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ARTICLE

Extraction of Non-Volatile Chemical Compounds in High-Quality and Traditional Coffee

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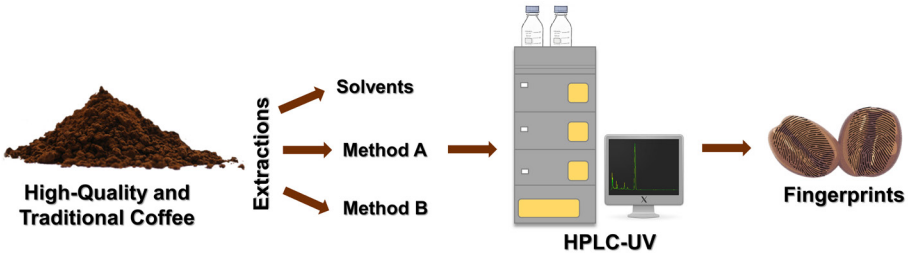

Coffee contains different volatile and non-volatile compounds, which are responsible for its characteristic flavor and aroma attributes. The extraction of non-volatile compounds from high-quality and traditional coffee by different methods was evaluated to determine the chemical compounds that discriminate between coffee types. Standard methods of preparing the coffee drink by consumers were evaluated. Method A corresponded to boiling water with coffee, and method B to the strained coffee method. Extraction with different solvents did not distinguish the compounds chosen as markers for coffees. In addition to being non-toxic and low-cost, water was the most suitable solvent, conforming to the principles of green chemistry while enabling direct comparison with sensory analysis. The total dissolved solids, percentage extraction, and non-volatile compounds were quantified to select the most satisfactory extraction method. The TDS value ranged from 1.7 to 3 between methods and coffee types, and the extraction percentage ranged from 25 to 45%. Significant differences in the extracts obtained using methods A and B high-quality versus traditional coffees were detected using the Student's *t*-test. Although method A extracted the chemical compounds in more substantial amounts, method B was also efficient in extracting the compounds and was easily executed given its similarity to the usual way of preparing coffee beverages used by consumers. The evaluated non-volatile compounds were identified in both high-quality and traditional coffee samples. In the chosen extraction method (method B), the average concentrations in mg 100 g^{-1} of the sample found for the compounds were: 5-hydroxymethylfurfural (11±0.5), 3,4-hydroxybenzoic acid (62±4), catechin (58±5), 4-hydroxybenzoic acid (58±2), caffeine (1152±44), chlorogenic acid (598±23), caffeic acid (0.7±0.1), and gallic acid (3±0.2).

Keywords: coffees, extraction, non-volatile compounds

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INTRODUCTION

Coffee is the second most widely consumed beverage worldwide and has high economic importance, being one of Brazil's main export products. There are more than 100 species of the genus L. (*Rubiacea*e); thus most types of coffee in this class are *Coffea arabica* and *Coffea canephora*, also called 'robusta' of the cultivar 'conilon'.[1] The coffee drinks made from these two varieties are significantly different in aroma and flavor because the arabica species have better sensorial properties than the robusta species,[2,3] providing the highest value and most consumer appreciation. In general, commercially available coffee drinks are produced from arabica coffee, robusta, or mixtures of these species.[4]

Coffee blends are a common practice in the coffee industry to standardize sensory properties such as bitterness, flavor, and aroma.[5] According to the Brazilian Coffee Industry Association (ABIC), roasted and ground coffees can be classified into three categories: Traditional (arabica blended with conilon up to a limit of 30%), Superior (blend with up to 15% conilon), and Gourmet (arabica only).[6] This classification considers the different proportions of conilon coffee and the maximum percentage of defects and sensory analysis scores, associated with the final quality.[7]

Sensory analysis is widely used in classifying coffee worldwide, but can still be seen as subjective. Therefore, analysis of the physicochemical and chemical composition is a complementary resource because the constituents of each species can be directly related to the attributes of the coffee beverage.[8,9] Thus, the chemical compounds in roasted coffee grains confer a series of attributes that give coffee its flavor and peculiar aromas.[10,11] In roasted coffee, these chemical components can be grouped into volatile substances, responsible for the aroma, and non-volatile substances, for the acidity sensations, bitterness, and astringency.[12]

Phenolic compounds contribute to the flavor and aroma of coffee drinks due to their high concentration in coffee and their physiological and pharmacological properties.[13] These compounds are characterized by one or more aromatic rings attached to at least one hydroxyl radical and/or other substitutents. Furthermore, they can be divided according to the number of phenolic rings and the structures to which they are attached.[14] The main phenolic compounds in coffee are phenolic acids, such as hydroxybenzoic (gallic, vinylic, and syringic) and hydroxycinnamic (caffeic, ferulic, sinapic, and *p*-coumaric). Esterified quinic acid, tartaric acid, or carbohydrates and their derivatives can also be found in most foods.[14–16]

Phenolic compounds represent a significant fraction of the coffee composition and can be used as chemical descriptors and markers of the authenticity of foods.[17] These compounds can be extracted with water, organic solvents, or polar organic solvent mixtures. The polar solvents used most frequently in the extraction of these compounds from food are methanol, ethanol, and acetone, often mixed with water in ratios of 80:20 (v/v) or 50:50 (v/v).[18]

Brewing is an essential step in preparing coffee beverages to achieve maximum extraction of the constituent compounds and to ensure aroma and flavor characteristics. The extraction efficiency is the ratio between the mass of ground coffee powder that passes through the cup and the total amount of ground coffee used.[19] In this context, coffee shops have introduced instruments to ensure quality control of the extraction process. Thus, baristas and coffee enthusiasts worldwide have started using scales, gauges, proportions, and control charts to prepare better-quality coffee.

Refractometers are used to evaluate the percentage of coffee extraction by determining the total dissolved solids (TDS) in brewed coffee, where the percentage of coffee extracted by a given extraction method can be estimated.[20] The TDS can be determined from the Brix degree (°Bx), which is a measurement of the refractive index. Due to the linear correlation between the °Bx and TDS, it is possible to convert the °Bx to the TDS through the mathematical equation: %TDS = 0.85 × % °Bx given that refractometers are usually more accessible than TDS meters.[20] The TDS measurement can be used to calculate the percentage coffee extraction (PE) through the correlation: Extraction = TDS × Beverage/Dosage. The TDS value is the same as found from the °Bx conversion; thus, the TDS of drink corresponds to the amount of water, and the 'Dosage' represents the serving in grams of coffee.

Although there are works in the literature that evaluate different extraction methods, the TDS and percentage of extraction in evaluating these methods as a parameter of quality and efficiency are still little

explored. Still, many of the methods investigated address coffee preparation methods such as espresso, mocha, V60, cold brew, and french press,[19] which use water as an extractor solvent since it is a drink for consumption is capable of extracting the compounds that represent characteristics sensory the drink. On the other hand, when looking for non-volatile markers, it is necessary to investigate other solvents in the extraction. There is a hypothesis that possible classification markers for coffees are extracted by solvents other than water due to the difference in polarity of the bioactive compounds present in coffee. There may still be varying effects when different solvents are used in the extraction, increasing the chances of observing important spectral changes.[21]

Liquid chromatography (LC) is one of the most commonly employed chromatographic fingerprinting methodologies. It has been widely applied to identify, classify and evaluate the quality of different types of foods. Furthermore, several classes of food solutions, in polar and non-polar solvents, can be directly and quickly analyzed by LC without the need for derivatization. Finally, the versatility of the chromatographic methods allows the interaction both in the separation steps and in the measurement ones to acquire an analytical signal with the maximum of useful information. These methods are excellent candidates for obtaining fingerprints for food identification, classification, and authentication.[22]

Thus, this exploratory study aims to evaluate the efficacy of different solvents and processes in extracting the characteristic compounds that discriminate high-quality and traditional coffee types using an High-performance liquid chromatography (HPLC) method with UV detection.

MATERIALS AND METHODS

Reagents, equipment, and accessories

All solutions and extracts were prepared using deionized water (18.2 MΩ cm at 25 °C) and analytical-grade reagents. The following analytical standards were used: 5-hydroxymethylfurfural (5-HMF), 3,4-hydroxybenzoic, catechin, 4-hydroxybenzoic, caffeine, chlorogenic acid (CGA), caffeic acid, and gallic acid from Sigma Aldrich.

The stock solutions of the standards were prepared at known concentrations: 3,4-hydroxybenzoic, catechin, and 4-hydroxybenzoic at 6250 mg L^{-1}; caffeine 12500 mg L^{-1}; gallic acid 2510 mg L^{-1}; CGA 5000 mg L^{-1}; caffeic acid 126 mg L^{-1} and 5-HMF 508 mg L^{-1}.

Chromatographic separation was achieved using HPLC (Agilent, model 1100 series) in reverse phase, equipped with a pre-column and C18 column (4.6 × 250 mm – 5 µm), at a flow rate of 0.8 mL min^{-1}.

Coffee samples and extract preparation

Samples of 100% arabica coffee were analyzed from the Alta Mogiana region (*Gourmet* Coffee) and a traditional coffee sample acquired in a local market in the city of Piracicaba, SP, Brazil. The ground coffee grains of the samples were passed through a granulometric sieve (20 mesh) for standardization, stored in a Falcon tube®, and protected from light until extraction.

Extraction procedure

The extracts were filtered through conventional filter paper and a syringe filter (hydrophilic PTFE membrane; filter diameter and pore of 13 mm and 0.45 µm, respectively) before chromatographic injection. Extraction methods A and B were performed in triplicate.

Extraction employing different solvents

In a 50 mL Falcon tube®, 1.0 g of sample and the volume of solvent (totaling 15 mL) were added as described in the experimental design (Table I), followed by agitation for 30 min at 150 rpm on an orbital table (Quimis, SP, Brazil; Model Q225M). Thereafter ethanol, ethyl acetate, acetone, water, and combinations of the organic solvents with water 50:50 (v/v) were evaluated as extraction solvents.

Table I. Experimental design for extraction employing different solvents

Extracts	Water (%)	Ethanol (%)	Ethyl acetate (%)	Acetone (%)
1	0	100	0	0
2	0	0	100	0
3	0	50	50	0
4	0	0	0	100
5	0	50	0	50
6	0	0	50	50
7	0	33.3	33.3	33.3
8	100	0	0	0
9	50	50	0	0
10	50	0	50	0
11	50	0	0	50
12	100	0	0	0

Extraction methods

Method A: The sample (10 g) and 150 mL of water were heated at 90 °C in a beaker for 2 min.

Method B: On a commercial support, 10 g of sample was added to filter paper, and 150 mL of water at 90 °C was poured onto the coffee.

Separation and quantification of non-volatile compounds

The non-volatile compounds were separated under the following chromatographic conditions: mobile phase: 95% (A) 5% of acetic acid in water (v/v), and 5% (B) acetonitrile; injected sample volume: 30 µL; run time: 55 min, with UV detection at 280 and 320 nm, adapted the Alves et al. and Alcantara, Melchert, and Dresch.[1,23]

The chromatographic profiles of the analytical standards were obtained under the same chromatographic conditions and used to identify the compounds by UV detection at: 280 nm for 5-HMF, 3,4-hydroxybenzoic, catechin, 4-hydroxybenzoic, caffeine, and gallic acid and 320 nm for CGA and caffeic acid.

The reference solutions 3,4-hydroxybenzoic, catechin, and 4-hydroxybenzoic, were prepared by dissolving 62.5 mg of each standard in 10 mL of deionized water; gallic acid was prepared by dissolving 25.1 mg in 10 mL of deionized water. The 5-HMF and caffeic acid reference solutions were prepared by dissolving 50.8 and 12.6 mg, respectively, in 100 mL of deionized water. The caffeine and CGA reference solutions were prepared by dissolving 312.5 and 125.0 mg, respectively, in 25 mL of deionized water.

5-HMF, 3,4-hydroxybenzoic, catechin, 4-hydroxybenzoic, caffeine, gallic acid, CGA, and caffeic acid were identified and quantified from the calibration curve through triplicate measurements based on the peak areas. Table II presents the linear equations obtained from the calibration curve of each compound. The limit of detection (LOD) was estimated through the parameters of the analytical curve, being expressed by the equation $LOD = 3{,}3 \times s/a$, where $\boldsymbol{s}$ is the standard deviation of the linear coefficient and $\boldsymbol{a}$ is the value of the angular coefficient. The concentrations of these compounds found in the coffee samples are expressed in mg 100 g^{-1} of ground-roasted coffee.

Table II. Calibration curves of the compounds identified in the coffee samples

Compound	Concentration (mg 100 g^{-1})	Straight equation	R^2	LOD (mg 100 g^{-1})	Retention time (min)
Gallic acid	0.05 – 0.75	Area = 0.48 + 103.46 C	0.999	0.002	4.5
5-HMF	0.2 – 4	Area = 33.19 + 263.80 C	0.999	0.036	6.4
3,4- Hydroxybenzoic	1.25 – 20	Area = -11.13 + 57.17 C	0.999	0.091	7.1
Catequina	2.5 – 25	Area = 0.90 + 23.43 C	0.999	0.346	10.5
4- Hydroxybenzoic	2.5 – 20	Area = -291.19 + 87.85 C	0.997	0.766	12.5
Caffeine	50 – 175	Area = 6352.75 + 83.60 C	0.998	5.015	20.7
CGA	10 – 125	Area = -117.77 + 61.23 C	0.999	0.966	12.5
Caffeic acid	0.0125 – 0.25	Area = 7.38 + 120.20 C	0.999	0.003	18.3

°Bx, TDS, and PE

The TDS and PE were calculated from the °Bx of all the extracts prepared with water by using a portable refractometer and conversion equations (1) and (2).

$$TDS = 0.85 \times \% \text{ °Bx} \quad (1)$$

$$PE = TDS \times \text{Drink/Dosage} \quad (2)$$

The beverage value corresponds to the amount of water, and the 'Dosage' represents the serving (g) of coffee.

Statistical analysis

The Student's *t*-test was performed at a significance level of 95% ($\alpha = 0.05$) to evaluate the difference between the extraction methods and coffee types. OriginPro 2022 software (Student Version 9.9.0.220) was used for the statistical analysis and construction of the figures.

RESULTS AND DISCUSSION

Screening solvents for discrimination of high-quality and traditional coffees

To maximize the extraction efficiency, different parameters such as the solvent, agitation, extraction time, solute/solvent ratio, temperature, and mass transfer efficiency[16] should be evaluated, permitting determination of the chemical markers that distinguish different coffees. The evaluated solvents were selected according to the guidelines of Bunzel and Schendel[18] who analyzed solvents for extracting phenolic compounds from foods, including water, polar organic solvents, or a mixture of polar organic solvents. The frequently used polar solvents include methanol, ethanol, and acetone (polarity index 5.1, 4.3, and 5.1, respectively) and less polar ethyl acetate (polarity index 4.4).[24] Moreover, detection at 280 and 320 nm was used for identification and quantification, as an essential method for analyzing the phenolic compounds in coffee. Caffeine and phenolic compounds such as CGA and caffeic acid are abundant compounds in coffee that carry out characteristics responsible for its flavor, aroma, and nutritional characteristics.[5,25] In the literature, the absorption spectrum of CGA presents a band at 300 nm, with a maximum of 326 nm. This absorption band can be attributed to organic foods and lipids.[26] For methylxanthines (caffeine, theobromine, and theophylline) extracted with water, the maximum absorption wavelength reported in the literature is between 270 and 280 nm.[27] Furthermore, phenolic compounds present in their organic

structure groups, usually unsaturated, called chromophores, absorb electromagnetic radiation in the UV-Vis regions,[28] thus allowing the detection of these compounds in this spectrum region.

The wavelength for the detection of the compounds was chosen after a previous study of the maximum absorption wavelengths of each compound, and monitoring the wavelengths between 280 and 320 nm allowed the simultaneous detection of important compounds for the characterization of coffee.

The proportion of the extraction solvent can be determined through statistical mixture design to optimize the quantity and variety of extracted metabolites. The statistical mixture design was applied using ethanol, ethyl acetate, acetone, and water (Table I); the chromatographic profiles are shown in Figure 1.

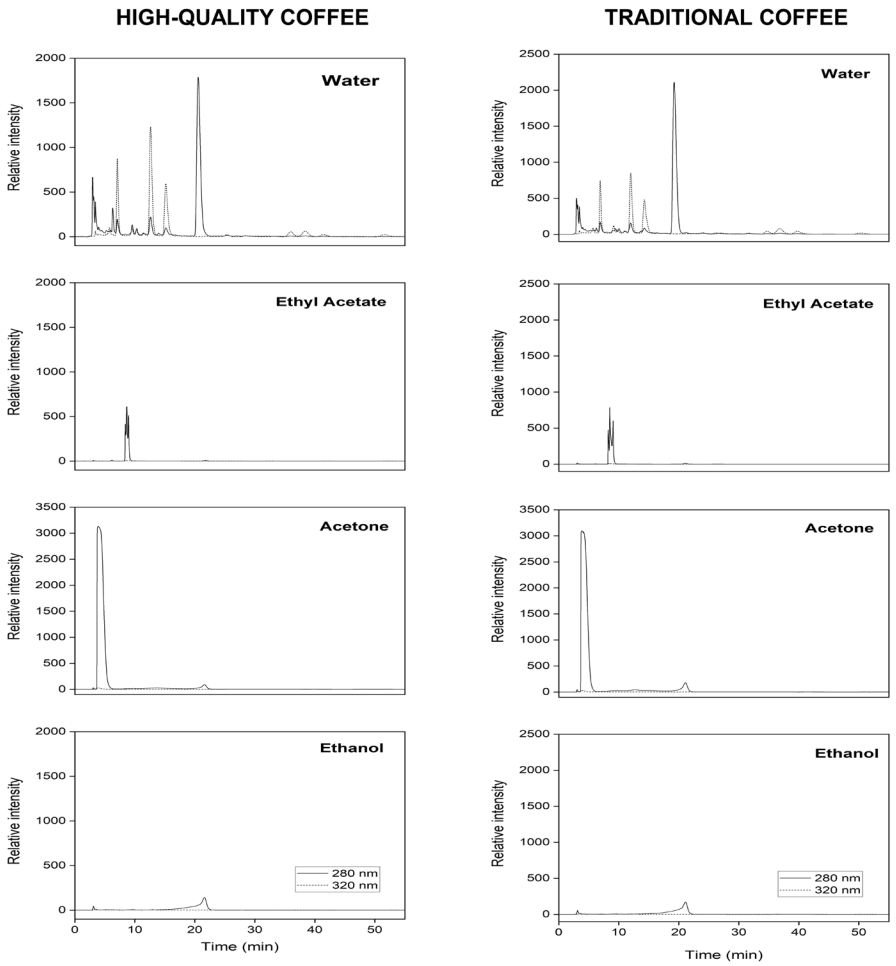

Figure 1. Chromatographic profiles in 280 and 320 nm for analysis of high-quality and traditional coffee using water, ethyl acetate, acetone, and ethanol as extractor solvent (100%). Chromatographic conditions: mobile phase consisting of 95% (A) 5% acetic acid in water (v/v) and 5% (B) acetonitrile; injection volume: 30 µL; and flow rate: 0.8 mL min^{-1}.

The profiles obtained at 280 and 320 nm, it was found that water enabled the extraction of a wider variety of compounds than the other solvents used in this study (Figure 1). Still showed a resolution value equal to 2.54 and 2.35 for neighboring peaks (6 min and 7 min) at 280 nm for the high-quality and traditional coffee, respectively, and a resolution equal to 3.62 and 2.93 for neighboring peaks (12 min and 15 min) at 320 nm for high-quality and traditional coffee respectively. As resolution values were more significant than 1.5, baseline separation was achieved.[28] Furthermore, depending on the solvent used, there was less extraction and separation of the compounds, baseline resolution was not achieved, and

the different peaks that appear in the chromatographic profiles refer to the solvent evaluated. Hence, using water as an extraction solvent proved advantageous for, extracting more compounds, conforming to the guidelines of green chemistry, and allowing direct comparison with the sensory analysis of coffee, while being inexpensive. The effectiveness of water as a solvent is expected due to the polarity of water (polarity index 10.2) and the compounds present in coffee, which are easily solubilized in the water, such as trigonelline, caffeine, and CGA.[29]

Furthermore, Abreu et al.[26] evaluated the effect of water, ethanol, and dichloromethane on the extraction of secondary metabolites from special and traditional coffees through blend planning, where water was the most effective extraction solvent. Thus, water enable the best discrimination between high-quality and traditional coffees and enabled corroboration with the results found in this work.

The interaction of solvents and water in the extraction (50:50 v/v) was evaluated as described in the experimental design (Table I); the chromatographic profiles are shown in Figures 2 and 3. The compounds found in the water were also extracted with a solvent and water mixture by evaluating the chromatographic profiles obtained.

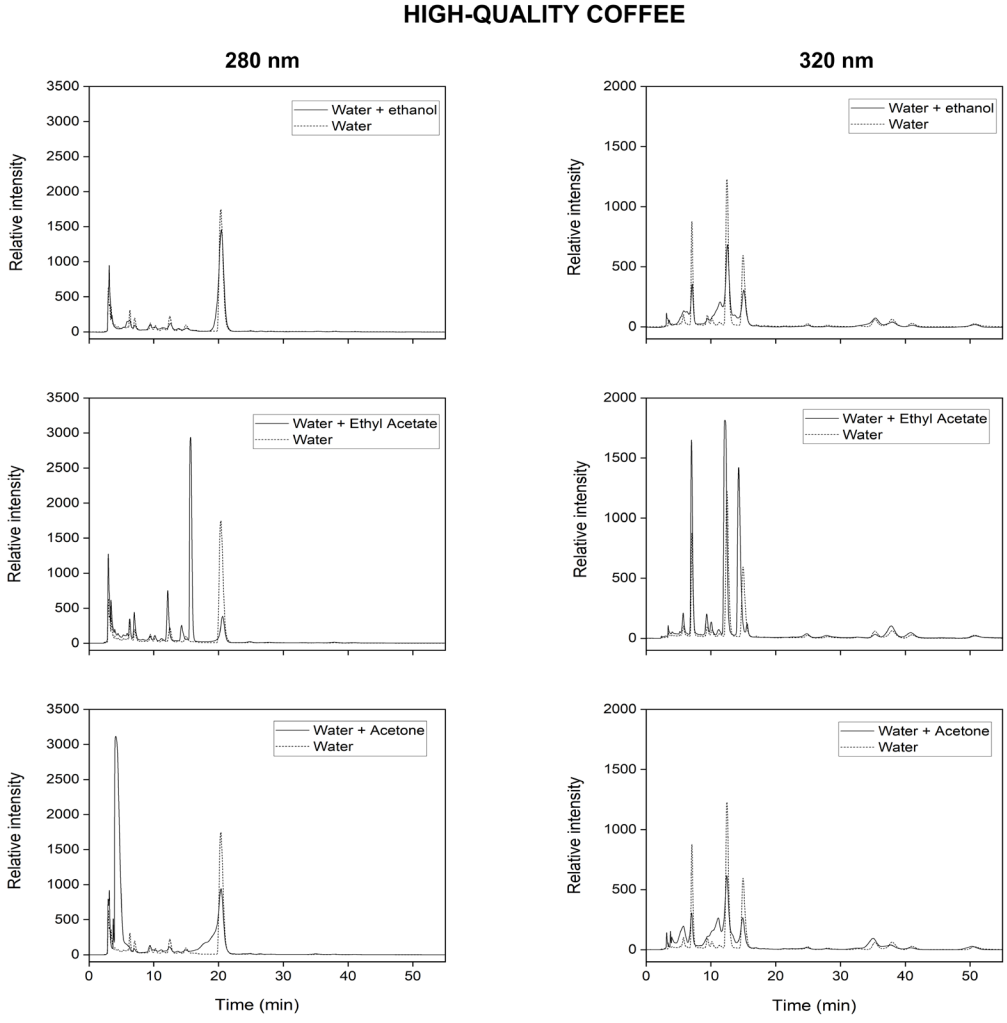

Figure 2. Chromatographic profiles obtained at 280 and 320 nm for high-quality coffee employing water and solvent mixture (50:50 v/v) as extractant. Chromatographic conditions: mobile phase consisting of 95% (A) 5% acetic acid in water (v/v) and 5% (B) acetonitrile; injection volume: 30 µL; flow rate: 0.8 mL min^{-1}.

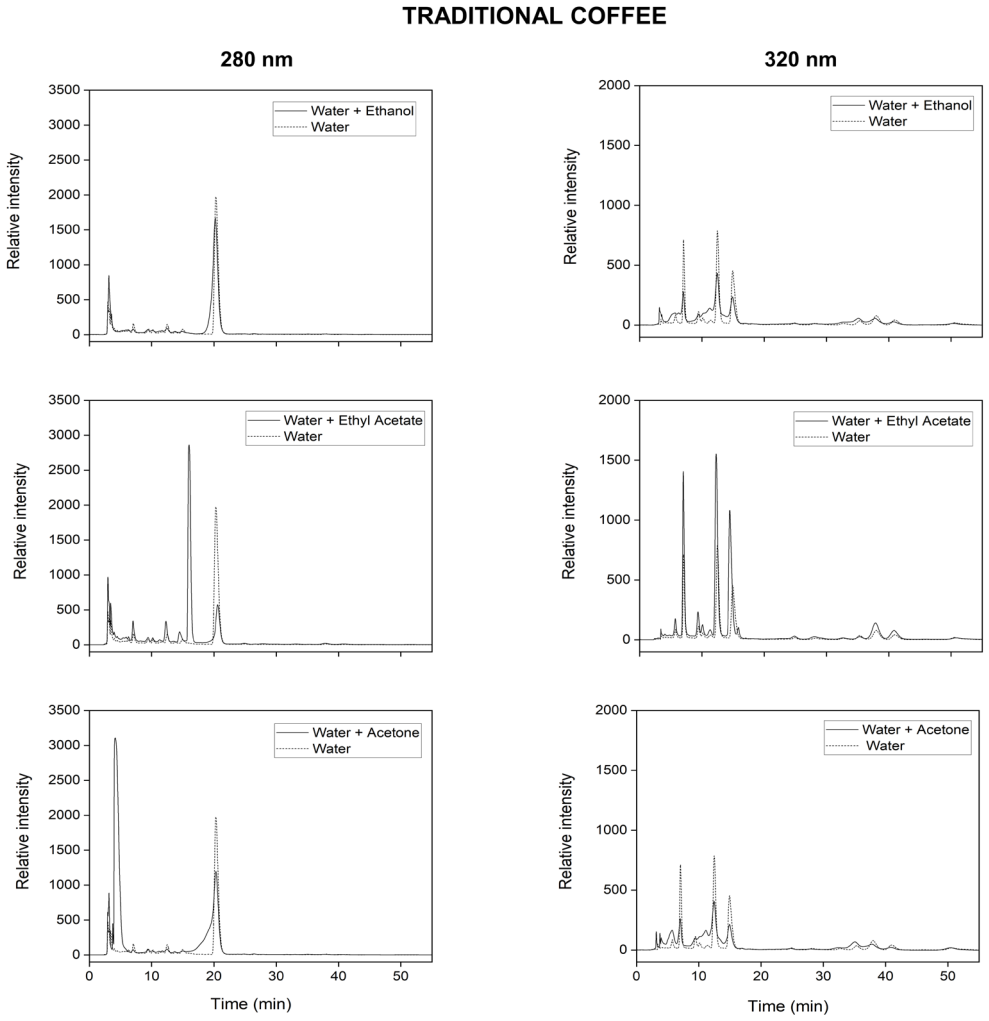

Figure 3. Chromatographic profiles obtained at 280 and 320 nm for traditional coffee employing solvent extraction using water and solvent (50:50 v/v). Chromatographic conditions: mobile phase consisting of 95% (A) 5% acetic acid in water (v/v) and 5% (B) acetonitrile; injection volume: 30 µL; flow rate: 0.8 mL min^{-1}.

In the literature, methanol was also cited as a solvent for coffee extraction. However, the chromatographic profiles were similar to those obtained with the other solvents, where no different compounds were extracted compared to those obtained by extraction with water.

The comparative exploratory evaluation of the chromatographic profiles obtained made it possible to judge the efficiency of solvent extraction for the work. Applying the experimental design (Table I) was an effective tool for optimizing the extraction conditions. It is possible to evaluate the solvents individually and their interactions using the experimental design. However, the different assessed solvents in the extraction in this work did not allow the discrimination of chemical compounds between the coffees. However, the differentiation between the types of coffee samples can be made by quantifying these compounds. So, choosing the method and the solvent is crucial, and the maximum extraction was achieved when using water as the extraction solvent.

Discrimination between high-quality and traditional coffees via extraction using methods A and B

Coffee preparation is a solid-liquid extraction process that involves three steps: (1) water absorption by ground coffee; (2) mass transfer of the soluble solids from the ground coffee to hot water; and (3) separation of the extract from the spent solids. Several variables can modify the quality of coffee beverages, such as

the contact time between the water and ground coffee, extraction time, ratio between ground coffee and water, water temperature and pressure, filter type, and boiling process.[25]

This work evaluated two extraction methods aiming at maximum extraction and the search for discriminating compounds between coffee types for high-quality and traditional coffee according to the comparison of the analysis of chromatographic profiles, as presented in Figure 4.

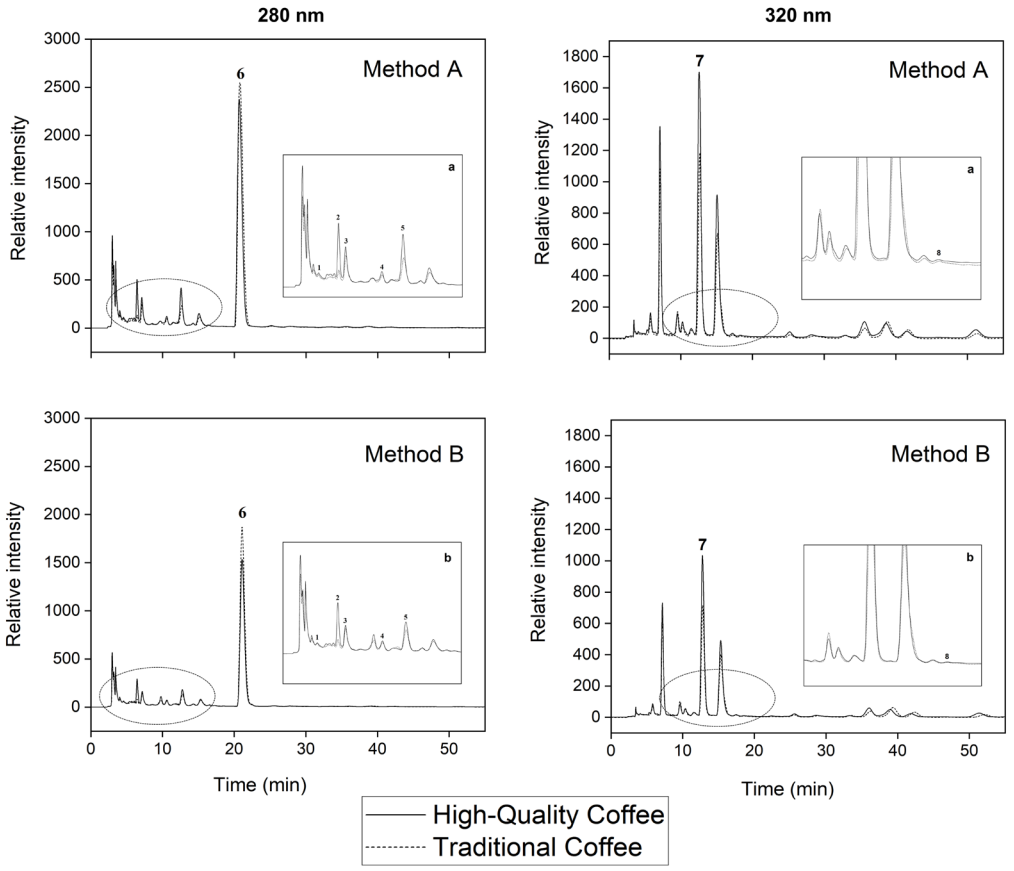

Figure 4. Chromatographic profiles of high-quality and traditional coffee, obtained at 280 and 320 nm. Images *a* and *b* are magnifications of the circulated parts. The compounds are (1) gallic acid, (2) 5-HMF, (3) 3,4-hydroxybenzoic, (4) catechin, (5) 4-hydroxybenzoic, (6) caffeine, (7) CGA, and (8) caffeic acid. Chromatographic conditions: mobile phase consisting of 95% (A) 5% acetic acid in water (v/v) and 5% (B) acetonitrile; injection volume: 30 µL; flow rate: 0.8 mL min^{-1}.

Evaluation of the chromatographic profiles at the two wavelengths (280 and 320 nm) verified the similarity between the extraction methods (Figure 4).

There were no significant differences in the chromatographic profiles of the high-quality and traditional coffee samples. Nonetheless, eight (5-HMF, 3,4-hydroxybenzoic, catechin, 4-hydroxybenzoic, caffeine, CGA, caffeic acid, and gallic acid) non-volatile compounds were identified and quantified in the high-quality and traditional coffee samples. The concentrations of these substances are presented in Table III.

Table III. Quantity of compounds in high-quality and traditional coffees extracted by methods A and B

Compound	mg 100 g^{-1} of sample			
	High-quality coffee		Traditional coffee	
	Method A	Method B	Method A	Method B
Gallic acid	4 ± 1^{aA}	3 ± 0.3^{bA}	3 ± 0.1^{aB}	2 ± 0.1^{cC}
5-HMF	33 ± 0.3^{aA}	18 ± 1^{cB}	5 ± 0.2^{bC}	3 ± 0.1^{dD}
3,4- Hydroxybenzoic	124 ± 1^{aA}	61 ± 4^{cB}	101 ± 4^{bC}	62 ± 4^{cD}
Catechin	97 ± 2^{aA}	58 ± 7^{cB}	89 ± 2^{bC}	58 ± 2^{cD}
4- Hydroxybenzoic	150 ± 3^{aA}	69 ± 3^{cB}	79 ± 2^{bC}	47 ± 1^{dD}
Caffeine	1799 ± 12^{aA}	962 ± 39^{cB}	2108 ± 29^{bC}	1342 ± 49^{dD}
CGA	1289 ± 5^{aA}	695 ± 30^{cB}	816 ± 15^{bC}	501 ± 16^{dD}
Caffeic acid	2 ± 0.1^{aA}	0.5 ± 0.1^{cB}	2 ± 0.1^{bC}	0.9 ± 0.1^{dD}

*Averages followed by the same letter, lowercase (comparison between classification) and uppercase (comparison between methods) in the line do not differ from each other, by Student's *t*-test, at a significance level of 95% (α = 0.05).

Different levels of the same compounds were found in the high-quality and traditional coffees, as presented in Table III. There was no significant difference in the content of gallic acid in the high-quality coffee samples extracted using methods A and B, according to the Student's *t*-test at the 95% confidence level. However, there were significant differences in the contents of 5-HMF, 3,4-hydroxybenzoic, catechin, 4-hydroxybenzoic, caffeine, CGA, and caffeic acid. Furthermore, the content of these compounds in high-quality and traditional coffees can be used as a marker, except for gallic acid, catechin, and 3,4-hydroxybenzoic for which there was no significant difference at the 95% confidence level.

From comparison of the extracts of the high-quality and traditional samples prepared using methods A and B, the concentrations of 5-HMF (33±0.3 mg 100 g^{-1} in the sample obtained by method A and 18±1 mg 100 g^{-1} in the sample obtained by method B) and CGA (1289±5 mg 100 g^{-1} in the sample obtained by method A and 695±30 mg 100 g^{-1} in the sample obtained by method B) were higher for high-quality coffee than traditional coffee. Thus, the content of these compounds is associated with the type of roast used and the sensory characteristics of higher-quality coffee.[23]

The highest caffeine content was found in traditional coffee. This result can be correlated to the coffees classified because blends between arabica and canephora species[5,30] constitute the traditional coffees.

Table IV presents some concentrations of CGA, caffeine, caffeic acid, and 5-HMF compounds found in the literature for different samples of roasted coffee.

Table IV. Contents of compounds quantified in different samples of the coffee

Description	Compounds				Ref.
	mg 100 g^{-1} of sample				
	CGA	Caffeine	Caffeic acid	5-HMF	
Gourmet	270 - 1200	990 - 1290	-	-	7
Traditional	140 - 690	1070 - 1790	-	-	
High-quality	2110	3440	790	100	23
Traditional	860	4890	300	-	

(continues on the next page)

Table IV. Contents of compounds quantified in different samples of the coffee (continuation)

Arabica	220 - 5960	4700	-	< 230	27
Robusta	130 - 6190	7200	-	< 40	

Comparing the concentrations found in this work (Table III) with those found by Souza et al.[7] (Table IV), the caffeine concentration was higher for the traditional classification coffee, and the CGA concentration was higher for the gourmet coffee. The concentration values were similar between the works. In work by Alcantara et al.,[23] 5-HMF was not detected for traditional coffee. The values found by the authors were higher than those found in this work for caffeine, caffeic acid, and 5-HMF, which may be linked to the coffee characteristics and the extraction method used by the authors. In the literature, levels of up to 230 mg 100 g^{-1} of 5-HMF were found for Arabica coffee and 40 mg 100 g^{-1} for Robusta coffee, with a marked decrease of the compound being observed in coffees with roasting.[27]

For works that investigated different conditions of extraction and concentration of chemical compounds in coffees, among these compounds caffeine and CGA, the results show differences in the concentrations of the compounds according to the extraction condition.[19,25] The concentrations of the compounds increase with temperature, regardless of the extraction method, flow rate, or contact time. Table V presents some concentrations of CGA and caffeine compounds found in the literature for different extraction conditions.

Table V. Contents of compounds quantified in different conditions of extraction

Description	**Compounds** mg mL^{-1}		**Ref.**
	CGA*	**Caffeine**	
Cold Drip	0.45 ± 0.04	1.27 ± 0.15	25
Cold Brew	0.35 ± 0.04	0.97 ± 0.12	
French Press	0.40 ± 0.03	1.09 ± 0.11	
Espresso Caffè Firenze	1.56 ± 0.17	1.43 ± 0.07	19
Espresso high-quality	4.80 ± 0.30	4.20 ± 0.09	
Espresso classical	4.46 ± 0.10	4.10 ± 0.16	
V60	0.80 ± 0.08	0.74 ± 0.09	
Cold Brew	1.39 ± 0.15	1.25 ± 0.12	
Aeropress	0.72 ± 0.11	0.78 ± 0.09	
French Press	0.53 ± 0.07	0.52 ± 0.06	
Moka	1.22 ± 0.18	1.28 ± 0.04	
Method A High-quality coffee	0.86 ± 0.01	1.20 ± 0.01	This study
Method B High-quality coffee	0.46 ± 0.02	0.64 ± 0.03	
Method A Traditional coffee	0.54 ± 0.01	1.41 ± 0.02	
Method B Traditional coffee	0.33 ± 0.01	0.89 ± 0.03	

*The CGA contents shown refer to 5-caffeoylquinic acid (5-CQA).

Despite the different extraction conditions presented in Table V, comparing the concentrations of CGA and caffeine, were found similar concentration values among the works.[19,25]

The same non-volatile compounds were identified in both extracts evaluated and significantly differed in the Student's *t*-test between methods (A and B) and the coffee type (high-quality and traditional). Although method A extracted a greater quantity of the compounds, method B was chosen due to its ease of execution compared to method A. The method chosen also had an efficient method for extracting compounds chosen as possible markers and is the method most similar to the usual method used by consumers in preparing the coffee beverage.

Total dissolved solids and extraction percentage

The °Bx of the coffee extracts prepared by methods A and B was evaluated. The TDS and PE were 3 and 45% and 1.7 and 25% for high-quality coffee extracted using methods A and B, respectively. For traditional coffee, the TDS and PE obtained with methods A and B were 3 and 39% and 1.8 and 26%, respectively.

The extraction percentage was higher for both coffees when method A was used (45 and 39%, respectively, for high-quality and traditional coffee). With method B, the average PE was 26%, which is closer to the ideal extraction value (18 and 22%), representing Lockart's quality and pleasant drink sensory characteristics proposed in 1957 in the Coffee Preparation Control Chart.[31]

Angeloni et al.,[19] when investigating eight different coffee beverage preparation methods, found a TDS variation from 1.35 ± 0.03 to 8.44 ± 0.38, and the range for PE was 28.60 ± 1.03 to 13.46 ± 1.56. The highest PE was found for the Mocha method and the lowest for the Espresso Caffè Firenze method.

Methods A and B both afforded superior extraction of coffee (PE > 22%), which is advantageous for quantifying the compounds. However, the coffee beverage may present notes of bitterness and astringency.

Despite being widely used by baristas and recommended by the Association of Specialty Coffees for evaluating the correct degree of extraction,[25] there are few studies on the TDS of coffees in the literature. In this study, a relationship between the highest extraction percentage and the highest levels of compounds quantified by method A was found.

CONCLUSIONS

Different extraction methods and variables were evaluated in the preparation of coffee extract. The TDS and PE results contributed to the choice of the extraction method. In addition to being non-toxic and low-cost, water was the optimal solvent for conforming to the principles of green chemistry and allowing direct comparison with sensory analysis. Among the extraction methods, method A enable the extraction of the largest amount of non-volatile compounds. Method B also showed satisfactory results for extracting the compounds of interest, with a PE closer to the ideal value (18 and 22%). This extraction method was chosen for further studies due to its ease of execution and similarity to the usual way of preparing coffee beverages used by consumers. Furthermore, the contents of the compounds can be used to discriminate between different coffees, where 5-HMF, 4-hydroxybenzoic, CGA, and caffeic acid can be used as possible markers.

Conflicts of interest

The authors declare that they have no conflict of interest.

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