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Antioxidants, phenols, caffeine content and volatile compounds in coffee beverages obtained by different methods

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Abstract

The objective of the research was to evaluate the antioxidant activity, phenols and volatile compounds of different types coffee infusions. We worked with the Catimor coffee variety and used five methods to obtain the infusion (espresso, V60, siphon, French press and a traditional local method). For each infusion, the antioxidant capacity was determined with the 2,2-Diphenyl-1-Picrylhydrazyl and 2,2′-azinobis-3-ethylbenzothiazoline-6-sulfonic acid techniques, the phenolic content was determined with the Folin-Ciocalteu technique, and aromatic volatile compounds were determined with gas chromatography coupled with mass spectrometry. The extraction method that yielded the coffee infusions with the most antioxidant activity, phenolic compounds and caffeine content was espresso; however, this coffee had the fewest aromatic volatile compounds. Although they had lower antioxidant activity, the infusions obtained with the French press had the highest content of volatile aromatic compounds and produced a cup that was free of pyridine, an undesirable compound in coffee due to its rotten smell.

Keywords: antioxidant; arabic coffee; coffee beverage; extraction method; phenols; volatile compounds.

Practical Application: Preparation method influences the bioactive and volatile aroma compounds of the coffee beverage.

1 Introduction

Coffee is the most consumed beverage in volume in the world after water. Although two-thirds of the world's demand comes from the United States, the European Union, Brazil and Japan, coffee is only produced in tropical regions. There is also a growing market of young people, especially in Asia, with specific characteristics (Vegro & Almeida, 2019) who expect to consume coffee that is prepared innovatively in ways that improve the experience.

Among consumer mega-trends is the search for healthy and nutritious products (Maciejewski & Mokrysz, 2019). Coffee, as one of the most consumed beverages worldwide, is not exempt from this market phenomenon, and therefore, there is a need to improve production processes to meet this demand.

One of coffee's widely demonstrated properties is its antioxidant composition, which has made it, with certain restrictions, a superfood (Pozo et al., 2020). However, the concentration of antioxidants depends on many factors; one is the processing conditions, the most important of which is roasting, which is continuously being studied to determine optimal parameters.

Although world coffee exports have decreased slightly due to the COVID-19 pandemic, in the last year, 80.45 million bags of arabica coffee and 47.37 bags of the Robusta variety have been exported (International Coffee Organization, 2022). Obviously, coffee is an agricultural product of great importance for developing countries such as Peru. Peru produces 4.3 million bags of coffee annually, mainly for export (International Coffee Organization, 2020).

In the coffee production chain, there are many actors involved from field production to the final cup (Vegro & Almeida, 2019). Therefore, the final quality depends on many elements throughout the chain.

In addition to cultivation, postharvest (Pereira et al., 2019), storage and transport, roasting is a fundamental stage in the processing of coffee and can occur in either an industrial system or a cafeteria. During the roasting process, aromas are formed, bioactive compounds are removed and/or produced, and the characteristic color develops (Gómez-Ruiz et al., 2008) and its composition in the beverage depends on the brewing method.

Coffee consumption has many benefits for the human body. The most important property attributed to coffee is that it is a source of antioxidants for the organism. Extensive data from experimental tests can be found in the literature; for example, it has been shown that coffee antioxidants can protect the DNA structures of cells from oxidation (Tomac et al., 2020).

Furthermore, chlorogenic acid is known to influence the functional properties of coffee while caffeine influences the sensory profile. These components are the most abundant and have an effect on human health (Farah, 2012; Yalçinkaya et al., 2022). However, its excessive consumption has potential health risks that are often associated with the caffeine content. High levels of caffeine consumption are required to produce undesirable effects such as increased risk of cardiovascular disease, diuresis, increased secretion of gastric acids, and even anxiety problems (Mitchell et al., 2014; Zulak et al., 2006).

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There is scientific evidence that has shown that moderate daily caffeine consumption does not represent health risks for healthy adult populations (Heckman et al., 2010; Knight et al., 2004). The US Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA) state that intake of 400 mg of caffeine per day from different sources of 200 mg/day is not associated with adverse health effects. In the case of pregnant women and children, the intake should be less than 200-300 mg/day and < 3 mg/kg of body weight, respectively (Bernstein et al., 1994; ACOG Committee on Obstetric Practice, 2002; EFSA Panel on Dietetic Products, Nutrition and Allergies, 2015; Mitchell et al., 2014; Mostafa, 2022).

Antioxidant compounds can be found in all parts of the coffee cherry, including the parchment coffee husk (endocarp) (Neves et al., 2019; Pozo et al., 2020; Puga et al., 2017) and endosperm (Kwak et al., 2017), which could be used in the formulation of diets with nutraceutical characteristics (Nzekoue et al., 2020). Additionally, solid coffee residues remaining after extraction are a potential source of bioactive compounds (Balzano et al., 2020) that could be incorporated into traditional products (Moreira et al., 2018; Salamat et al., 2019; Severini et al., 2020).

The antioxidant activity of roasted coffee depends on the roasting conditions. The temperature and roasting time are very important factors that must be controlled; additionally, whilst it is not taken into account, the air flow in the roasting chamber can affect the antioxidant content of the final sample (Kwak et al., 2017).

Although it is expected that the antioxidant activity of the different types of coffee infusions will be high, the exact level depends on the specific process; for example, espresso, filtered and French press coffees have very similar antioxidant levels but differ from Turkish and mocha coffees (Çelik & Gökmen, 2018).

The volatile compounds responsible for aroma also depend on the processing conditions; therefore, they are likely to vary according to the technique used to obtain the infusion (González et al., 2011).

This research sought to study the antioxidant activity, phenolic content and volatile compounds of coffee according to the technique used to obtain the infusion (that is, the preparation or type of coffee). In other words, it sought to determine which preparation technique yields coffee with greater antioxidant activity and greater phenolic contents.

2 Methodology

2.1 Obtaining the material

We worked with the *Coffea arabica* variety Catimor from the province of Jaén, Department of Cajamarca, Peru. Parchment coffee was purchased, and all subsequent processing was carried out at the Coffee Processing and Quality Control Laboratory of the Universidad Nacional Toribio Rodríguez de Mendoza de Amazonas (UNTRM).

2.2 Experimental procedure

Parchment coffee in samples loads of 140 g was roasted in an electric induction roaster (Probat, Germany) at 170 °C and 60% power, for 8 to 12 min depending on the extraction method. It was grounded, sorted, sieved (15 mesh) and infusions were obtained using five extraction methods: espresso, V60 filter, French press, siphon and traditional method used in Chachapoyas. Then, infusions were obtained in triplicate according to the protocol of each technique. The antioxidant activity, total phenolic content and volatile compounds were determined for all infusions, as described in Figure 1.

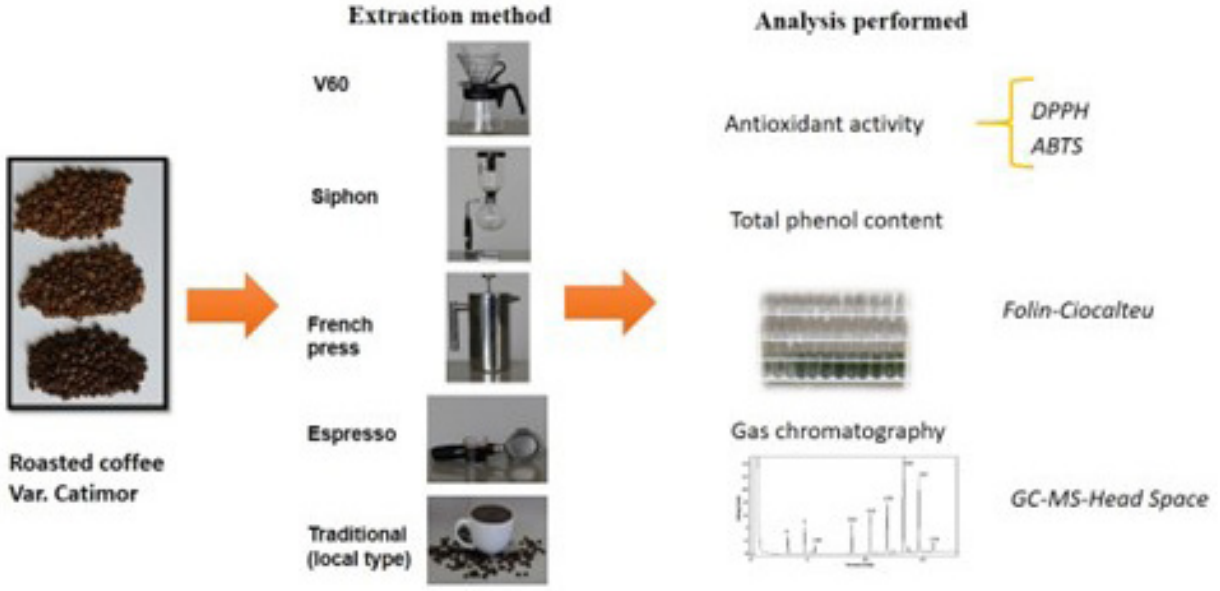

Figure 1. Summary of the experimental procedure.

2.3 Coffee extraction methods

Roasting and grinding conditions

The coffee beans were roasted according to the requirements of each extraction method. The roast grade for the siphon, French press and V60 filter methods was medium roast (n° 95); for espresso it was medium dark (n° 75) and for the traditional method dark (n° 45), according to the SCAA, AGTRON classification system. For the espresso and traditional methods, a fine grind was performed, for the French press a coarse grind and for the other methods a medium grind was performed (Figure 2).

Espresso method

A Ruby Pro espresso machine (Quality Espresso, Spain) was used. For each batch (long espresso cup), 10 g of roasted coffee was finely ground (level 1) in a coffee mill (G3HD brand BUNN, USA). The extraction parameters were as follows: water temperature 95 °C, water pressure 9 bar and 30 s percolation time, assuming an optimal flow rate of 1 mL/s.

French press

Ten grams of coarsely ground coffee was weighed and placed in an 800 mL French press coffee maker, and 180 mL of hot water (95 °C) was added. After 4 min, the plunger (with a metal filter attached) was pressed, and the filtrate was immediately poured into beakers for further analysis.

V60

Ten grams of ground coffee was placed in the filter paper-lined funnel of a 500 mL V60 coffee maker. Subsequently, 180 mL of hot water (95 °C) was added slowly using a gooseneck kettle until the liquid flowed into the container. The filtering process was expected to take 4 min to complete.

Japanese siphon

Ten grams of ground coffee and 180 mL of water were placed in a 500 mL extraction instrument (siphon) with an alcohol burner, and the vacuum filtering process lasted 4 min.

Traditional method

A hundred and eighty milliliters of water were boiled in a beaker and 10 g of medium-ground coffee was added. The beaker was immediately removed from the flame and stirred with a stainless-steel spoon. The mixture was left to stand for 5 min and then filtered and gauged in test tubes for later analysis.

2.4 Determination of antioxidant activity in coffee beverages

The antioxidant activity was determined using two techniques: 1) The first one involved the uptake of the free radical 2,2-diphenyl-1-picrilidrazil (DPPH) and was based on the technique developed by Brand-Williams et al. (1995) and adapted by Çelik & Gökmen (2018) to determine the antioxidant activity in coffee. Twenty milligrams of DPPH were weighed per liter of methanol to obtain an absorbance of approximately 0.45. DPPH solution (3.9 mL) was placed in glass cuvettes to measure the initial absorbance of DPPH (A0) at a wavelength of 516 nm. Then, 100 μL of the sample extract was pipetted and placed in the cuvette containing the DPPH solution, and the solution was stirred. The cuvettes were left in the dark for 10 min, and then the final absorbance (At) was measured.

The decrease in the absorbance of the resulting solution was measured spectrophotometrically at 516 nm (UV/VIS

Figure 2. Coffee roasting degrees according to the requirements of the extraction method.

spectrometer). All experiments were performed in triplicate, and the mean values are reported. The scanning capacity was calculated using the following equation and was expressed as the inhibition of DPPH (Equation 1).

$$\% \text{ inhibition of DPPH} = \frac{(A0 - AS) - (AT - AS)}{(A0 - AS)} X\,100 \quad (1)$$

A0: Absorbance of the DPPH solution, AS: Absorbance of methanol, AT: Absorbance of the sample.

2) The second technique was the uptake of the 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid ($ABTS^{\cdot+}$) radical, as described by Castillo et al. (2002). The Trolox standard was used for all measurements, and the values are expressed in mMol Trolox equivalent/L of infusion. To generate the $ABTS^{\cdot+}$ cation, 19.2 mg of 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) was weighed and dissolved in 5 mL of distilled water to obtain a concentration of 7 mM. Then, 88 µL of 140 mM potassium persulfate was added. The resulting solution was homogenized and incubated at room temperature (25 °C ± 1) in the dark for 16 h. Once the $ABTS^{\cdot+}$ radical was generated, it was adjusted with methanol to obtain an absorbance of 0.7 ± 0.1 at 754 nm. For the analysis of the sample, 3.9 mL of $ABTS^{\cdot+}$ solution was used; 100 µL of the aqueous coffee extract was added and the solution was vigorously stirred. The sample was read immediately in a UV/VIS spectrophotometer at 754 nm. The calibration curve was constructed with Trolox using a range of 0 to 1.0 mM.

2.5 Total phenols content in coffee beverages

The total polyphenol content was determined using the Folin-Ciocalteu technique, following the procedure described by Çelik & Gökmen (2018). Gallic acid was used as a standard; 10 mg of gallic acid was weighed and diluted with ultrapure water to a volume of 100 mL to prepare the stock solution. This solution was used to prepare the calibration curve using the range of 0-16 mg/L gallic acid. The extract of each sample (50 µL) was diluted in 950 µL of ultrapure water and introduced into test tubes. Folin-Ciocalteu reagent diluted in distilled water (1:10 v/v) in a total volume of 2.5 mL was added followed by 2 mL of Na_2CO_3 (20% aqueous solution). The test tubes were left in an oven at 50 °C for 5 min to develop the blue complex. All samples were prepared in triplicate. Absorbance measurements were performed using a UV/VIS spectrophotometer at a wavelength of 765 nm.

2.6 Chromatographic conditions for the determination of caffeine in coffee beverages

Caffeine content was identified and quantified by high-performance liquid chromatography (HPLC) following the method described by Brunetto et al. (2007), on a Hitachi-Chromaster chromatograph, Tokyo, Japan, (LC-20AD), equipped with a SIL-20A/HT autoinjector, a CBM-20A communication module and a SPD-M20A diode array detector (DAD) and UV detection was recorded at 278 nm. Separation was carried out on a 5 µm Supelco-LiChrospher RC C-18 column (25 cm x 4.6 mm). A methanol/water mixture (30/70 v/v) was used as mobile phase in isocratic mode at a flow rate of 1.0 mL/min. Caffeine standard 99.9% (Sigma-Aldrich, USA) dilutions were used for identification and quantification.

2.7 Determination of the volatile compounds profile

The volatile compounds present in the infusions were determined using automatic injection into a gas chromatograph (GC System 7890B) coupled with mass detector (5977B MSD) Agilent Technologies (USA) for headspace technique (HS-GC/MS), according to the procedure described by Rahn & Yeretzian (2019). For each of the obtained solutions, 2 mL was placed undiluted in 20 mL vials and hermetically sealed. A capillary column DB-5MS UI (60 m long, 0.25 mm i.d. and 1 µm thickness) was used to determine the volatile compounds. Three runs of each sample were performed to reduce the measurement error. The NIST 14.L library was used for the identification of the compounds.

2.8 Statistical data processing

Treatments were compared using analysis of variance and Tukey's multiple comparisons to determine statistical differences.

3 Results and discussion

The beverages obtained from the espresso machine had higher phenolic, antioxidant and caffeine compounds, as shown in Table 1. In addition, the content of these compounds differed for each type of beverage obtained according to previous work (Górecki & Hallmann, 2020).

3.1 Total phenolic content of coffee infusions

The coffee extracted using the espresso method had the highest phenolic content of up to two times higher than the other methods evaluated. No significant differences were found between the siphon and French press methods, which yielded beverages with lower phenolic contents (Figure 3).

The phenolic contents of the infusions obtained depend on the extraction method, taking into account that in addition to the differences in the instrumental material used, each method requires a different degree of roasting, which could also influence the amounts these compounds that are extracted (Cruz et al., 2018; Muñoz et al., 2020). Therefore, the functionality of the coffee beverage is conditioned by the method used to obtain the infusion.

3.2 Antioxidant activity of coffee infusions

As expected, the highest antioxidant activity values in the two techniques used (DPPH and ABTS) were observed for the infusion obtained using the espresso method, which may be due to its high capacity to extract phenolic compounds; however, there were some differences in the sequence (from lowest to highest antioxidant activity) according to the free radical capture technique used (Figures 4-5). In general, we observed that the antioxidant activity of coffee is determined mainly by the ability

Table 1. Total phenolic content (TPC), antioxidant activity (DPPH and ABTS) and caffeine content (CC) of coffee infusions.

Extraction method	TPC GAE (mg/g)		DPPH (mmol TE/L)		ABTS (mmol TE/L)		CC (mg/50mL)*	
	Average	SD	Average	SD	Average	SD	Average	SD
Espresso	73.275 a	4.423	1587.7 a	29.5	22.606 a	0.183	58.70 a	3.234
French press	32.646 d	0.910	628.9 c	37.7	10.644 d	0.070	34.90 c	4.374
V60	36.873 c	1.247	810.6 b	12.6	11.494 b	0.055	42.53 bc	0.407
Siphon	30.542 d	1.501	829.9 b	10.7	11.431 b	0.033	43.40 b	2.827
Traditional	43.944 b	0.662	584.4 c	4.51	11.009 c	0.071	45.90 b	2.580

*Different letters indicate statistically significant differences ($p < 0.05$). SD: standard deviation (n = 3).

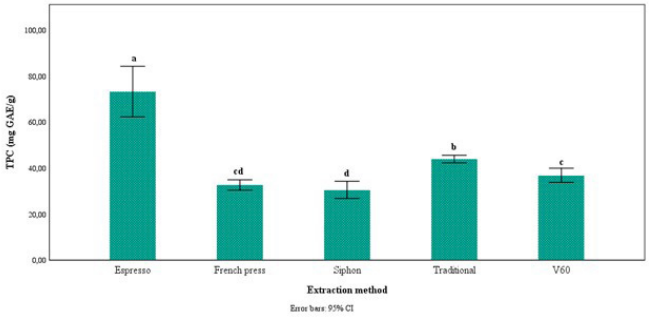

Figure 3. Total phenolic content of coffee infusions according to the extraction method. Different letters indicate statistically different groups ($p<0.05$; n=3).

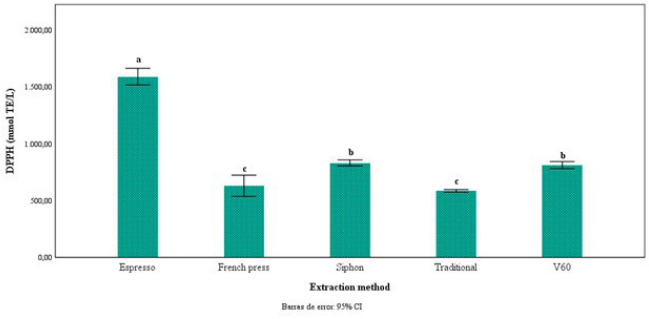

Figure 4. Capture of the free radical DPPH by coffee infusions obtained using different methods. Different letters indicate statistically different groups ($p<0.05$; n=3).

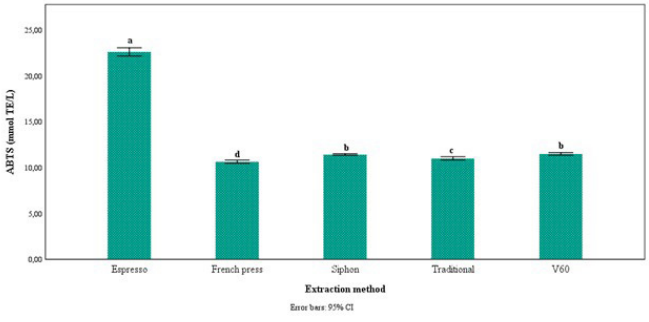

Figure 5. Capture of the free radical ABTS by coffee infusions obtained by different methods. Different letters indicate statistically different groups ($p<0.05$; n=3).

of the infusion method to extract phenolic compounds from roasted ground coffee beans.

3.3 Volatile compounds of coffee infusions

The five evaluated methods allowed us to obtain between 11 and 18 volatile compounds from coffee infusions. The espresso and V60 methods extracted the lowest amount and diversity of volatile compounds, while the French press, siphon and traditional local methods yielded higher volatile contents (Table 2).

Although furans and their derivatives (2-methylfuran and 3-methylfuran) are compounds that give coffee pleasant aromas (chocolate, caramel, roast), high levels of these compounds are potentially carcinogenic (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2018), as are other polycyclic aromatic hydrocarbons generated by roasting (Binello et al., 2021). Recent studies have shown that the amounts of these compounds depend on the degree of roasting and the extraction method used (Rahn & Yeretzian, 2019) In our study, these compounds were not detected in the infusions obtained using the espresso, siphon and French press methods.

The infusion obtained in an espresso machine has the fewest aromatic volatile compounds and pyridine, an unwanted compound in coffee that causes a putrefied, fishy odor, was not detected (Pereira et al., 2019; Liu et al., 2019; Rahn & Yeretzian, 2019); thus, along the French press method, the espresso method yields less aromatic but cleaner infusions. In comparison, the filter methods extracted and preserved a greater number of desirable aromatic volatile compounds and also was detected pyridine. Therefore, it will be important to research more deeply the trade-off between beverage with complex aromatic compounds and the presence of undesirable volatile organic compounds.

Coffee infusions obtained using different extraction methods differ in phenolic compounds, antioxidant capacity and the volatile compounds responsible for the aroma, since each depends on a specific degree of roasting, degree of grinding (particle size) and instrument (Vivo et al., 2019).

Therefore, the method by which coffee infusion is obtained directly influences the extraction of compounds that confer functional activity and sensory quality (Cordoba et al., 2020).

3.4 Caffeine content of coffee infusions

The coffee obtained in the espresso machine (Figure 6) had a higher caffeine content (58 mg/50 mL) than that obtained by

Table 2. Composition of the volatile fraction of coffee infusions obtained by five extraction methods.

Name	RT	Espresso	French press	Siphon	Traditional	V60	Characteristic smell
Dimethyl ether	4.446	ND	0.79%	1.79%	1.53%	ND	---
Acetone	4.644	ND	1.17%	ND	ND	ND	---
Diazene, dimethyl-	4.838	ND	ND	2.04%	1.93%	2.44%	---
Propene	5.624	ND	0.78%	ND	ND	ND	---
2-butanone	5.636	ND	1.30%	1.78%	0.56%	ND	Ethereal, fruity, camphorous[d].
Propane, 2-nitro-	5.641	ND	2.67%	ND	1.21%	ND	---
Propanal, 2-methyl-	5.649	1.86%	ND	ND	ND	1.29%	Roasted, dark chocolate, fruity, malt[a].
Acetic anhydride	5.651	ND	1.26%	ND	ND	ND	Vinegar.
Acetic acid	5.804	0.91%	0.57%	0.82%	0.51%	0.48%	Sour, organic acid[c].
2,3-butanedione	6.001	1.65%	0.73%	1.15%	ND	ND	Butter, creamy, fatty, oily, sweet, vanillaa.
Furan, 3-methyl-	6.272	ND	ND	ND	0.73%	ND	---
Furan, 2-methyl-	6.286	ND	0.44%	0.53%	0.54%	ND	Burned, chocolate, ethereala.
Oxirane, trimethyl-	7.192	ND	ND	ND	ND	0.97%	---
Pentanal	7.194	1.46%	1.89%	2.15%	ND	ND	---
Succindialdehyde	7.198	ND	ND	ND	1.60%	ND	---
Butanal, 3-methyl-	7.201	ND	1.80%	ND	1.65%	1.34%	Fruity, almonds, ethereal, peaches[b].
Diazene, bis (1,1-dimethylethyl)-	7.280	0.66%	ND	ND	ND	2.10%	---
di-tert-butyl dicarbonate	7.360	ND	ND	3.85%	ND	ND	---
Propane, 2-methyl-1-nitro-	7.360	ND	3.15%	ND	ND	ND	---
Butanal, 2-methyl-	7.365	2.08%	2.29%	3.33%	2.76%	ND	Toasted bread, roasted peanuts, and roasted almondsa.
Neopentane	7.370	ND	ND	ND	2.72%	1.18%	---
Propanal, 2,2-dimethyl-	7.371	ND	1.32%	ND	ND	ND	---
2-furancarboxaldehyde, 5-methyl-	7.796	ND	ND	ND	0.97%	ND	---
2,3-Pentanedione	7.798	2.17%	1.31%	2.27%	0.94%	0.97%	Butter, caramel, creamy, penetrating, sweeta.
Pyridine	8.981	ND	ND	0.83%	0.61%	0.88%	Rotten fishy smella.
3(2H)-furanone, dihydro-2-methyl-	10.113	0.62%	ND	0.55%	ND	ND	Sweet, bread, butter, nutsa.
Furfural	10.672	1.81%	2.69%	3.41%	1.18%	1.85%	Almonds, sweet, bread, caramelizeda.
3-furaldehyde	10.679	3.40%	2.17%	3.25%	1.66%	2.03%	Honey, floral.
Methylenecyclopropanecarboxylic acid	10.952	ND	ND	0.77%	ND	ND	---
2,5-dimethylpyrimidine	12.209	ND	ND	0.42%	ND	ND	---
2-furancarboxaldehyde, 5-methyl-	13.231	0.71%	0.52%	0.85%	0.50%	0.63%	Sweet spice, caramelized, coffeea.
2-furanmethanol, acetate	13.581	ND	ND	0.53%	ND	ND	Onion, garlic, sulfurous, spicy, vegetablea.
Other unidentified		82.67%	73.15%	69.68%	78.40%	83.84%	
Number of volatile compounds		11	18	18	17	12	

ND: not detected.; RT: Retention time. [a]Yeretzian, 2017. [b]Yeretzian et al., 2019. [c]Liu et al., 2019. [d]Pereira et al., 2019.

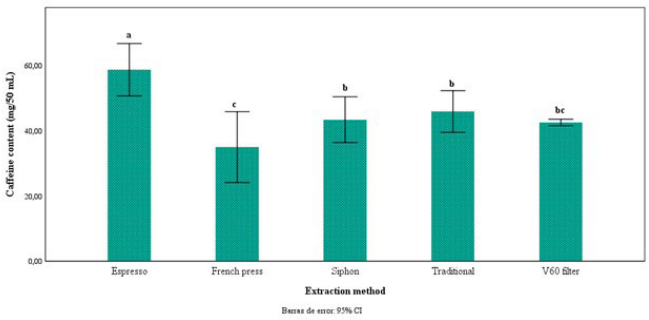

Figure 6. Caffeine content of coffee infusions obtained by different methods. Different letters indicate statistically different groups (p<0.05; n=3).

the other techniques, whose values are statistically equal ($p < 0.05$). The values obtained are lower than those reported by other studies (Hutachok et al., 2021; Passos et al., 2021), which could be due to the fact that we worked with the coffee beverage, as opposed to previous studies that used extracts to recover the highest caffeine content.

4 Conclusion

The extraction method that provided the coffee infusions with the most antioxidant activity, phenolic compounds and caffeine content was espresso; however, this coffee had the fewest aromatic volatile compounds.

Infusions free of pyridine, a compound responsible for an unpleasant aroma, were obtained by the French press and espresso methods.

The traditional Chachapoyas method yielded coffee infusions with a high number of volatile aromatic compounds comparable to those obtained with the French press and siphon methods.

Although the infusions obtained by the French press had lower antioxidant activity, they had the highest content of volatile aromatic compounds and were free of pyridine, an undesirable compound in coffee that causes a rotten smell.

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