0.07	0.97	0.09	0.84	0.10
1400	1397	4,5-dimethylthiazole	0.95	0.06	0.92	0.14	1.16	0.23
1410	1407	2-ethyl-3-methylpyrazine	0.78	0.09	1.64	0.12	0.75	0.08
1462	1459	2-methyl-5-propylpyrazine	0.24	0.03	0.53	0.11	0.24	0.06
1475	1473	Furfural	4.57	0.86	4.33	0.94	3.16	0.74
1480	1477	Acetol acetate	0.16	0.02	0.30	0.06	0.19	0.05
1496	1493	2-furfuryl-5-methylsulfide	0.65	0.05	1.91	0.33	0.79	0.06
1499	1497	2-methyl-3,5-diethylpyrazine	0.26	0.03	0.81	0.16	0.26	0.02
1511	1507	Furfuryl formate	1.70	0.13	1.80	0.18	0.60	0.08
1516	1513	2-acetylfuran	3.55	0.32	2.24	0.42	1.34	0.27
1526	1523	Pyrrole	0.40	0.07	0.43	0.04	0.42	0.09
1542	1540	3,3-dimethyl-2-butanone	0.55	0.14	0.82	0.14	0.63	0.12
1548	1547	Furfuryl acetate	10.09	0.52	11.25	1.05	10.72	0.68
1560	1557	Linalool	0.23	0.08	0.42	0.09	0.22	0.04
1565	1565	Linalyl acetate	0.09	0.02	0.17	0.02	0.05	0.00
1584	1582	5-methylfurfural	3.43	0.21	3.49	0.35	3.57	0.41
1619	1618	2-furfuryl furan	0.40	0.04	0.40	0.05	1.19	0.14
1631	1628	N-methyl-2-formylpyrrole	0.34	0.03	0.82	0.09	0.30	0.03
1640	1637	γ-butyrolactone	0.61	0.12	2.76	0.25	0.67	0.11
1656	1654	4-(2-furyl)-2-butanone	0.31	0.04	0.43	0.1	0.27	0.05
1660	1658	2,5-dihydro-3,5-dimethyl-2-furanone	0.99	0.24	1.00	0.18	1.33	0.22
1665	1663	2-acetyl-1-methylpyrrole	1.21	0.17	1.31	0.16	1.38	0.56
1677	1671	Furfuryl alcohol	12.43	0.68	13.22	1.03	7.45	0.9
1735	1731	N-acetyl-4(H)pyridine	0.34	0.04	0.47	0.09	0.33	0.03
1790	1787	1-(5-methyl-2-furyl)-2-propanone	0.58	0.06	0.59	0.01	1.98	0.26
1808	1804	Butyl diethylene glycol	0.16	0.03	0.44	0.12	0.17	0.03
1841	1839	Furfuryl pyrrole	0.91	0.18	4.45	0.84	0.86	0.06
1874	1871	Guaiacol	0.98	0.16	1.80	0.33	1.12	0.04

Table 6. *Cont.*

RI_{exp}	RI_{lit}	Compound	Espresso		Moka		Kamira	
			Area %	RSD	Area %	RSD	Area %	RSD
1890	1886	Benzyl alcohol	0.14	0.02	0.64	0.13	0.11	0.00
1920	1921	Phenethyl alcohol	0.09	0.01	0.26	0.08	0.14	0.00
1981	1983	2-acetylpyrrole	0.23	0.06	0.64	0.04	0.25	0.02
1995	1996	Furfuryl ether	0.65	0.06	0.80	0.04	0.91	0.05
2035	2038	Pyrrole-2-carboxaldehyde	0.56	0.04	2.02	0.24	0.61	0.03
			84.91	9.14	92.94	12.24	80.35	10.35

3.5.2. Multivariate Analysis and Discriminant Characterization of Volatile Profiles

The multivariate structure of the volatile dataset was investigated by hierarchical heatmap analysis (Figure 3) using the relative abundance values obtained from HS-SPME-GC analyses of the three coffee beverages. Prior to statistical analysis, the dataset was log-transformed and autoscaled (z-score normalization by variable) in order to reduce variability associated with differences in compound abundance and allow for direct comparison among analytes.

In the heatmap, positive z-score values (yellow-to-red scale) indicate compounds relatively enriched in a specific brewing method, whereas negative z-score values (light-blue-to-dark-blue scale) indicate comparatively lower relative abundances. Volatile compounds were grouped according to their chemical families (furans, pyrazines, pyridines, pyrroles, and sulfur-containing compounds), and hierarchical clustering was performed using Euclidean distance and Ward's linkage algorithm.

The clustering analysis revealed a clear separation among the brewing methods. Espresso and Kamira clustered more closely together, whereas moka formed a distinct branch, indicating a markedly different volatile profile.

Nevertheless, the heatmap demonstrates that the similarity between espresso and Kamira is not homogeneous across all chemical classes and that each brewing method is characterized by specific enrichments and depletions within distinct groups of volatile compounds. Among the analyzed families, furans were predominantly associated with espresso.

Compounds such as furfuryl acetate, furfural, 2,5-dimethylfuran, 1-(5-methyl-2-furyl)-2-propanone, and 2-acetylfuran displayed strongly positive z-score values in espresso, while showing negative standardized values in moka. Kamira generally exhibited intermediate or moderately positive values for these compounds. Furans derive mainly from sugar degradation and Maillard-related thermal pathways and are typically associated with sweet, caramel-like, toasted, and bread-like aromatic notes. The enrichment of these compounds in espresso therefore suggests a volatile profile characterized by a stronger contribution of thermally derived sweet-roasted notes [35].

Pyrazines exhibited an opposite trend compared with furans. Espresso showed predominantly negative z-score values for most pyrazines, whereas moka and Kamira displayed positive or near-positive standardized abundances. In particular, 2-ethyl-5-methylpyrazine, 2,6-dimethylpyrazine, ethylpyrazine, and 2-methyl-5-propylpyrazine were relatively enriched in moka and Kamira compared with espresso. Pyridine derivatives showed a more selective distribution pattern with a markedly positive z-score value in espresso, while Kamira showed strongly negative standardized values for pyridine and 3-ethylpyridine. Moka generally displayed intermediate values for this chemical family. The strongest discrimination of moka emerged within the pyrrole and sulfur-containing compound families. Pyrrole derivatives, including methyl-1H-pyrrole, pyrrole, 2,5-dimethylpyrrole, pyrrole-2-carboxaldehyde, and furfuryl pyrrole, displayed strongly positive z-score values in moka, whereas espresso

and Kamira showed predominantly negative standardized abundances. Similarly, sulfur-containing compounds such as dimethyl disulfide, thiophene, 4-methylthiazole, and 4,5-dimethylthiazole were comparatively enriched in moka and depleted in espresso, while Kamira again exhibited intermediate behavior. These compounds are commonly associated with roasted, smoky, sulfur-like, and burnt aromatic nuances and originate from advanced Maillard and thermal degradation reactions [35].

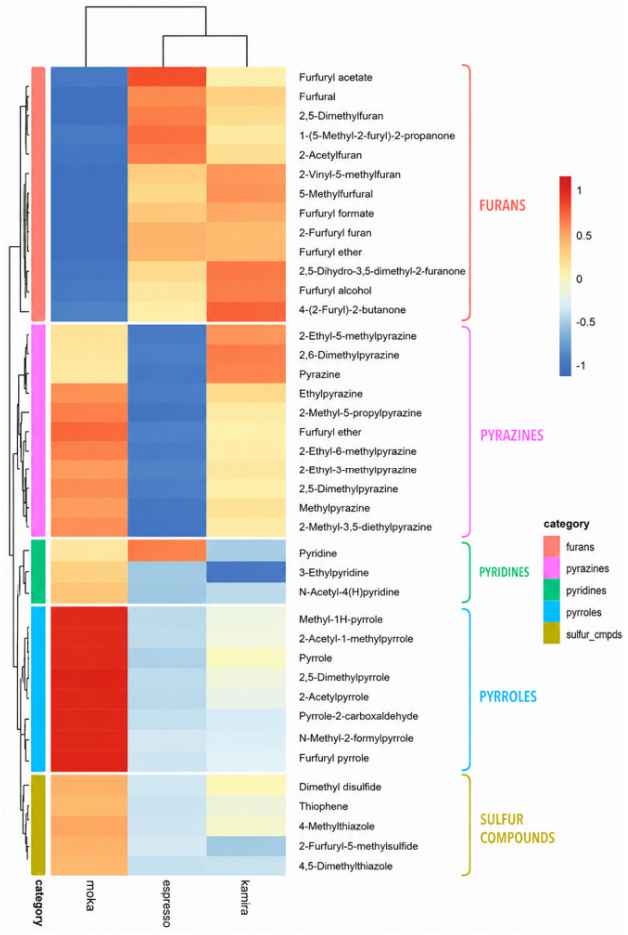


Figure 3. Heatmap of volatile compounds detected in coffee prepared by moka, espresso, and Kamira methods.

The multivariate patterns observed in this study are consistent with previous findings reported in the literature. In particular, a comparable separation of samples subjected to more intense processing conditions was previously reported, where darker roasting levels occupied a distinct region of the PCA space and were associated with increased contributions from furans, pyrazines, and sulfur-containing compounds [36]. Similarly, a clear differentiation of coffee beverages was observed according to extraction technology, demonstrating that brewing methods significantly influence the organization of volatile and sensory-related molecular profiles [31]. Also, furans, pyrazines, and sulfur-containing compounds were identified among the major discriminant variables in PCA models comparing coffees prepared under different brewing conditions [37]. As can be seen in Figure 4, in the present study, furans were the main compounds associated with PC1, while pyrroles and sulfur-containing compounds contributed more strongly to the separation of moka samples. This suggests that the different brewing methods influence the relative abundance of roasting-derived heterocyclic compounds in the final beverages. In particular, the closer clustering of espresso and Kamira compared with moka indicates that, despite the different extraction principles underlying the two systems, Kamira may partially reproduce the se-

lective extraction behavior characteristic of espresso beverages. These observations support the hypothesis that the distinct clustering observed among brewing methods primarily reflects differences in extraction dynamics and physicochemical transfer phenomena rather than variations in roasting chemistry alone. To quantitatively assess the discriminant contribution of individual compounds, a composite discriminant score was calculated by integrating differences between group means and intra-group variability (coefficient of variation, CV). The results are reported in the top marker plot (Figure S5). The consistency between PCA loadings and marker-based discrimination supports the robustness of the observed separation. Similar variations in these compound classes across extraction conditions were also reported elsewhere, further supporting their role as key contributors to variability in coffee volatile profiles [37].

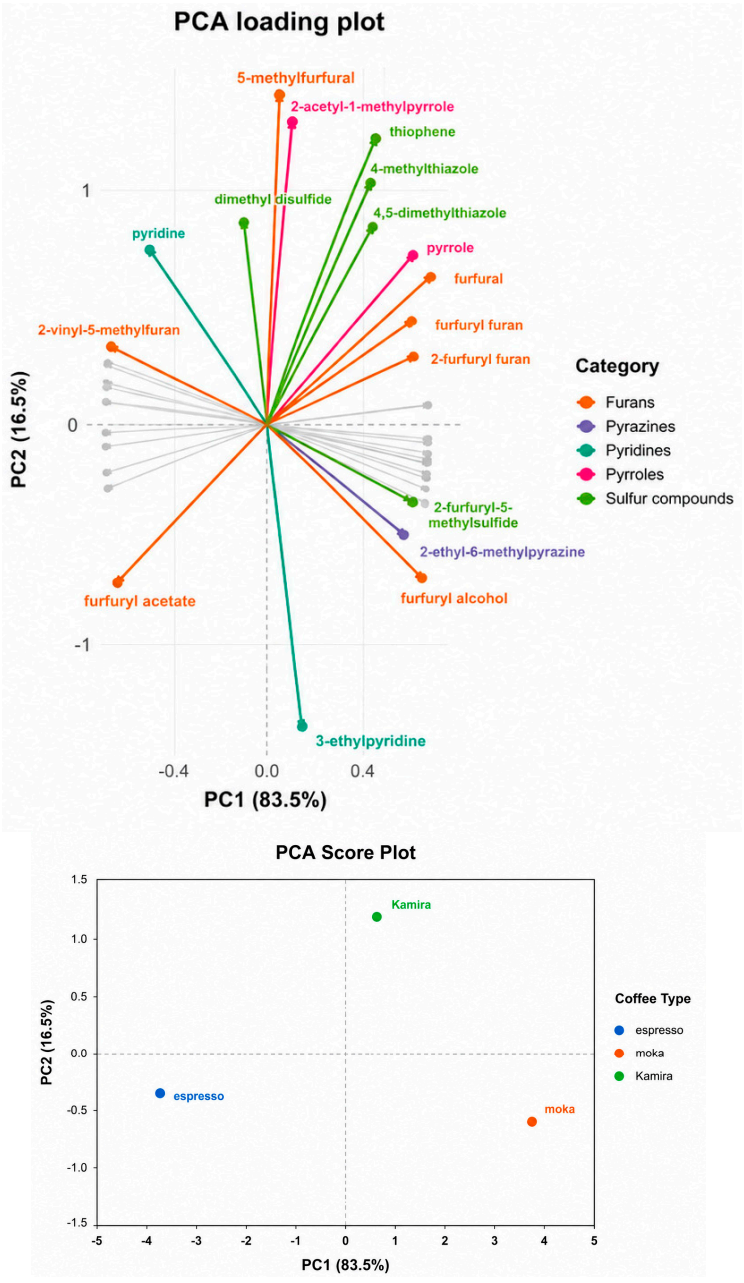


Figure 4. (**Top**) PCA loading plot of volatile compounds; highlighted vectors indicate the main contributors to PC1–PC2. (**Bottom**) PCA score plot showing differences among espresso, moka, and Kamira coffee-brewing methods.

4. Conclusions

Coffee prepared by traditional moka, conventional espresso, and a novel Italian brewing device (Kamira) was investigated through an integrated analytical and sensory approach, with particular emphasis on separation-based techniques. Volatile constituents were characterized by headspace solid-phase microextraction coupled with gas chromatography–mass spectrometry and gas chromatography–flame ionization detection (HS-SPME/GC–MS and GC–FID), highlighting the occurrence of furan, pyrrole, and pyrazine derivatives typical of roasted coffee. Fatty acids were determined by gas chromatography, whereas caffeine and chlorogenic acids were quantified by HPLC-PDA. In addition, total solids, pH, and refractive index were measured to support the analytical characterization of the beverages. Sensory evaluation was performed by a trained panel who observed distinct patterns among the three brewing systems.

In particular, espresso and Kamira brews presented similar volatile compositions, while moka coffee diverged for a distinct aromatic fraction. In moka brews, relative abundances of typical Maillard compounds, such as furans and pyrazines, were higher, as well as for sulfur compounds. Qualitative results from the compositional assays are in agreement with those coming from the sensory panel. On the other hand, both espresso and Kamira revealed a more balanced aroma, with slightly higher percentages of pyridines. The clusterization of Kamira and espresso separately from moka has been further confirmed by the PCA analysis that evidenced discriminant molecules linked to roasting and heat. Overall, our findings demonstrate that brewing technology markedly affects coffee composition and sensory perception, and provide the first analytical characterization of the Kamira system.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/separations13060166/s1, Figure S1: Illustration of the Kamira® coffee maker; Figure S2: Agreement between replicate A and replicate B for each sensory descriptor and brewing method. Each point represents the paired scores assigned by the same assessor to duplicate samples. The dashed diagonal indicates perfect agreement between replicates; Figure S3: Boxplots of all sensory descriptors by brewing method. Scores are based on panel-level aggregated values obtained from duplicate evaluations. Points represent individual assessors, boxes indicate the interquartile range, and the central line represents the median; Figure S4: Three overlapped HS-SPME-GC-FID chromatograms of coffee brews prepared with moka (purple color), espresso (black color), and Kamira (blue color); Figure S5: Top discriminant volatile markers for each coffee-brewing method.

Author Contributions: Conceptualization, R.C.; methodology, G.L.V. and R.V.; software, G.T.; validation, R.C. and R.V.; formal analysis, G.L.V., R.C., L.D.M. and R.D.P.; investigation, G.L.V., R.C., L.D.M. and R.D.P.; resources, N.C.; data curation, R.C., R.V. and G.T.; writing—original draft preparation, R.C.; writing—review and editing, R.V.; visualization, N.C.; supervision, R.C. and N.C.; project administration, N.C.; funding acquisition, N.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors upon request.

Acknowledgments: The authors would like to thank Santoro from Kamira s.r.l. company for kindly providing the coffee maker used in this study and for his valuable technical guidance on its operation.

Conflicts of Interest: Nicola Cicero has been involved as a Scientific Consultant in Science4life Srl. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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