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ARTICLE

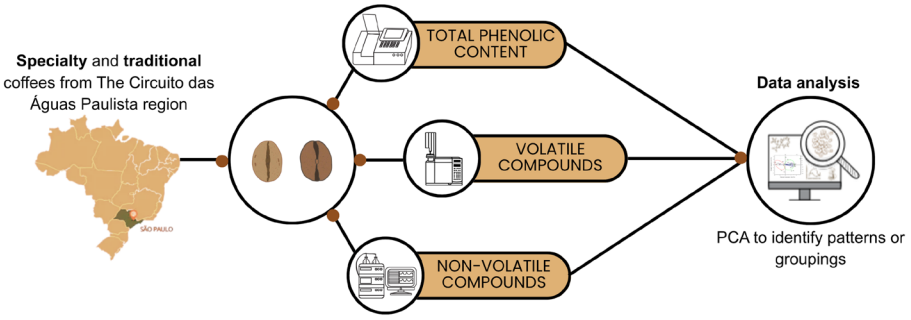
Evaluation of Volatile and Non-Volatile Compounds in Specialty and Traditional Coffees from the *Circuito das Águas Paulista* Region

Bruna Luiza Duarte Guedes[1], Winston P. C. Gomes[2], Gabriela Maria R. N. de Alcantara[2], Gisele G. Bortoleto[3], Wanessa R. Melchert[1]*

[1]*Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo, PO Box 9, 13418-970, Piracicaba, SP, Brazil*

[2]*Centro de Energia Nuclear na Agricultura da Universidade de São Paulo (CENA/USP), Av. Centenário, 303, 13416-000, Piracicaba, SP, Brazil*

[3]*Centro Estadual de Educação Tecnológica Paula Souza/CEETEPS, Escola Técnica de Piracicaba Deputado Roque Trevisan, 13414-141, Piracicaba, SP, Brazil*



Coffee, renowned for its aroma and flavor, ranks second in global consumption. Key compounds in coffee beans significantly influence their sensory properties in green and roasted forms. Brazil, a leading coffee producer and exporter, benefits from the adaptability of coffee plants due to its diverse geographical features. The *Circuito das Águas Paulista* region, in particular, provides an ideal environment for high-quality coffee cultivation, producing coffees that surpass the 80-point threshold needed to attain specialty coffee status. This study evaluated 17 roasted *Coffea arabica* samples: 12 from the 2020/2021 harvest (six specialty and six traditional) and 5 from the 2022/2023 harvest. Chemical composition was assessed using UV-Vis spectrophotometry, HPLC, GC-FID, and chemometric tools. Total phenolic content, measured by the Folin-Ciocalteu method, ranged from 3371 to 3968 milligrams of gallic acid equivalents per 100 grams (mg GAE 100 g^{-1}). Caffeine and chlorogenic acid contents (507–1006 mg 100 g^{-1} and 453–1004 mg 100 g^{-1}, respectively) were determined by HPLC. Volatile compounds such as diacetyl (37.01–108.28 µg 100 g^{-1}) and 2-methylpyrazine (2.41–3.38 µg 100 g^{-1}) were quantified by GC-FID with headspace sampling. Significant differences were found between specialty and traditional coffees, particularly in diacetyl, which was more abundant in specialty samples and may act as a marker. Principal component analysis effectively distinguished the two groups, with 2-methylpyrazine playing a key role in traditional coffees. Comparison between harvests

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revealed notable variations in caffeine, gallic acid, chlorogenic acid, 3,4-dihydroxybenzoic acid, and 2-methylpyrazine, suggesting that environmental conditions, such as frost, can affect coffee chemistry and quality. The analytical advance of this work resides in the integration of complementary analytical techniques with chemometric analysis, providing a robust approach to discriminate coffee categories and evaluate environmental influences on their chemical composition.

Keywords: specialty coffees, chromatography, volatile compounds, phenolic compounds, chemometrics

INTRODUCTION

Coffee is a widely recognized stimulant beverage known for its distinctive aroma and flavor, ranking second globally in consumption, just behind water.[1,2] In the global coffee trade, Brazil leads in production and export. This leadership can be attributed to the adaptability of coffee plants to Brazil's diverse environmental conditions, including varied altitudes, latitudes, climates, and terrains.[3]

According to CONAB (*Companhia Nacional de Abastecimento*) in 2022, the Brazilian states with the highest coffee production rates are Minas Gerais, Espírito Santo, São Paulo, Paraná, Bahia, Rondônia, Rio de Janeiro, Goiás, Mato Grosso, Amazonas, and Pará. The *Circuito das Águas Paulista* region is particularly notable for its favorable geography and the differentiated quality/composition of its waters, which support the cultivation of high-quality coffee.[4-6] Therefore, due to these unique edaphoclimatic conditions, altitude, nutrient-rich soils, water, and mild microclimates, it is essential to map the chemical profile of the coffees produced in this region in detail.

The designation of specialty coffee is determined through sensory evaluations, such as cupping scores, following guidelines established by the Specialty Coffee Association of America.[7] Coffee must score at least 80 points and have certified traceability to be classified as a specialty. Therefore, many producers seek certifications from specialized evaluation entities to demonstrate the quality and excellence of the coffee's sensory characteristics.[5,8]

Sensory characteristics can be directly related to the compounds (volatile and non-volatile) present in the composition of coffee beans, as they influence the beverage's aroma and flavor, thereby enhancing its appeal and consumer acceptance. The chemical composition of coffee includes carbohydrates, lipids, proteins, minerals, amino acids, and bioactive compounds. Additionally, edaphoclimatic factors can influence this set of elements, with altitude and exposure to light being significant factors.[9-11]

Caffeine, chlorogenic acid, gallic acid, 5-hydroxymethylfurfural (5-HMF), and 3,4-dihydroxybenzoic acid are bioactive compounds commonly found in coffee, each with distinct nutritional significance and contributing significantly to the sensory richness and uniqueness of coffee.[9-11] Caffeine has a psychoactive stimulant effect, but high doses can lead to adverse effects like insomnia and tachycardia.[12,13] Chlorogenic acid and gallic acid are antioxidants with anti-inflammatory potential, and are often used in functional foods and nutraceuticals; both are generally considered safe at dietary levels.[14–17] 5-HMF, formed during thermal processing, is valued as a quality marker but may be linked to potential mutagenic effects.[18,19] Meanwhile, 3,4-dihydroxybenzoic acid shows antioxidant activity with low toxicity reported at low doses.[20,21]

Recent research in the literature has employed high-performance liquid chromatography (HPLC) and gas chromatography (GC) to evaluate the non-volatile and volatile compounds in coffee, respectively. However, few studies still focus on evaluating specialty and traditional coffees, particularly roasted ones, using uniform standards for roasting, extraction, and preparation with beans from the same species and region, and correlating these aspects with sensory analysis parameters.[22,23] In this field, the works of Alcantara *et al*. and Abreu *et al.* stand out.[24,25]

In light of this, the present study aimed to analyze and compare the chemical composition of specialty and traditional coffees from cities of the *Circuito das Águas Paulista* region employing chromatographic, spectrophotometric, and chemometric techniques. Only through in-depth knowledge of the chemical signatures that reflect the local terroir will it be possible, in subsequent studies, to establish comparative criteria with other producing regions and demonstrate the peculiarities of this region. Thus, this study establishes an

analytical framework that will enable us to evaluate, in future stages, regional differences and support specific quality claims for coffees from the *Circuito das Águas Paulista*. Furthermore, the specific objectives of this study were to quantify the total phenolic compounds (TPC) in samples of specialty and traditional coffees, identify and quantify non-volatile compounds based on retention time and established analytical standards, and obtain the chromatographic profile of these non-volatile compounds. It also aimed to identify and quantify volatile compounds in the samples and establish correlations between the results obtained and the sensory scores, cultivation altitude, and classification of the coffee samples.

The novelty of this study lies in the integrated application of complementary analytical techniques (UV-Vis spectrophotometry, HPLC, GC-FID with headspace sampling) combined with chemometric tools. This analytical strategy enabled a comprehensive chemical characterization of roasted coffee, allowing the identification of discriminant compounds between specialty and traditional samples and the evaluation of environmental influences across harvests. In this sense, the work contributes to advancing coffee quality assessment and authentication by demonstrating the potential of established methods when applied in an integrative and systematic approach.

MATERIALS AND METHODS

Reagents and equipment

For all analyses, deionized water (conductivity of 18.2 MΩ·cm at 25 ºC) and analytical-grade reagents from Sigma-Aldrich (≥99% purity), including acetic acid, methanol, acetonitrile, gallic acid, Folin-Ciocalteu reagent, caffeine, 3,4-dihydroxybenzoic acid, chlorogenic acid, 5-hydroxymethylfurfural, sodium carbonate, acetaldehyde, acetone, methanol, ethanol, diacetyl, and 3-methyl-butanol, were used.

The following types of equipment were utilized during the analyses: an ultrasonic bath (Ultra Cleaner, model 1450), an analytical balance (Mettler Toledo, model ME104), a UV-Vis spectrophotometer (Agilent, model Cary 60), a high-performance liquid chromatography (Agilent, model 1100), and a gas chromatograph (PerkinElmer, model Clarus 600).

Sample preparation

Twelve samples of Arabica coffee beans were obtained from producers in the *Circuito das Águas Paulista* region during the 2020/2021 period, including the cities of Serra Negra, Socorro, Águas de Lindóia, and Monte Alegre do Sul, all located in the state of São Paulo, Brazil (Table I). Subsequently, all samples underwent a roasting process for uniformity. The coffee beans were ground using an analytical mill (Tecnal, model TE-631/4) and passed through a 20-mesh sieve for proper standardization, according to protocol by the Specialty Coffee Association.[7] Subsequently, five additional samples of Arabica coffee beans from the 2022/2023 harvest were collected from the same region for further comparison.

Table I. Specialty and traditional coffee samples

Samples	Classification	Plant variety	City	Altitude (m)	SCAA* Score
S1	Specialty	*Arara*	Socorro	1000 - 1200	80.175
S2	Specialty	*Bourbon Amarelo*	Monte Alegre do Sul	900	83.325
S3	Specialty	*Mundo Novo*	Monte Alegre do Sul	1100	80.15
S4	Specialty	*Mundo Novo*	Serra Negra	1150	80.275
S5	Specialty	*Bourbon Amarelo*	Socorro	1300	81.6
S6	Specialty	*Arara*	Serra Negra	1100	84.175
T1	Traditional	*Arara, Mundo Novo*	Serra Negra	825	78.975
T2	Traditional	*Catuaí Vermelho*	Serra Negra	680	78.625

(continues on next page)

Table I. Specialty and traditional coffee samples (continuation)

Samples	Classification	Plant variety	City	Altitude (m)	SCAA* Score
T3	Traditional	*Catuaí*	Águas de Lindóia	1200	78.425
T4	Traditional	NOS**	Serra Negra	720	77.7
T5	Traditional	*Catuaí*	Serra Negra	1120	79.075
T6	Traditional	*Mundo Novo*	Serra Negra	1100	73.925

*Specialty Coffee Association of America. **Not otherwise specified.

In the spectrophotometric analyses performed, the beverage was prepared using the infusion method described in the coffee sensory analysis protocol by the Specialty Coffee Association of America.[7] In this process, 1.37 g of ground coffee was brought into contact with 25 mL of water at a temperature of 90 ºC for 5 minutes. After this time, the beverage was filtered using conventional filter paper and then diluted with water at a 1:50 (v/v) ratio.

The beverage preparation was carried out using the percolation method, adapted from Alcantara, Spíndola, and Melchert, for the chromatographic analyses of non-volatile compounds.[24] In this process, 15 mL of preheated water at 90 ºC was poured over 1.0 g of ground coffee. Subsequently, the mixture was filtered using conventional filter paper. The resulting extract was filtered using a 0.45 µm PTFE syringe filter for future injection into the chromatograph.

Determination of total phenolic compounds

Total phenolic compounds were determined using the Folin-Ciocalteu method with a UV-Vis spectrophotometer (Agilent, model Cary 60) equipped with a 1 cm path length cuvette for reading, and gallic acid was used as the analytical standard.[26]

A 600 µL aliquot of the diluted sample (1:50, v/v) was transferred to a Falcon® tube. Subsequently, 3000 µL of 10% (v/v) Folin-Ciocalteu reagent solution was added. After 5 minutes, 2250 µL of a 4% (w/v) sodium carbonate solution was added. The resulting mixture was kept at room temperature and protected from light for 2 hours. Subsequently, the spectrophotometer measured the solution at a wavelength of 770 nm.[26]

The analytical curve was established in a concentration range of 10 to 50 mg L^{-1} of gallic acid (GAE). The results were expressed in milligrams of GAE per 100 g of ground-roasted coffee. All analyses were performed in triplicate to ensure greater precision in the results.[26-28]

Determination of non-volatile compounds

Non-volatile compounds were separated using a high-performance liquid chromatograph (Agilent, model 1100) equipped with a UV detector (Agilent, model VWD G1314A). A 30 µL sample was injected into a reverse-phase C18 column (Agilent, model Eclipse XDB, 4.6 x 250 mm, 5 µm). The mobile phase consisted of solvent A (5% v/v acetic acid in water) and solvent B (acetonitrile), using isocratic elution with a composition of 95% A and 5% B. The flow rate was set at 0.8 mL min^{-1}, with a total run time of 55 minutes.[28,29]

Signals were measured and identified by comparing the chromatographic profile with that of analytical standards at 280 nm for caffeine, 5-hydroxymethylfurfural, 3,4-dihydroxybenzoic acid, and gallic acid, and 320 nm for chlorogenic acid.

Determination of volatile compounds

Volatile compounds were determined using a gas chromatograph (PerkinElmer, model Clarus 600) equipped with a flame ionization detector (FID) and an automatic headspace sampler (CTC Analytics, Pal System). The column used was NOVA-WAX (Nova Analytics), with dimensions of 30 m in length, 0.25 mm in diameter, and a stationary phase of 0.25 µm.[23,30,31] In the headspace method, a sample weighing 0.55 g

was placed in a 20 mL vial. Heating occurred for 5 minutes at an oven temperature of 80 °C, with agitation at 500 rpm. The collected and injected volume was 1.5 mL, injected at a speed of 500 µL s^{-1} with a split ratio of 1:30.[23,30,31] Additionally, the injector temperature was maintained at 150 °C, and the detector at 300 °C. The column temperature was initially programmed to 45 °C for 3 minutes. It was then gradually increased at a rate of 7.5 ºC min^{-1} until reaching 60 ºC, followed by a rate of 15 ºC min^{-1} up to 165 °C, with a total run time of 12 minutes. High-purity gases (99.999%) were employed, including nitrogen at a flow rate of 1.2 mL min^{-1}, hydrogen at 45 mL min^{-1}, and synthetic air at 450 mL min^{-1}.[23,30,31]

The identification of the compounds (acetaldehyde, acetone, methanol, ethanol, diacetyl, 3-methyl-butanol alcohol and 2-methylpyrazine) was based on the comparison of the retention time with the injection of the analytical standards and by the values obtained from the linear retention indexes (LRI), which were determined according to Equation 1.

$$LRI = 100 \times \left(\frac{t_c - t_n}{t_{n+1} - t_n} + n \right) \qquad \text{Equation 1}$$

where:

t_c is the retention time of the compound of interest

t_{n+1} is the retention time of the subsequent hydrocarbon

n is the number of carbons of the previous hydrocarbon

To calculate the LRI, the retention times of linear alkanes (C7-C40, Sigma-Aldrich, 49452-U) were obtained under the same experimental conditions. The values obtained were compared with the literature and with the NIST Chemistry WebBook.[32-38]

Furthermore, the ethanol/methanol ratio was calculated using the concentration values of the compounds as reported by Gibson apud Flament.[39] Since this ratio presents a flavor known as “Solai,” a higher ratio is associated with higher-quality coffees.[39]

Limit of detection (LOD) and quantification (LOQ)

For both total phenolic compounds and volatile and non-volatile compounds, the limit of quantification (LOQ) was calculated using the minimum concentration of each sample, and the limit of detection (LOD) was determined using Equation 2.[40]

$$LOD = 3.3 \times \frac{s}{b} \qquad \text{Equation 2}$$

where:

s is the estimate of the standard deviation of the regression curve

b is the slope of the analytical calibration curve

Calibration curve precision was assessed by the percentage relative standard deviation (RSD) of triplicate signals at each concentration level. All RSD values were below 20%.[41]

Statistical analysis

The obtained contents of the evaluated compounds were subjected to the unpaired Student’s *t*-test with a significance level of 95% (α = 0.05). The Shapiro-Wilk, Mann-Whitney, and Levene tests were also applied to verify the normality and homogeneity of the results. In addition, patterns or groupings that could differentiate specialty coffees from traditional coffees were investigated using principal component analysis (PCA). All analyses were performed using **OriginPro® 2024b software**.

RESULTS AND DISCUSSION

Total phenolic compounds

The analytical curve for the total phenolic compounds (TPC) analysis is described as follows: for concentrations ranging from 10 to 50 mg L^{-1}, the regression equation is *A*bs = 0.006 + 0.0088 C, with a coefficient of determination (R^2) of 0.999. The LOD and LOQ were estimated at 0.3 and 10 mg L^{-1}, respectively. Table II presents the content of total phenolic compounds for all coffee samples, including both specialty and traditional varieties.

Table II. Total phenolic compounds content in specialty and traditional coffee samples

Sample	Mean content (mg GAE 100 g^{-1} of coffee)
S1	3490 ± 129
S2	3751 ± 28
S3	3856 ± 68
S4	3638 ± 96
S5	3831 ± 49
S6	3584 ± 108
Mean	3692 ± 106a (RSD 3%)
T1	3377 ± 25
T2	3968 ± 29
T3	3673 ± 86
T4	3666 ± 79
T5	3371 ± 34
T6	3806 ± 40
Mean	3643 ± 207a (RSD 6%)

Note: means followed by the same letter in the column do not differ by Student's *t*-test at the 95% confidence level (α = 0.05). RSD = Relative Standard Deviation.

The mean content of GAE in mg 100 g^{-1} of roasted coffee was 3692 ± 145 for specialty and 3643 ± 236 for traditional. The samples with the highest and lowest concentrations of TPC were the traditional samples T2 and T5, with 3968 and 3371 mg GAE 100 g^{-1} of coffee, respectively. Furthermore, the results of the Student's *t*-test at 95% confidence did not indicate a statistically significant difference between the coffees due to standardized roasting processes, as more intense roasts tend to degrade phenolic compounds, as stated by Alcantara, Dresch, and Melchert.[24]

The average values of total phenolic compounds obtained fall within the range reported by Alcantara, Dresch, and Melchert[24] which ranged from 1368 to 4332 mg GAE 100 g^{-1} of roasted coffee. The study by Almeida and Benassi[42] reported a range of 1910 ± 40 to 3550 ± 40 mg GAE 100 g^{-1} of roasted coffee for total phenolics in commercial traditional coffees, with values in this study falling at the upper end of that range. It is noteworthy that neither study standardized the roasting process.

Furthermore, it is noted that the relative standard deviation (RSD - Table II) for the Special samples was 3%, while for the Traditional samples it was 6%, demonstrating that the traditional samples have a greater dispersion in their phenolic composition. The greater variability of the traditional samples is likely due to less standardized agricultural practices and edaphoclimatic factors, which differ from those observed and practiced in samples of specialty coffees.

Non-volatile compounds

Table III presents the retention time, regression equations, correlation coefficients, LODs, and LOQs for each non-volatile compound analyzed. The chromatographic analysis enabled the identification and quantification of the following non-volatile compounds in specialty and traditional coffee samples: caffeine, chlorogenic acid, gallic acid, 5-HMF, and 3,4-dihydroxybenzoic acid (Table IV). When evaluating the RSD range observed in Table IV (13–22% for the Special samples and 14–36% for the Traditional samples), it essentially reflects the intrinsic heterogeneity of the coffee samples, since the grinding and roasting procedure were standardized. Factors such as origin, cultivar, and post-harvest conditions will significantly impact the concentration of these compounds.

Table III. Analytical parameters of non-volatile compounds

Compounds	Retention time (min)	Concentration (mg L^{-1})	Regression equation	R^2	LOQ (mg L^{-1})	LOD (mg L^{-1})
Caffeine	21.6	200 – 950	Area = -355 + 88.2 C	0.999	200	6.1
Chlorogenic acid	12.6	100 – 1000	Area = 380.3 + 59.7 C	0.999	100	13.2
Gallic acid	4.2	10 – 100	Area = 720.2 + 70.4 C	0.992	10	9.0
5-hydroxymethylfurfural	6.2	2 – 40	Area = 15.9 + 261 C	0.999	2.0	0.3
3,4-dihydroxybenzoic acid	7.1	12.5 – 200	Area = -11.1 + 57.2 C	0.999	12.5	1.0

Table IV. Non-volatile compound content in specialty and traditional coffees

Sample	Mean of non-volatile compounds ± standard deviation (mg 100 g^{-1} of ground roasted coffee)				
	Caffeine	Chlorogenic acid	Gallic acid	5-HMF	3,4-dihydroxybenzoic acid
S1	871 ± 12	1004 ± 11	24 ± 1	31 ± 1	122 ± 2
S2	881 ± 43	969 ± 41	23 ± 2	31 ± 1	111 ± 6
S3	607 ± 31	755 ± 44	12 ± 1	28 ± 2	84 ± 5
S4	909 ± 79	910 ± 81	19 ± 1	27 ± 3	102 ± 14
S5	939 ± 31	729 ± 45	28 ± 1	18 ± 1	87 ± 5
S6	1006 ± 87	965 ± 31	28 ± 4	36 ± 1	112 ± 5
Mean	860 ± 144a (RSD 17%)	889 ± 118a (RSD 13%)	23 ± 5a (RSD 22%)	28 ± 6a (RSD 21%)	103 ± 15a (RSD 15%)
T1	507 ± 35	453 ± 15	6 ± 1	15 ± 4	47 ± 13
T2	759 ± 90	645 ± 83	16 ± 5	18 ± 2	82 ± 12

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Table IV. Non-volatile compound content in specialty and traditional coffees (continuation)

Sample	Mean of non-volatile compounds ± standard deviation (mg 100 g^{-1} of ground roasted coffee)				
	Caffeine	Chlorogenic acid	Gallic acid	5-HMF	3,4-dihydroxybenzoic acid
T3	642 ± 16	595 ± 35	12 ± 1	20 ± 1	71 ± 5
T4	670 ± 11	570 ± 10	18 ± 1	16 ± 1	69 ± 2
T5	540 ± 5	505 ± 37	11 ± 1	11 ± 1	65 ± 4
T6	748 ± 42	544 ± 99	20 ± 2	15 ± 3	65 ± 11
Mean	635 ± 104b (RSD 16%)	558 ± 78b (RSD 14%)	14 ± 5b (RSD 36%)	16 ± 3b (RSD 19%)	66 ± 13b (RSD 20%)

Note: means followed by the same letter in the column do not differ by Student's *t*-test at the 95% confidence level (α = 0.05).
RSD = Relative Standard Deviation.

According to the results obtained for caffeine concentrations, traditional coffees generally had lower caffeine content compared to specialty coffees, as shown in Table IV, with mean values of 860 ± 144 and 635 ± 104 mg 100 g^{-1} for specialty and traditional coffees, respectively. The specialty and traditional coffee samples showed a statistically significant difference when performing the Student's *t*-test at a 95% confidence level. These resulting values were slightly below those found by Kitzberger, Scholz, and Benassi,[43] whose caffeine variation ranged from 1038 to 1386 mg 100 g^{-1}, and by Duarte, Pereira, and Farah,[44] who reported a variation from 990 to 1540 mg 100 g^{-1}. In both studies, the analyzed coffees were classified as traditional and belonged to the Arabica species, having undergone different post-harvest treatments. On the other hand, when analyzing non-volatile compounds in roasted and ground Brazilian coffees, Alcantara, Dresch, and Melchert[24] obtained an average of 3440 mg 100 g^{-1} for specialty coffees and 4890 mg 100 g^{-1} for traditional coffees to caffeine content. Preparation methods, grain grinding type, and the origin and variety of the coffee may influence differences between the values found in the literature. It is worth noting that caffeine is present in higher amounts in the *Coffea canephora* species. Furthermore, commercially marketed coffees are typically composed of blends that combine the species *C. canephora* and *C. arabica*.[45-47]

Regarding chlorogenic acid, specialty coffees exhibited a range of 729 ± 45 to 1004 ± 12 mg 100 g^{-1}, resulting in an average of 889 ± 118 mg 100 g^{-1}. For traditional coffees, the range for this compound was from 453 ± 15 to 645 ± 83 mg 100 g^{-1}, with an average of 558 ± 78 mg 100 g^{-1}. According to the Student's *t*-test analysis with a 95% confidence level, specialty and traditional coffees exhibited statistically significant differences. The values obtained for this compound were slightly lower than those found by Alcantara, Dresch, and Melchert,[24] whose range was from 1502 ± 5 to 2276 ± 19 mg 100 g^{-1} for specialty coffees and from 559 ± 24 to 1237 mg 100 g^{-1} for traditional coffees. Similarly, both coffee categories showed statistically significant differences, with the specialty category showing higher levels of chlorogenic acid. The presence of chlorogenic acids significantly influences the sensory qualities of coffee due to their considerable thermal degradation during the roasting process. This process leads to the formation of volatile compounds that are crucial to the beverage's flavor characteristics. However, severe roasting conditions can result in substantial losses of chlorogenic acids, with only 5% of the compound potentially remaining. Moreover, chlorogenic acids are also associated with parameters such as acidity, astringency, and bitterness, playing an essential role in the overall acceptance and quality of the beverage.[48-50]

Like caffeine, sample T1 was also the traditional category sample with the lowest amount of gallic acid, at 6 ± 1 mg 100 g^{-1}. The highest value for this acid (28 ± 4 mg 100 g^{-1}) was found in specialty sample S6. The average for specialty samples was 23 ± 5 mg 100 g^{-1}, while for traditional samples, it was 14 ± 5 mg 100 g^{-1}. The Student's *t*-test results at a 95% confidence level indicated statistical differences

between the two classifications. The results obtained in this study were consistent with those presented by Alkaltham *et al*.[51] In their investigation of the effects of different roasting methods, the researchers quantified the presence of gallic acid in samples of green coffee, microwave-roasted coffee, and oven-roasted coffee. The values found were 7 mg 100 g^{-1} for green coffee, 16 mg 100 g^{-1} for microwave-roasted coffee, and 20 mg 100 g^{-1} for oven-roasted coffee.

Regarding the results obtained for the 5-HMF compound, the average from chromatographic analyses was 28 ± 6 mg 100 g^{-1} for specialty coffees and 16 ± 3 mg 100 g^{-1} for traditional coffees. As observed with non-volatile compounds evaluated earlier, specialty sample S6 exhibited the highest content, while the lowest was found in traditional sample T5. The range for 5-HMF varied from 12 ± 1 to 51 ± 5 mg 100 g^{-1}, and according to the Student's *t*-test at a 95% confidence level, specialty and traditional coffees were statistically different. The 5-HMF content for specialty coffee samples was lower than that obtained by Alcantara, Dresch, and Melchert,[24] whose range was approximately 80 to 120 mg 100 g^{-1}, and no detectable levels of 5-HMF were found in traditional samples. On the other hand, the resulting values fall within the range obtained in the study by Vignoli *et al*.,[29] where the highest content of 5-HMF reached 230 mg 100 g^{-1} when evaluating the effects of roasting processes on various bioactive compounds of Arabica coffee. Three traditional coffee samples were evaluated by Francisco *et al*.[52] obtained 72, 58, and 26 mg 100 g^{-1} of this compound. The variation in 5-HMF quantification in the literature can be explained by the degree of roast used in each sample, as 5-HMF is considered a thermal marker and is present in lower quantities at the beginning of this process.[29] Murkovic and Bornik[53] observed an approximately 160% increase in 5-HMF after a roasting process lasting 3 minutes at 240 °C.

For 3,4-dihydroxybenzoic acid, the analyzed samples ranged from 87 ± 5 to 122 ± 2 mg 100 g^{-1} of ground roasted coffee. Among the specialty samples, S1 exhibited the highest content of this compound, averaging 103 ± 15 mg 100 g^{-1}. Traditional coffee samples had an average of 66 ± 13 mg 100 g^{-1}, with sample T1 showing the lowest content of 3,4-hydroxybenzoic acid. Statistically, these two coffee classifications differed after applying for the Student's *t*-test at a 95% confidence level. These values were lower than those found by Alkaltham *et al*.[51] who analyzed the effects of different roasting methods and obtained quantifications of 463 mg 100 g^{-1} for 3,4-hydroxybenzoic acid in green coffee, 599 mg 100 g^{-1} for microwave-roasted coffee, and 617 mg 100 g^{-1} for oven-roasted coffee. For Brazilian coffees, research conducted by Uslu[54] observed variations in levels of 3,4-hydroxybenzoic acid ranging from 15 to 40 mg 100 g^{-1} of coffee. Similarly, in Colombian coffees, this substance exhibited an even wider range, varying from 13 to 61 mg 100 g^{-1}. These variations were noted during the investigation of the influences of different extraction methods and times on the phenolic compound content in coffee beans, and were significantly smaller than those obtained in the current study. Among specialty coffees, sample S6 exhibited the highest quantities of caffeine and 5-hydroxymethylfurfural, while sample S5 had the highest levels of gallic acid. Sample S1 showed the highest amount of 3,4-hydroxybenzoic acid. On the other hand, traditional coffee samples such as T1 and T5 generally showed the lowest quantities of these compounds.

Volatile compounds

The calculated linear retention index (LRI) values were systematically compared with those reported in the literature for columns of similar polarity to ensure the identification and characterization of volatile compounds. Seven compounds (Table V) were identified by GC-FID using external standards and validated with LRI values referenced in previous studies. The LRI values obtained in this study for each compound analyzed showed strong agreement with the values established in the literature, highlighting the reliability of the identification process.

Table V. Compounds identified in coffee samples by GC-FID and comparison of linear retention indices (LRI) with literature values

Compound	LRI experimental	LRI literature	Ref. literature	LRI NIST	Ref. NIST
Acetaldehyde	706	702	37	700	
Acetone	823	823	37	814	
Methanol	915	915	33	911	
Ethanol	952	944	34	950	38
Diacetyl	990	985	32	988	
3-methyl-butanol	1229	1229	36	1229	
2-methylpyrazine	1296	1297	35	1288	

Table VI presents the linear regression equations, correlation coefficients, LODs, and LOQs for each volatile compound analyzed. Through chromatographic analysis, the following volatile compounds were identified and quantified in samples of both traditional and specialty coffees: acetaldehyde, acetone, methanol, ethanol, diacetyl, 3-methyl-butanol, and ethanol/methanol. These results are detailed in Table VII, in which the average density of 0.343 g mL^{-1} for roasted coffee beans[55,56] was adopted to express the concentrations in µg 100 g^{-1} of coffee samples. Furthermore, the RSD values in Table VII reflect the intrinsic variability of volatile compounds between the batches of the *Circuito das Águas Paulista*, even with standardized roasting and grinding, evidencing the strong influence of edaphoclimatic factors (altitude, microclimate, and seasonal events) on the aromatic composition.

Table VI. Analytical parameters of volatile compounds

Compounds	Concentration (mg L^{-1})	Regression equation	R^2	LOQ (mg L^{-1})	LOD (mg L^{-1})
Acetaldehyde	0.25 – 40	Area = -0.56 + 89.52 C	0.999	0.25	0.07
Acetone	0.25 – 40	Area = -2.07 + 83.04 C	0.999	0.25	0.08
Methanol	5 – 900	Area = -0.95 + 3.82 C	0.997	5.00	2.63
Ethanol	0.5 – 100 100 – 750	Area = 1.82 + 16.39 C Area = 1241.24 + 6.93 C	0.999 0.992	0.50	0.10
Diacetyl	0.5 – 20	Area = -7.76 + 26.12 C	0.978	0.50	0.26
3-methyl-butanol	0.01 – 0.5 0.5 – 2.5	Area = 0.58 + 62.39 C Area = 0.27 + 63.82 C	0.999 0.999	0.01	0.009
2-Methylpyrazine	1.99 – 100	Area = -4.77 + 9.17 C	0.999	1.99	0.18

The result of the Student's *t*-test at a 95% confidence level indicated no statistically significant difference between the mean acetaldehyde content in samples of specialty and traditional coffees (Table VII). In the specialty coffee group, the variation ranged from 0.04 ± 0.01 to 0.29 ± 0.15 µg 100 g^{-1} of coffee, while in the traditional coffee group, it ranged from 0.12 ± 0.01 to 0.16 ± 0.03 µg 100 g^{-1} of coffee. These values were lower than those obtained by Kalschne *et al*.,[57] who evaluated the influence of steam treatment to

improve the volatile compound profile of defective roasted robusta coffees, obtaining a range of 32.74 to 57.59 µg 100 g^{-1} for acetaldehyde content. Discrepancies in results compared to the literature may be attributed to variations in coffee bean quality. Acetaldehyde can be considered an indicator of quality, as it is found in lower concentrations in higher-quality coffee beverages and is characterized by a pungent and putrid odor.[58,59] On the other hand, when comparing specialty and traditional green coffees, Gomes, Bortoleto, and Melchert[60] found statistically significant differences between the samples. With variations from 3.66 ± 0.25 to 37.68 ± 1.90 µg 100 g^{-1} for specialty green coffees and from 1.27 ± 0.30 to 11.73 ± 1.05 µg 100 g^{-1} for traditional green coffees, with acetaldehyde present in higher quantities in some specialty coffee samples. Despite contradicting the findings of Rodriguez *et al*.,[58] this difference in acetaldehyde content can be justified by climate characteristics, altitude, and the extraction process.[61,62]

Despite evaluating volatile compounds in green coffees, Gomes, Bortoleto, and Melchert[23] also did not obtain statistically significant values in differentiating between specialty and traditional coffees based on acetone quantification. The variation observed from 1.52 ± 0.15 to 60.54 ± 9.65 µg 100 g^{-1} in specialty coffee samples and from 6.08 ± 1.68 to 35.07 ± 1.42 µg 100 g^{-1} in traditional ones. These values were higher than those obtained in the present study, where the acetone content in roasted coffees was evaluated. The variation in acetone levels may be related to the extraction method used during beverage preparation. For instance, in a study conducted by Chavez, Mendoza, and Caetano,[39] where five different infusion methods were tested, this volatile compound was detected only in coffee prepared through the French press method. This suggests that the extraction method may play a significant role in determining the chemical composition of coffee, including the presence or absence of certain volatile compounds, such as acetone. Additionally, the quantification of this compound may also be influenced by the type of grain processing (wet or dry) and milder climatic conditions.[39,63]

Table VII. Content of volatile compounds in specialty and traditional coffees

Sample	Mean of volatile compounds ± standard deviation (μg 100 g^{-1} of coffee samples)							
	Acetaldehyde	**Acetone**	**Methanol**	**Ethanol**	**Ethanol/ Methanol Ratio**	**Diacetyl**	**3-methyl-butanol**	**2-Methylpyrazine**
S1	0.04 ± 0.01	0.21 ± 0.01	5.16 ± 4.10	3.92 ± 1.04	1.42 ± 0.02	108.28 ± 8.44	7.28 ± 0.11	2.56 ± 0.29
S2	0.04 ± 0.01	0.20 ± 0.02	8.00 ± 0.99	0.93 ± 0.03	0.11 ± 0.02	91.83 ± 2.29	6.63 ± 0.71	2.67 ± 0.09
S3	0.18 ± 0.04	0.20 ± 0.05	17.02 ± 0.75	0.87 ± 0.05	0.07 ± 0.03	97.23 ± 7.48	7.49 ± 0.63	2.41 ± 0.30
S4	0.14 ± 0.09	0.17 ± 0.02	18.18 ± 0.37	3.18 ± 0.06	0.21 ± 0.06	82.14 ± 13.35	13.45 ± 1.00	3.14 ± 0.06
S5	0.19 ± 0.02	0.24 ± 0.02	2.17 ± 0.73	0.44 ± 0.12	0.15 ± 0.03	81.31 ± 14.05	6.11 ± 0.51	2.57 ± 0.18
S6	0.29 ± 0.15	0.29 ± 0.01	10.99 ± 1.26	28.52 ± 0.45	2.61 ± 0.26	102.88 ± 15.43	8.91 ± 0.51	2.75 ± 0.29
Mean	0.15 ± 0.09a (RSD 60%)	0.22 ± 0.04a (RSD 18%)	10.34 ± 6.28a (RSD 61%)	6.31 ± 10.97a (RSD 174%)	0.76 ± 1.04a (RSD 18%)	93.94 ± 10.95a (RSD 12%)	8.31 ± 2.69a (RSD 32%)	2.68 ± 0.28a (RSD 10%)
T1	0.14 ± 0.02	0.18 ± 0.02	14.81 ± 1.19	1.10 ± 0.09	0.07 ± 0.01	37.01 ± 3.29	8.60 ± 0.72	2.80 ± 0.07
T2	0.15 ± 0.01	0.19 ± 0.01	10.49 ± 0.45	1.00 ± 0.04	0.10 ± 0.01	57.81 ± 2.49	6.98 ± 0.94	2.98 ± 0.16
T3	0.16 ± 0.03	0.19 ± 0.04	10.85 ± 0.95	1.00 ± 0.07	0.09 ± 0.01	51.60 ± 6.41	6.93 ± 0.94	2.68 ± 0.23
T4	0.13 ± 0.01	0.17 ± 0.01	9.18 ± 0.63	1.00 ± 0.06	0.11 ± 0.01	43.80 ± 0.73	7.29 ± 0.30	2.51 ± 0.10
T5	0.12 ± 0.01	0.17 ± 0.01	7.83 ± 1.20	0.91 ± 0.00	0.11 ± 0.01	44.18 ± 5.11	7.51 ± 0.45	2.41 ± 0.13
T6	0.16 ± 0.01	0.24 ± 0.01	8.03 ± 0.13	1.09 ± 0.02	0.14 ± 0.01	64.14 ± 4.69	7.41 ± 0.20	3.38 ± 0.19
Mean	0.14 ± 0.02a (RSD 14%)	0.19 ± 0.02a (RSD 11%)	10.20 ± 2.57a (RSD 25%)	1.02 ± 0.07a (RSD 105%)	0.10 ± 0.02a (RSD 14%)	49.76 ± 10.04b (RSD 20%)	7.45 ± 0.61a (RSD 8%)	2.79 ± 0.35a (RSD 13%)

Note: means followed by the same letter in the column do not differ by Student's *t*-test at the 95% confidence level (α = 0.05), RSD = Relative Standard Deviation.

Methanol and ethanol are the alcohols most frequently identified in the volatile fraction of roasted coffees.[64] For methanol, specialty samples ranged from 2.17 ± 0.73 to 18.18 ± 0.37 μg 100 g^{-1}, while traditional samples varied from 7.83 ± 1.20 to 14.81 ± 1.19 μg 100 g^{-1}. Compared to the literature, these values were lower than those reported by Rhoades,[65] whose average methanol content was 83.0 μg 100 g^{-1} in beverages made with fresh coffee beans. Regarding ethanol, traditional coffees ranged from 0.87 ± 0.05 to 28.52 ± 0.45 μg 100 g^{-1} and did not follow a normal distribution, as indicated by the Shapiro-Wilk test. Ethanol showed a narrow range in traditional coffees, with samples ranging from 0.91 ± 0.0 to 1.10 ± 0.09 μg 100 g^{-1}. Moreover, this compound's quantification was closer to that of Rhoades[65] where the resulting averages ranged from 2.2 to 3.2 μg 100 g^{-1}. The variation in this compound may be related to coffee bean processing, with higher quantities found in wet processing.[66] The results obtained in the present study for both compounds also did not show statistically significant differences when comparing specialty and traditional coffee groups, as determined by the Mann-Whitney test and Student's *t*-test at a 95% confidence level.

Diacetyl was the only volatile compound evaluated that showed a statistically significant difference between the two coffee classifications, as determined by Student's *t*-test at a 95% confidence level. As shown in Table VII, mean values of 93.94 ± 10.95 μg 100 g^{-1} and 49.76 ± 10.04 μg 100 g^{-1} were found for specialty and traditional coffees, respectively. These results suggest the potential use of this volatile compound to differentiate between specialty and traditional coffees. Conversely, Toci and Farah[67] identified higher quantities of this compound in coffees made from defective beans, as its presence is generally undesired in other food types, such as beer.[68] However, these values were lower than those obtained in the study conducted by Procida *et al*.,[69] diacetyl concentrations ranged from 195.9 to 881.8 μg 100 g^{-1} in roasted coffees of robusta and arabica species from various geographic regions. The coffee bean roasting process can influence the diacetyl content. Hyong *et al.*[70] observed that the concentration of this compound significantly increased as roasting temperature and time increased. The quantification of diacetyl may also be influenced by the method of beverage preparation.[71]

Specialty coffee samples showed a variation range of 6.11 ± 0.51 to 13.45 ± 1.00 μg 100 g^{-1} for 3-methyl-butanol content with a resulting mean of 8.31 ± 2.69 μg 100 g^{-1}, while traditional coffee samples ranged from 6.93 ± 0.94 to 8.60 ± 0.72 μg 100 g^{-1} with a mean of 7.45 ± 0.61 μg 100 g^{-1}. Despite the higher mean of specialty samples, there was no significant difference between these two classifications when applying the Student's *t*-test at a 95% confidence level.

3-methyl-butanol is associated with coffee processing, especially wet processing, and its presence is linked to microbial metabolic reactions during the process, being found in higher quantities in green coffees.[43] However, the results obtained in this study for roasted coffees were relatively close to those obtained by Gomes, Bortoleto, and Melchert[60] for green coffees, the variation in specialty samples was from 2.57 ± 0.48 to 7.67 ± 0.5 μg 100 g^{-1} and from 0.33 to 16.89 ± 2.28 μg 100 g^{-1} in traditional samples.

In the specialty coffee group, concentrations of 2-methylpyrazine ranged from 2.41 ± 0.30 to 3.14 ± 0.06 μg 100 g^{-1}, resulting in a mean of 2.68 ± 0.28 μg 100 g^{-1}. Meanwhile, in the traditional coffee group, the variation was from 2.41 ± 0.13 to 3.38 ± 0.19 μg 100 g^{-1}, with a mean of 2.79 ± 0.35 μg 100 g^{-1}. Upon conducting a Student's *t*-test at a 95% confidence level to compare the means between the two sample groups, it was found that there was no significant difference in the levels of 2-methylpyrazine between specialty and traditional coffees.

Based on the comparison of the results obtained in this study with data found in the literature, it was observed that the values of 2-methylpyrazine were significantly lower compared to those reported by Wang *et al*.[72] The range for this compound varied between 2041 and 3418 μg g^{-1} when evaluating the chemical composition of roasted coffee beans from 12 different cultivars.

Similarly, the results for 2-methylpyrazine were considerably lower than those obtained by Cheong *et al.*,[73] who evaluated Arabica coffees from various geographical regions. Thus, the discrepancy in 2-methylpyrazine levels may be related to the geographical origin of the coffee beans, as evidenced in the study by Toledo *et al.*[74] In that study, the use of 2-methylpyrazine as a marker for geographical origin achieved approximately 90.9% correct classifications, highlighting the importance of geographical context in the chemical composition

and sensory characteristics of the analyzed coffees. No statistically significant differences were found in the quantification of the most volatile compounds investigated in this study between traditional and specialty coffee samples.

Principal Component Analysis (PCA)

The analysis incorporated various variables, including non-volatile compounds: caffeine (CAF), chlorogenic acid (CGA), gallic acid (EGA), 5-hydroxymethylfurfural, and 3,4-hydroxybenzoic acid (3,4-HB); and volatile compounds: acetaldehyde (AcH), acetone, methanol (MeOH), ethanol (EtOH), ethanol/methanol ratio, diacetyl, 3-methyl-butanol (3-MeB), and 2-methylpyrazine (2-MeP).

Additionally, altitude and cupping scores were considered. PCA was conducted to identify patterns or groupings that differentiate specialty coffees from traditional ones based on these chemical and sensory variables. Figure 1 displays the plot from principal component analysis encompassing the variables of non-volatile compounds, altitude, and cupping scores.

When analyzing the plots from Figure 1, two distinct groups were formed between specialty and traditional coffees based on non-volatile compounds, altitude, and cupping scores (Figure 1a), except for samples S3 and T2. Coffee sample S3 stood out among the specialty coffees, positioned on the negative side of the x-axis. The behavior of this sample in PCA can be attributed to its lower levels of caffeine, gallic acid, and 3,4-hydroxybenzoic acid, resulting in a lower score compared to other specialty coffees. Additionally, sample S3 has the second lowest altitude (after S6) and the second lowest levels of chlorogenic acid and 5-hydroxymethylfurfural.

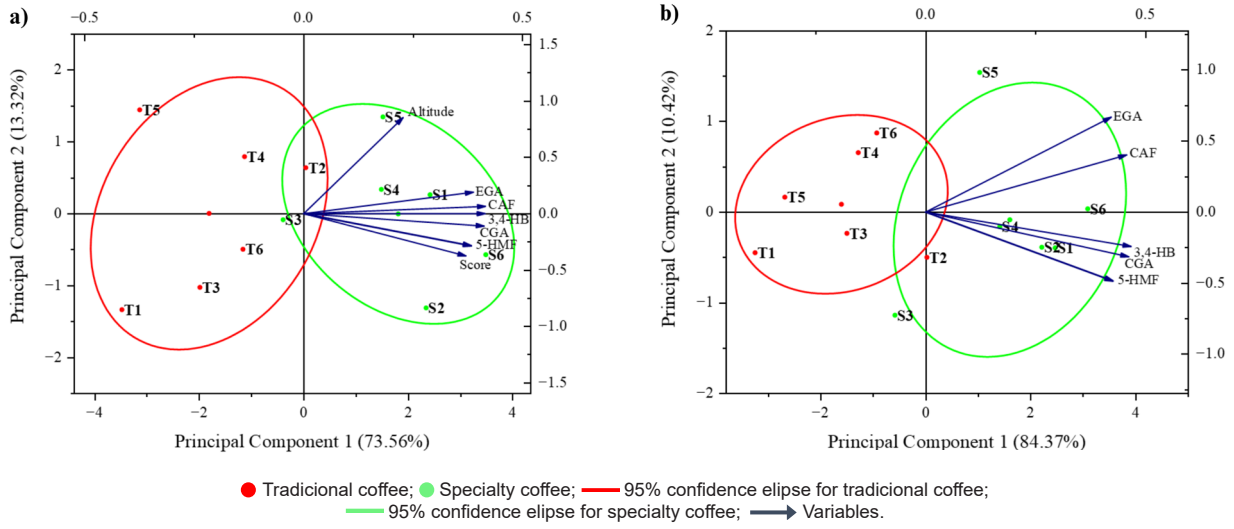

Figure 1. Biplot of the first two principal components with non-volatile compound variables, altitude, and scores (a) and (b), considering only non-volatile compounds for specialty and traditional coffees. (caffeine – CAF, chlorogenic acid – CGA, gallic acid – EGA, 5-hydroxymethylfurfural – 5HMF, and 3,4-hydroxybenzoic acid – 3,4-HB).

To provide a comprehensive evaluation, additional principal component analyses were conducted to investigate the impact of volatile compounds, considering both altitude and cupping scores. Furthermore, the relationship between these volatile and non-volatile compounds was examined; the results of these analyses are depicted in Figure 2.

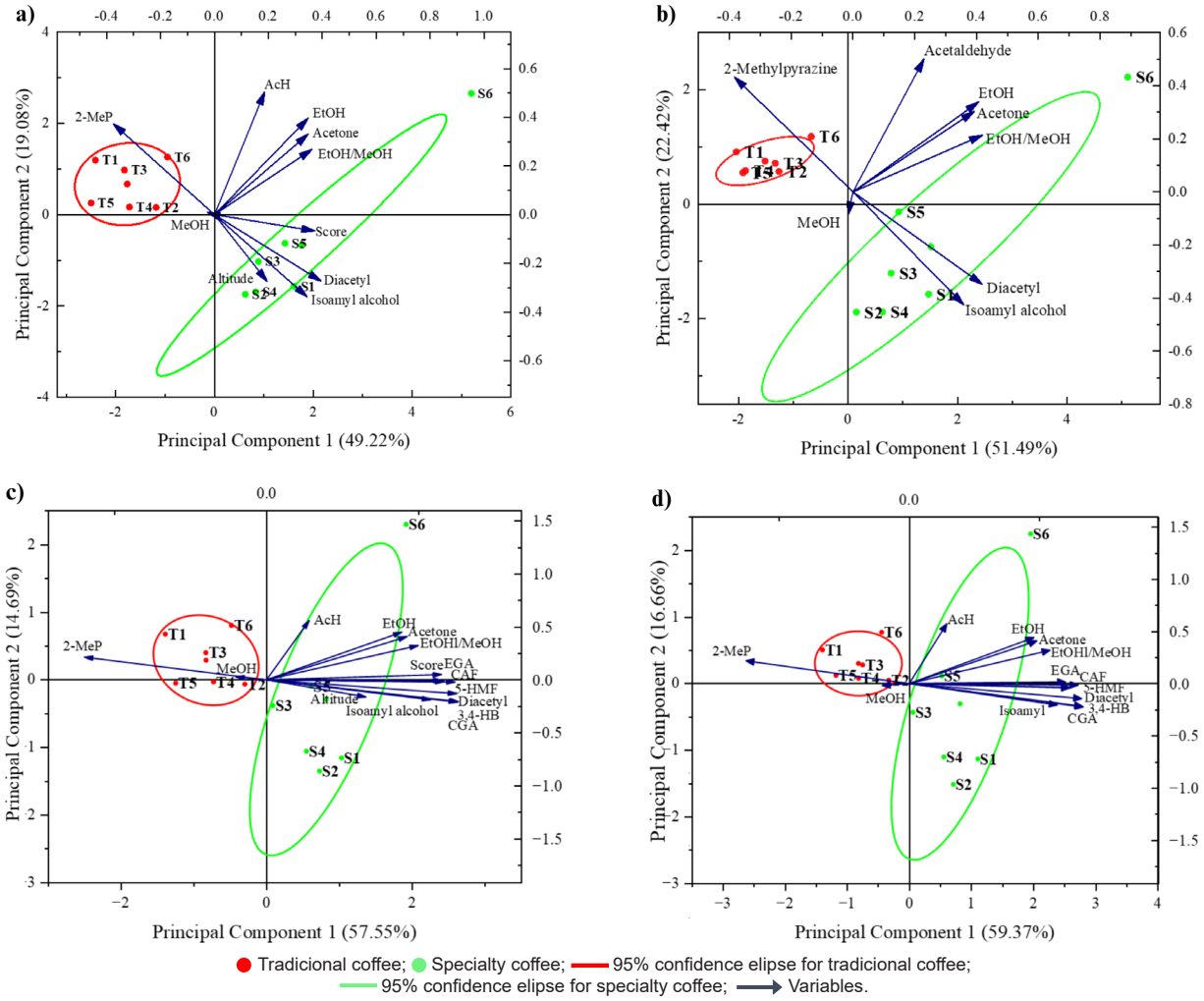

Figure 2. Biplot of the first two principal components with volatile compound variables, altitude, and scores (a); volatile compounds excluding altitude and ratings (b); all evaluated variables (c); and all evaluated variables excluding altitude and ratings (d) for specialty and traditional coffees. (caffeine – CAF, chlorogenic acid – CGA, gallic acid – EGA, 5-hydroxymethylfurfural – 5HMF, 3,4-hydroxybenzoic acid – 3,4-HB, acetaldehyde – AcH, methanol – MeOH, ethanol – EtOH, 3-methyl-butanol – 3-MeB, and 2-methylpyrazine – 2-MeP).

The analysis of Figure 2 reveals the identification of two distinct clusters: one formed by specialty coffee samples (in green) and another by traditional coffee samples (in red), with no overlapping samples. This separation is most pronounced along the first principal component (PC1), essential in distinguishing the two coffee categories. Optimal clustering was achieved without including altitude and cupping scores, with PC1 accounting for 51.49% (Figure 2b) and 59.37% (Figure 2d) of the total variance.

Notably, the volatile compound 2-methylpyrazine was particularly influential in traditional coffee samples, suggesting its significant role in differentiating these coffees, which may be due to variations in processing methods. Although prior studies indicate a stronger association between 2-methylpyrazine and wet-processed specialty coffees, this study also highlights its relevance in traditional coffee samples.[43]

Further, diacetyl and 3-methyl-butanol appear to characterize specialty coffee samples. While diacetyl is typically deemed undesirable in food products,[67,68] 3-methyl-butanol is consistent with findings linking it to wet processing, commonly employed in specialty coffee production.[75]

Comparison between harvests

To assess the impact of the frost that occurred during the 2020/2021 harvest period, five samples were collected from the same local producers during a non-frost harvest period (2022/2023), following the same methodology for total phenolic compounds, non-volatile compounds, and volatile compounds. These comparisons provide insight into how environmental stressors, such as frost, affect coffee quality and sensory characteristics.

Table VIII quantifies the total phenolic content and non-volatile and volatile compounds in coffee from the 2020/2021 and 2022/2023 harvests. The analysis shows that 5-hydroxymethylfurfural, acetone, and ethanol were the only compounds that did not exhibit statistically significant differences between the two harvest periods, as determined by a *t*-test at a 95% confidence level. In contrast, caffeine, along with other compounds, showed significant variations between the two periods, suggesting a potential correlation to the occurrence of frost. These findings highlight the impact of environmental stress on the chemical composition of coffee.

Table VIII. Compounds content by harvest

	mg 100 g^{-1} of coffee sample	
Compounds	**2020/2021**	**2022/2023**
TPC	3626 ± 166a	4314 ± 174b
5-hydroxymethylfurfural	21 ± 8a	25 ± 4a
3,4-dihydroxybenzoic acid	77 ± 23a	161 ± 17b
Chlorogenic acid	678 ± 181a	1189 ± 103b
Caffeine	758 ± 209a	3489 ± 126b
Gallic acid	19 ± 9a	11 ± 1b
	µg 100 g^{-1} of coffee sample	
Compounds	**2020/2021**	**2022/2023**
Acetaldehyde	0.18 ± 0.07a	0.43 ± 0.17a
Acetone	0.21 ± 0.03a	0.40 ± 0.16a
Methanol	7.88 ± 3.45a	1.78 ± 0.21b
Ethanol	1.99 ± 2.43a	3.07 ± 0.71a
Diacetyl	69.47 ± 19.07a	0.05 ± 0.03b
3-methyl-butanol	7.31 ± 0.78a	0.004 ± 0.001b
2-Methylpyrazine	2.90 ± 0.44a	1.16 ± 0.23b

Note: means followed by the same letter in the line do not differ by Student's *t*-test at the 95% confidence level (α = 0.05).

Figure 3 illustrates the Biplot of the first two principal components, including volatile and non-volatile compound variables, for specialty and traditional coffees from both harvest periods. PC1 accounts for 46.65% and PC2 for 21.38%. The samples identified by the letter N correspond to those obtained in the 2022/2023 harvest. When analyzing the plots from Figure 3, two distinct groups were formed between specialty and traditional coffees based on volatile and non-volatile compounds, except for sample N5, standing out among the specialty coffees, positioned on the negative side of the x-axis.

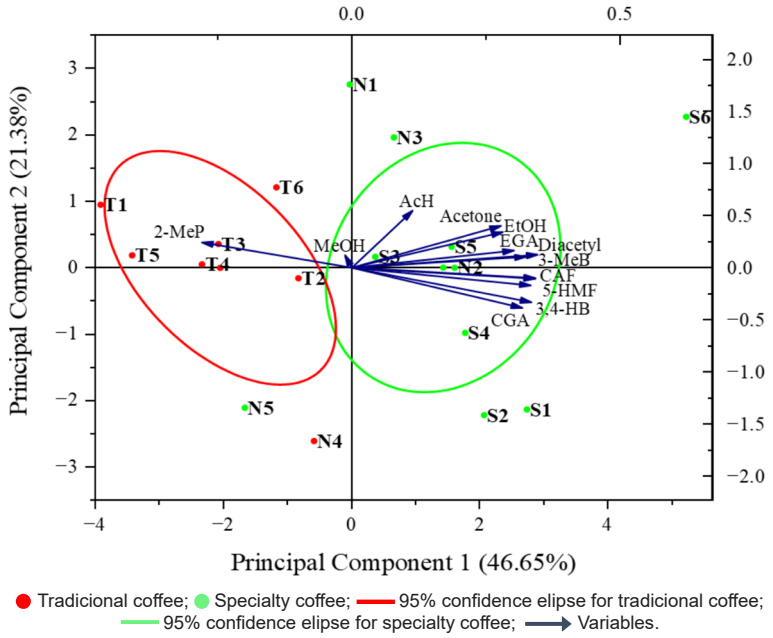

Figure 3. Biplot of the first two principal components with volatile and non-volatile compound variables for specialty and traditional coffees of both harvest periods. (caffeine – CAF, chlorogenic acid – CGA, gallic acid – EGA, 5-hydroxymethylfurfural – 5HMF, 3,4-hydroxybenzoic acid – 3,4-HB, acetaldehyde – AcH, methanol – MeOH, ethanol – EtOH, 3-methyl-butanol – 3-MeB, and 2-methylpyrazine – 2-MeP).

CONCLUSIONS

The chromatographic analysis of non-volatile compounds provided deeper insights into the distinctive characteristics between specialty and traditional coffees. This approach revealed significant differences in quantifying all evaluated non-volatile compounds: caffeine, chlorogenic acid, gallic acid, 5-hydroxymethylfurfural, and 3,4-hydroxybenzoic acid. These results highlight the chemical complexity of these samples and underscore the importance of examining a range of non-volatile compounds for a comprehensive understanding of the chemical profile and its relationship to the sensory aspects of coffee.

Regarding volatile compounds, diacetyl stood out as the only volatile compound assessed that showed statistically significant differences between the two coffee categories, according to the Student's *t*-test at a 95% confidence level. These findings suggest that diacetyl plays a crucial role in differentiating between specialty and traditional coffees.

PCA analysis proved to be extremely relevant for differentiating between specialty and traditional coffees. When addressing non-volatile compounds, including or excluding sensory scores and altitude, PCA showed a slight overlap of the confidence ellipses. However, this distinction became possible when volatile compounds were analyzed independently in a PCA encompassing all variables considered in this study. In both cases, analyses were conducted with and without sensory scores and altitude, yielding better results when these parameters were excluded. The volatile compound 2-methylpyrazine stood out in samples of coffees categorized as traditional, thus indicating a possible marker for lower-quality coffees from the *Circuito das Águas Paulista* region.

Combining chemical analyses with statistical tools played a prominent role in exploring the chemical composition of volatile and non-volatile species present in coffee. This approach facilitated correlating chemical composition with beverage classification, identifying clustering based on the similarity between specialty and traditional coffees.

Conflicts of interest

The authors declare no conflicts of interest regarding the publication of this article.

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