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Analysis of polyphenols and xanthines in yerba mate (*Ilex paraguariensis*) infusions by high-pressure extraction and ultra-high performance liquid chromatography

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ABSTRACT

Yerba mate infusions are highly consumed and increasingly popular in the world. The evaluation of their chemical profiles representing the actual dietary intake may present analytical and interpretation challenges due to the diversity of available products, their drinking procedures, and transfer rates of the compounds into the infusions. There is a general interest in assessing the amounts of polyphenols in human diets to evaluate their potential health-promoting benefits. Thus, the objective of this work was to provide a fast and robust method for the analysis of infusions of yerba mate to evaluate teas with different particle sizes, degree of processing and type. A simple extraction using an espresso machine and ultra-high performance liquid chromatography with diode array detection (UHPLC-DAD) was developed and validated for the determination of theobromine, caffeine, caffeoylquinic and dicaffeoylquinic acids in yerba mate infusions. The chemical profiles of twenty-six yerba mate samples reflected their industrial processes. The dietary intake and the ratio of chlorogenic acids to caffeine of yerba mate was evaluated for different products (aged, green, and roasted yerba mate). The new method proved to be a fast, simple, and fit-for-purpose procedure for the aqueous extraction and determination of bioactive compounds in yerba mate products.

1. Introduction

The infusions of *Ilex paraguariensis* (yerba mate) are staples of the diet in the southern cone of South America, a drink that is also increasingly popular in the world. In 2019, the top importers of yerba mate were Uruguay, Syria, Chile, United States, and Spain (Datawheel, 2021). *Ilex paraguariensis* is a native plant of the subtropical and temperate regions of South America (Heck & de Mejia, 2007), grown in Argentina, Paraguay and Brazil. Through its industrialization process, involving heat treatments, grinding, and ageing, several products are made available to the final consumer. The main product consists of loose leaves of yerba mate, with distinct types according to its processing: aged, green or roasted; finely ground, coarsely ground or with twigs/stems; and special products such as yerba mate with the addition of aromatic herbs or sugar. Each of these products is associated with a specific brewing process: in the long-established method, 30 to 50 grams of yerba mate (green or aged) are placed in a gourd, horn or cup and successive extractions with small portions of water (known as "mateada") are suctioned using a straw with a filter (called "bombilla") (Hartwig et al., 2012; Vazquez & Moyna, 1986). These infusions are called "mate" or "chimarrão" when prepared with hot water and "tereré" when cold water is used (Hartwig et al., 2012). Yerba mate leaves can also be roasted to obtain a different product, roasted yerba mate ("chá-mate"), which is brewed as a tea that is mainly consumed as a cold drink. Other products such as yerba mate extracts in capsules or pills and energy drinks have been recently developed (Becker et al., 2019).

Besides being highly consumed as part of the human diets for centuries, herbal infusions attract interest as potential health-promoting foods, effects that are generally associated with their polyphenol content (Cory et al., 2018). Among the polyphenols of yerba mate, hydroxycinnamate esters (chlorogenic acids) are prominent, with high concentrations of caffeoylquinic and dicaffeoylquinic acids (Bravo et al., 2007; Filip et al., 2001). The main polyphenols in coffee are chlorogenic acids (CGAs) as well, with high amounts caffeoyquinic acids and also containing ferruloylquinic and dicaffeoylquinic acids (Clifford, 1999). Black and green tea (*Camelia sinensis*), on the other hand, contain catechins, such as (−)-epigallocatechin gallate (EGCG), (−)-epigallocatechin (EGC), (−) epicatechin gallate (ECG), and (−)-epicatechin (EC), and the main tea phenolic acid is gallic acid (Zuo et al., 2002). The consump-

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tion of green coffee, both in infusions and as concentrated extracts has sparked interest because of the high amounts of caffeoylquinic acids that it provides. The type and amounts of polyphenols may change during roasting; CGAs are transformed into lactones and other compounds, whereas caffeine is more stable during the process (Farah et al., 2005). The relative amount of CGAs and caffeine in coffee is suggested as an indicator that correlates with the degree of coffee roasting (Ludwig et al., 2014), and as a quality parameter that consumers may use to evaluate their intake of polyphenols in different coffee products (Jeon et al., 2019). The beneficial effects of polyphenol-rich diets are well documented, but the required amounts of each specific compound and its matrix (within foods or as a supplement) are not defined (Cory et al., 2018). Thus, the evaluation of dietary intake of polyphenols from food sources becomes relevant, as is the case for yerba mate infusions due to their widespread consumption.

Analytical procedures for the characterization of the bioactive compounds in yerba mate leaves (Marx et al., 2003) have been carried out by several extraction methods, including protocols using organic solvents and their aqueous mixtures with maceration, ultrasound assisted extraction and supercritical fluid extractions (Dartora et al., 2011; Dugo et al., 2009; Konieczynski et al., 2017; Lima et al., 2016; Marques & Farah, 2009; Perrenoud et al., 2016; Souza et al., 2021). Laboratory extractions that mimic the way that yerba mate is consumed with hot or cold infusions ("mateadas") (Bravo et al., 2007; Colpo et al., 2016; da Silveira et al., 2016; Kaltbach et al., 2022; Mesquita et al., 2021) or by decoction (Boger et al., 2018; Isolabella et al., 2010), have also been reported using different experimental setups, some of which involve lengthy procedures. The main bioactive compounds of dried leaves of yerba mate are still subject to further characterization (Lorini et al., 2021; Mateos et al., 2018). However, the evaluation of aqueous infusions representing the actual dietary intake present analytical and interpretation challenges due to the diversity of available products, drinking procedures and transfer rates into the infusions (Bravo et al., 2007; Panzl et al., 2022; Theuma & Attard, 2020). As an alternative, an *espresso* machine could be employed as an easily available and low-cost extraction method, and it has been reported as a viable method for organic solvent extractions in matrices such as spices and cannabis (Leiman et al., 2018; Martinez-Sena et al., 2017). It is also suitable for aqueous extractions (Caprioli et al., 2012); it requires simple laboratory procedures, and it is amenable to standardization.

In order to evaluate the amounts and types of polyphenols and other bioactive compounds in human diets, there is a need for fast and robust analytical methods that can be applied to the evaluation of teas with different particle sizes, degree of processing and type of product. The objective of the present work was to design and validate an analytical method for the aqueous extraction and determination of bioactive compounds in yerba mate infusions.

2. Materials and methods

2.1. Instrumentation and materials

Chromatographic analysis was performed in an UHPLC chromatograph (Nexera, Shimadzu, Kyoto, Japan) equipped with DAD detector (SPD-M30A), column oven (CTO-20A) and auto sampler (SIL-30A). Chromatograms were acquired using the *LabSolutions* software (version 5.52 SP2, Shimadzu, Kyoto, Japan).

Aqueous extractions were performed using a commercial domestic *espresso* machine (Phillips Espresso Duo HD5661, Netherlands) working at 15 bars. Sample compaction of the different types of samples was avoided using glass boiling pearls.

Analytical standards used for the determinations were caffeine with a purity of 99.8% obtained from Carlo Erba (Barcelona, Spain), 3,4 and 4,5 dicaffeoylquinic acids (DCQ) both with a purity of ≥ 95% obtained from PythoLab (Vestenbergsgreuth, Germany), 3,5 DCQ with a purity of 98% obtained from Indofine (New Jersey, USA), theobromine with a purity of 98% and chlorogenic acid (5-O-Caffeoilquinic acid) with a purity of 95% obtained from Cayman (Ann Arbor, Michigan, USA). Acetonitrile and methanol HPLC grade were purchased from J.T. Bakers (Mexico), formic acid with a purity of 98-100% was purchased from Merck (Germany). Aqueous infusions and mobile phase were prepared using ultrapure water (18.2 MΩ cm) obtained from an ultrapure water system (Arium Mini, Sartorius, Germany).

2.2. Stock solutions and standard solutions

Stock solutions of caffeine and theobromine were prepared in methanol: water (50:50 v/v); and 5-caffleoylquinic acid (5-CQA) in methanol at a concentration of 1000 mg $L^{-1}$and stored at -20°C (conventional freezer) until use. Intermediate mix solutions with the three standards were prepared in ultrapure water. The final concentration of the mix calibration solution ranged from 1 to 60 mg L^{-1} for caffeine and 5-caffleoylquinic acid, and 0.2 to 10 mg L^{-1} from theobromine. A solution of 3,5-dicaffeoylquinic acid in methanol at a concentration of 500 mgL^{-1} was prepared and stored at -20°C and an intermediate solution of 100 mg L^{-1} was prepared in ultrapure water. The analytical curve concentrations ranged from 1.0 to 75 mg L^{-1}. Standard solutions of DCQs isomers (3,4; and 4,5) were used for identification by comparing the retention time in the yerba mate samples chromatograms.

2.3. Samples of yerba mate

Twenty-six samples of yerba mate from seventeen different brands purchased in grocery stores in Uruguay, Argentina and Brazil were used in this study. Brands were selected among the ones with the highest commercialization in the region, according to the data provided by the local retail sales data. The products consumed in Uruguay are produced in Brazil (usually referred to as "PU1 type" or "Uruguayan standard") and include both aged yerba mate and aged yerba mate with addition of aromatic herbs (a combination of aromatic plants such as *Mentha sp, Peumus boldus, Tilia tormentosa*, and others). Yerba mate produced and consumed in Argentina include aged yerba mate and "aged yerba mate with stems/twigs", whereas tereré, green and roasted yerba mate are produced and consumed in Brazil. Information is summarized in Table 1.

2.4. Particle size analysis

Particle size distribution were performed using a set of sieves of 150, 106 and 75 μm with a sieve-shaker machine (Bertel, Brazil). Samples of yerba mate were weighted (about 2 g) and subjected to five minutes of mechanical shaking and five minutes of vibration in the plate sieve. Subsequent sieves were used, and particle size ranges were measured by weighing each retained portion.

2.5. Extraction methods

2.5.1. Espresso extraction method

The espresso machine was purged with 100 mL of ultrapure water three times with the stainless-steel capsule containing boiling pearls to clean up the system. The samples (3 ± 0.1 grams of vegetal material) were placed on top of 40 grams of boiling pearls, and serial extractions up to a total volume of 480 mL of ultrapure water were performed, with a nominal pressure of 15 bars and at 97 ± 1°C. The vegetal material was moistened with 5 mL of ultrapure water to avoid water losses in the first extraction and for standardization of the initial conditions. Extracts were transferred to a flask and brought to a final volume of 500 mL with ultrapure water. One milliliter was filtered by 0.22 μm PVDF and five-fold diluted in water before the chromatographic analysis, except for sample YM 12 (roasted yerba mate) that was analyzed without dilution. Three replicates of each yerba mate extraction were performed. The *espresso* machine extraction method is schematized in Fig. 1.

Table 1
Samples of yerba mate.

Identification	Consumed in	Brand	Type of product
YM 01	Brasil	A	Green yerba mate
YM 02	Brasil	B	Green yerba mate
YM 03	Argentina	C	Aged yerba mate with stems
YM 04	Uruguay[a]	D	Aged yerba mate
YM 05	Brasil	E	Green yerba mate
YM 06	Brasil	D	Tereré [c]
YM 07	Brasil	E	Tereré [c]
YM 08	Brasil	A	Green yerba mate
YM 09	Brasil	D	Green yerba mate
YM 10	Uruguay[a]	E	Aged yerba mate
YM 11	Uruguay[a]	F	Aged yerba mate
YM 12	Brasil	G	Roasted yerba mate
YM 13	Argentina	C	Aged yerba mate with stems
YM 14	Argentina	H	Aged yerba mate
YM 15	Uruguay[a]	I	Aged yerba mate
YM 16	Uruguay[a]	I	Aged yerba mate with herbs
YM 17	Uruguay[a]	F	Aged yerba mate
YM 18	Uruguay[a]	F	Aged yerba mate
YM 19	Uruguay[a]	J	Aged yerba mate
YM 20	Uruguay[a]	K	Aged yerba mate with herbs
YM 21	Uruguay[a]	F	Aged yerba mate with herbs
YM 22	Uruguay[a]	L	Aged yerba mate with herbs
YM 23	Uruguay[a,b]	I	Aged yerba mate
YM 24	Uruguay[a,b]	I	Aged yerba mate with herbs
YM 25	Uruguay[a,b]	D	Aged yerba mate
YM 26	Uruguay[a,b]	D	Aged yerba mate with herbs

[a] Produced in Brazil only for its consumption in Uruguay.
[b] Available mostly in grocery stores of the Brazil-Uruguay border regions.
[c] Green yerba mate product mostly used for Tereré cold brewing

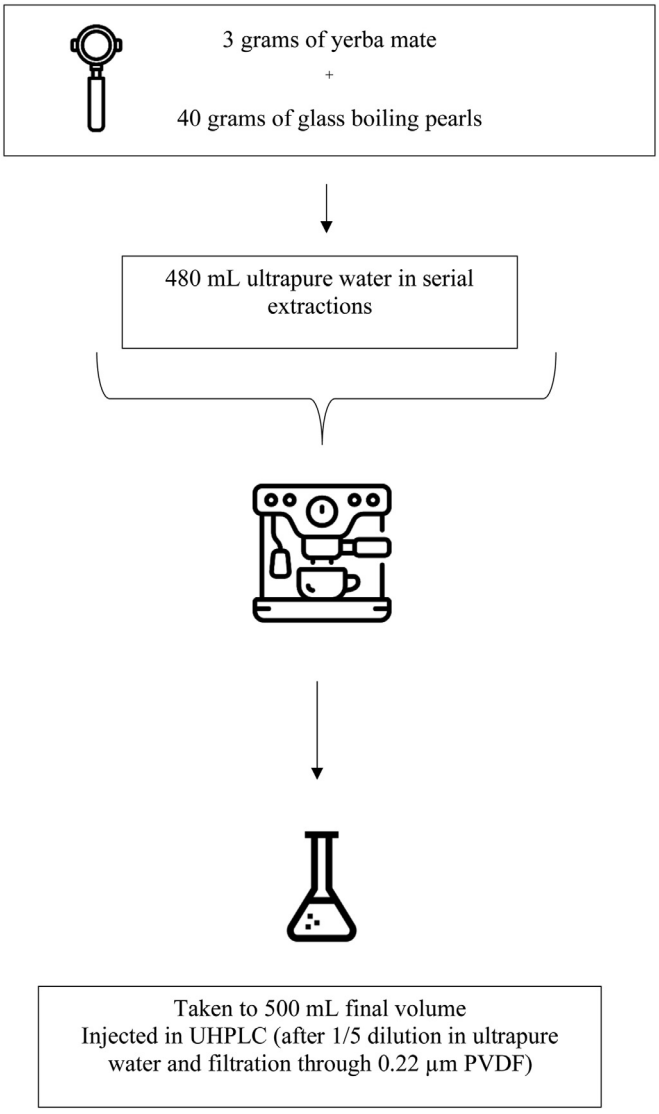

Fig. 1. Diagram of espresso machine extractions of yerba mate products.

2.5.2. Laboratory infusion extraction method

The simulation of the traditional infusion extraction method was carried out as described in Torterolo et al. (2014) with modifications. Briefly, 50 grams of yerba mate were poured into a beaker where 1 L of ultrapure water at a temperature of 80° C was added. The sample was kept in a thermostatic bath (80° C ± 2° C) for 15 minutes, stirring constantly. The liquid was extracted with a "bombilla" coupled to a vacuum system through a hose to suction the beverage. After cooling, the volume of the aqueous infusion was corrected to 1 L with ultrapure water. The extract was centrifuged for 10 minutes at 3,000 rpm. A few milliliters were filtered by 0.22 PVDF µm and ten-fold diluted before the chromatographic analysis.

2.6. Chromatographic analysis

Separation was performed using a C18 reversed-phase column (1.6 µm, 2.1 mm x 100 mm, CORTECS® UHPLC Waters, Milford, USA) with a C18 Security-Guard Ultra (AJ0-8782, California, USA), using a gradient elution of acetonitrile and water mobile phases (both with 0.1% formic acid) at a flow rate of 0.3 mL min^{-1}, a controlled temperature of 35 ± 0.2°C and an injection volume of 1.0 µL. Sample holder was kept at 10°C.

The mobile phase system consisted in 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B) used in a gradient elution as follows: 0-1 min, 7% B; 1-11 min, 30% B; and 11-13 minutes, 70% B before returning to the initial conditions for 3 min to re-equilibrate in a 16-minute run. Analytes were monitored at 272 nm for caffeine and theobromine, and 325 nm for caffeoyl and dicaffeoylquinic acids, and DAD signals were acquired in the 190-800 nm range.

2.7. Quantitative and semi-quantitative analysis of bioactive compounds

Caffeine and theobromine were quantified by external standard calibration with concentration ranges contemplating the different types of analyzed samples. 5-CQA analytical standard was used to quantify the compound and estimate its isomers 3-CQA and 4-CQA present in the samples, and the three analytes are expressed under the form of 5-CQA.

Three standard solutions of DCQs isomers (3,4; 3,5; and 4,5) were used for identification by comparing the retention time in the yerba mate samples chromatograms. A calibration curve using 3,5 DCQ (1.0 to 75 mg L^{-1}) was used to estimate the concentrations of the isomers present in the samples, and the analytes are expressed under the form of 3,5 DCQ.

2.8. Validation procedure for quantification of caffeine, theobromine and 5-CQA in aqueous extracts of yerba mate

The analytical method was validated for the determination of caffeine, theobromine, and 5-CQA in accordance with ICH and Eurachem guidelines (ICH, 2005; Magnusson & Örnemark, 2014) for linearity, accuracy by recovery of spiked samples, precision (instrumental precision and inter-day precision), LOD and LOQ, robustness and stability of the samples. The analytes in the samples were identified by comparison with the retention time of the standard and the UV-visible absorption spectra of the standard. The validation procedure of the method was carried out with the focus on the linearity range contemplating the different types of analyzed samples.

2.8.1. Linearity

Linearity was evaluated within a concentration of 50 and 150% of the expected concentration in the green, roasted and aged yerba mate samples. For this purpose, triplicate standard solutions of the analytes were prepared at seven concentration levels. The regression coefficient (R^2) was calculated, and visual inspection and residual distribution analysis were carried out. The selected model was lineal fitting.

2.8.2. LOQ and LOD

The limit of quantification (LOQ) and limit of detection (LOD) were defined by using $3\sigma/S$ and $10\ \sigma/S$, respectively, where σ is the standard deviation of ten consecutive blanks (blank extractions with ultrapure water) measurements and S is the slope of the linear curve.

2.8.3. Precision and accuracy by spike recovery

The intra-day and inter-day precision were determined by injecting five replicates of aqueous extraction of yerba mate, evaluating the percentage of relative standard deviation (%RSD) in four different days. The analysis was performed with five types of yerba mate products (green, aged, aged with stems, tereré and roasted yerba mate).

The instrumental precision was determined by the analysis of a medium concentration standard mix solution with five successive injections.

A recovery test was used to determine the accuracy of the proposed method. A known amount of each standard (caffeine, theobromine and 5-CQA) was added to 3 grams of yerba mate leaves. Triplicate analyses were performed for the test in three different levels (low, medium and high) and the method was evaluated based on the calculated RSD % value. The amounts of the three analytes present in the yerba mate were determined with five replicates of each sample without spikes.

2.8.4. Robustness

The method was evaluated by intentionally altering the optimized conditions in 10-15 % of the set point. The parameters were mobile phase composition (0.100 ± 0.015% acid formic), injection volume (1± 0.1μL), and column oven temperature (35± 3.5 ˚C). A control sample (quality control) was analysed in each series of experiments.

2.8.5. Sample stability

The fresh infusion of YM11 was filtered with 0.22 μm PVDF and aliquoted. These solutions were stored in several individual vials at -20˚ C. As validation and subsequent analysis of the samples were carried out, one vial was analyzed per experiment to evaluate the stability of the sample. For this purpose, the concentrations of caffeine, 5-CQA and theobromine were determined 20 times (in different days) over the course of 69 days.

2.9. Statistical analysis

Regression analysis of the calibration curves was performed by the least-squares method and analysis of variance (ANOVA) and Tukey test performed on the software Excel (Microsoft, USA). The data are expressed as means ± standard deviations (SD).

The calculation of the shelf life of the yerba mate extract solutions stored at -20°C was performed using the software Minitab 19 (Pennsylvania State University, USA), using as a mathematic model a linear regression analysis for the stability study with 95% confidence.

3. Results and discussion

The *espresso* machine extractions were optimized for yerba mate products. The particle size distribution and grinding type are among the parameters that affect extraction dynamics (Kaltbach et al., 2022; Meghwal & Goswami, 2010), thus the optimization for different products was achieved using glass boiling pearls to avoid the compaction of the plant material and to allow thorough contact with the extraction medium. The efficiency of the aqueous extraction using an *espresso* machine was evaluated with five types of yerba mate that differ in the sizes and proportions of leaves and stems in each product: green, roasted, aged, aged with stems/twigs and aged coarse ground. Estimated caffeine, theobromine and 5-CQA amounts were obtained using five serial infusions in the *espresso* machine, where the last infusion accounted for less than 5% of the total. After three consecutive infusions, 90 to 100% of the analytes of interest in yerba mate were extracted (Fig. 2). Samples like green yerba mate (YM01) and aged yerba mate (YM 11) required only one infusion step to extract 80 to 90% of caffeine, whereas samples with a higher proportion of larger size of leaves/stems and lower proportion of smaller size particles, such as roasted yerba mate (YM12), aged

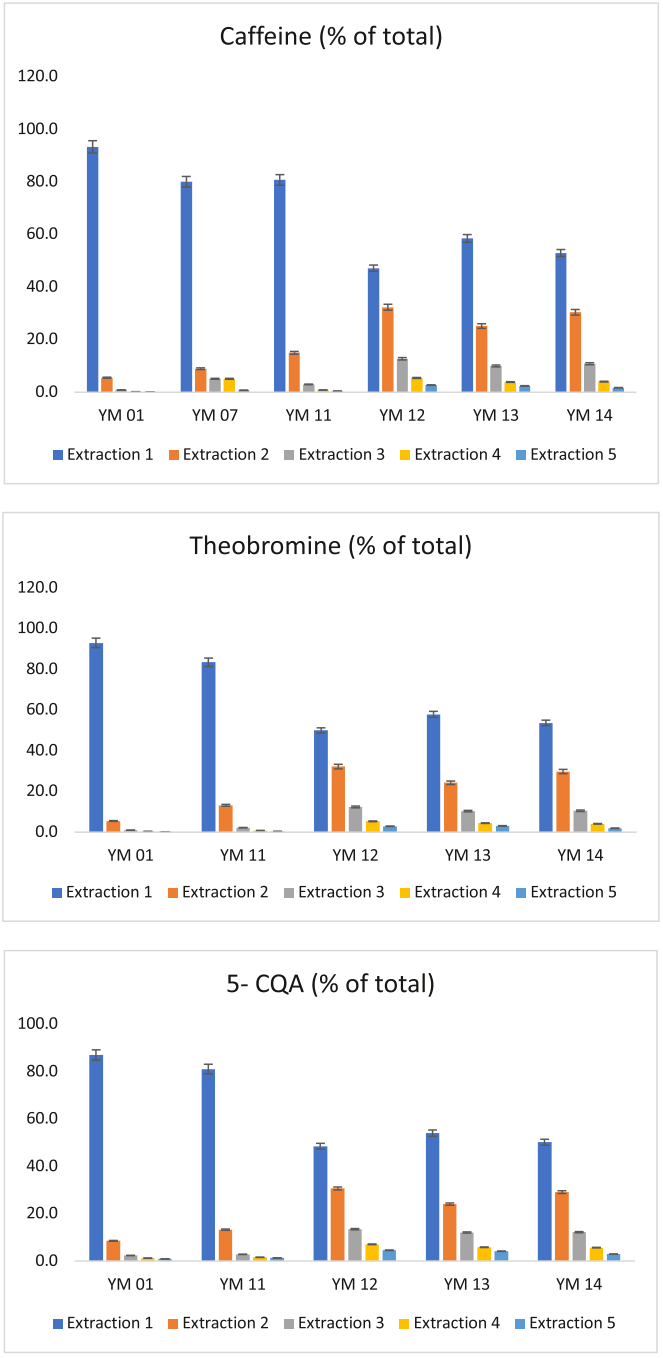

Fig. 2. Efficiency of extraction using the espresso machine method in five types of yerba mate products: green (YM01), tereré (YM07), roasted (YM12), aged (YM11), and aged with stems (YM13).

Table 2
Size and distribution of particles in yerba mate samples.

Sample	Sieve			
	150 mm	106 mm	75 mm	<75 mm
Aged yerba mate	79-84%	4-9%	5-7.5%	2-6%
Green yerba mate	59%	19%	10%	10%
Roasted yerba mate	99%	0	0	0
Aged yerba mate with stems	98%	0.1%	0	1.0%
Aged yerba mate (coarse ground)	98%	0.1%	0.1%	1.3%

coarse ground (YM14) or aged yerba mate with twigs/stems (YM13) presented a different pattern of extraction (Table 2).

The method was standardized to use 3 grams of yerba mate with 40 grams of boiling pearls in successive extractions up to 480 mL of ultrapure water. The espresso machine extraction method is schematized in Fig. 1.

A laboratory method that mimics the traditional mate drinking infusions with a "bombilla" was compared to the *espresso* machine method to evaluate the extraction efficiency and the overall procedure. Triplicate analysis of aged yerba mate YM11 with the *espresso* method resulted in 13.49 ± 0.13 mg g^{-1} for caffeine and 2.15 ± 0.01 mg g^{-1} for theobromine. A single extraction step (with 50 grams of yerba mate and 1 L of water) was used in the laboratory "bombilla" method, and the results (and amplitude) were 10.71 (0.16) mg g^{-1} for caffeine and 2.50 (0.30) mg g^{-1} for theobromine in duplicate analyses.

The usual form of drinking of yerba mate ("mateada") involves a process that is difficult to reproduce in a laboratory, requiring a time-consuming procedure with several successive steps that are not standardized (amounts of hot or cold water added to yerba mate, contact time, suction with the "bombilla", waiting interval, use of dry or moistened yerba mate, among other parameters). With the *espresso* machine method, all types of yerba mate products were processed in the same manner, with three successive extractions and a small amount of sample (3 grams) in a rapid procedure that reaches the same extraction end point for comparison of the samples.

The chromatographic separation for the determination of caffeine, theobromine, caffeoylquinic acids and dicaffeoylquinic acids was optimized in a UHPLC system and resulted in a short method of 16 minutes with low consumption of solvents (less than 1.5 mL of acetonitrile per run).

The high-pressure extraction method and UHPLC-DAD analysis were validated for the determination of caffeine, theobromine, and 5-CQA, and figures of merit are presented in Table 3. The analytical response showed a linear correlation with coefficients (R^2) of at least 0.999 calculated from external-standard calibration curves within the range chosen for the 3 analytes. The LOD and LOQ concentrations were calculated at 0.04 and 0.07 mg L^{-1} for theobromine, 0.58 and 0.62 mg L^{-1} for chlorogenic acid and 0.17 and 0.20 mg L^{-1} for caffeine, respectively. The recovery values for theobromine, chlorogenic acid and caffeine conducted at 3 spiking levels were between 92 and 99%. The method is robust to changes in mobile phase composition and column oven temperature, whereas variations in the injection volume affected the analytical results. The inter-day intermediate precision was evaluated by determination of the repeatability on four different days (n=3), and the analysis of variance (single factor, p 0.05) satisfied the acceptance limit. The intra-day precision analysis was performed with five types of yerba mate products (green, aged, aged with stems, tereré and roasted yerba mate). The replicates (n=5) had RSD % below the Horwitz value for their concentrations, except for Tereré (YM 07) (Table S1). Tereré yerba mate samples contain a large proportion of twigs or stems (see photos of the samples in Fig. 3), as well as finely ground leaves. This heterogeneity is reflected in a higher variation in the experimental results. Alternatively, samples could be ground to a specified particle size, an approach often used in herbal products analysis. However, the chemical profiles of the different yerba mate products ingested by the consumer depend on both

Table 3
Analytical figures of merit of the *espresso* machine extraction method.

Compounds	Analytical linear working range (mg L^{-1})	Analytical curve y = a X + b	R^2	LOD [a] (mg L^{-1})	LOQ [a] (mg L^{-1})	Intermediate precision (mg g^{-1})		Recovery (%)						
						YM 11	%RSD	Low	%RSD	Medium	%RSD	High	%RSD	
Theobromine	0.2-10	y = 10.402,0x - 6.203,57	0.999	0.04	0.07	2.18 ± 0.01	0.66	98 ± 1.6	1.65	97 ± 1.7	1.75	99 ± 1.0	1.03	
5-Caffeoylquinic acid	1.0-60	y = 11.567,5x - 359,16	0.999	0.58	0.62	16.49 ± 0.13	0.77	92 ± 1.7	1.9	95 ± 1.3	1.37	96 ± 0.1	0.08	
Caffeine	1.0-60	y = 10.333,3x - 1.105,93	0.999	0.17	0.2	13.33 ± 0.11	0.79	96 ± 1.5	1.61	97 ± 2.3	2.39	98 ± 1.6	0.62	

[a] LOQ= Limit of quantification; LOD= limit of detection.

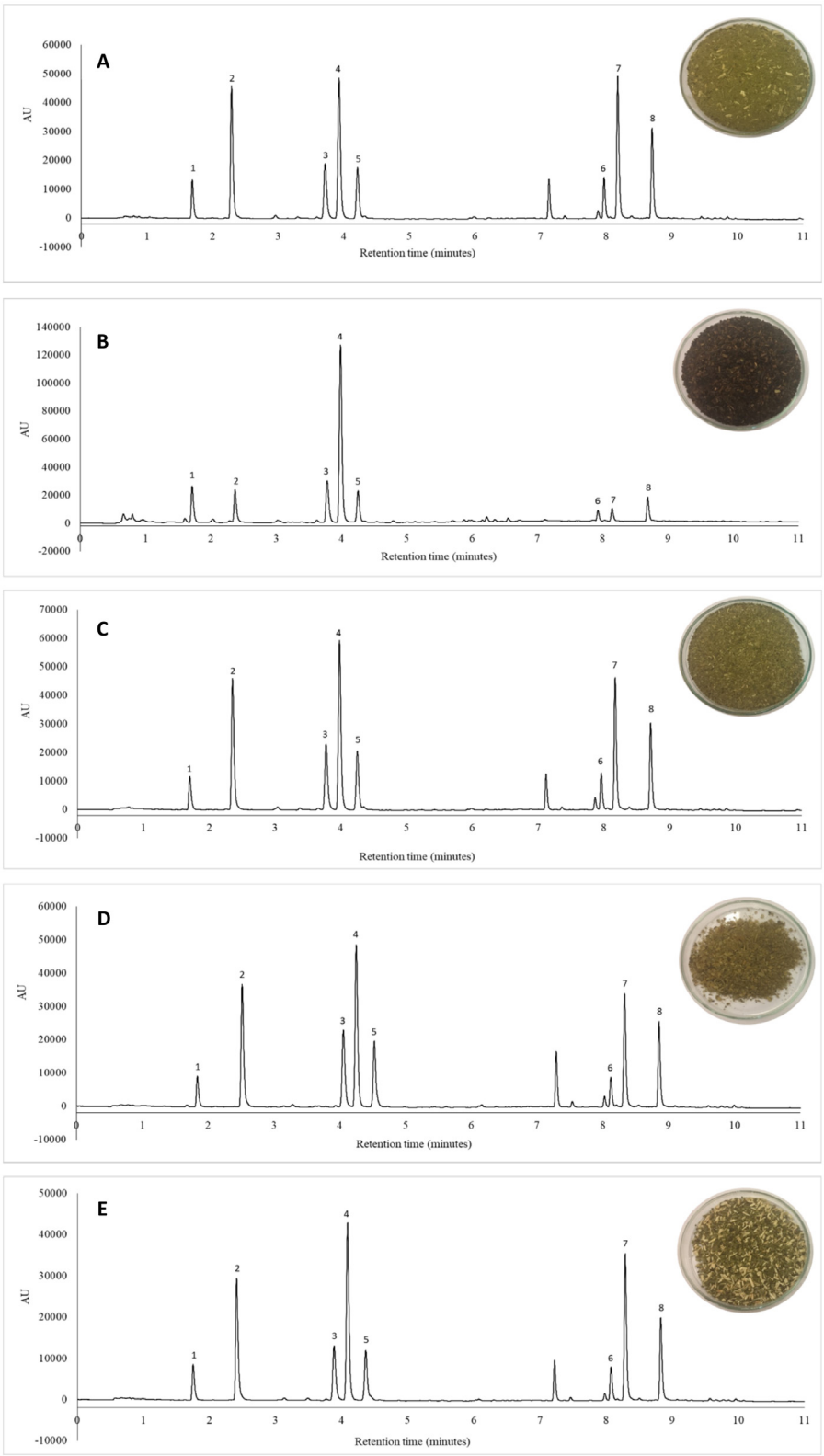

Fig. 3. UPLC-DAD chromatogram at 272 nm. A) Green yerba mate YM 01 (Brazil); B) Roasted yerba mate YM 12 (Brazil); C) Aged yerba mate YM 11 (Brazil, for export to Uruguay); D) Aged yerba mate without stems YM 14 (Argentina); E) Tererê YM 06 (Brazil). Peak identification: (1) theobromine; (2) 3-caffeoylquinic acid; (3) 5-caffeoylquinic acid; (4) caffeine; (5) 4-caffeoylquinic acid; (6) 3,4-dicaffeoylquinic acid; (7) 3,5-dicaffeoylquinic acid; (8) 4,5-dicaffeoylquinic acid.

the composition of the sample and the physical parameters involved in the brewing process. For this reason, the analyses were performed in the samples without modification.

For the study of stability of the yerba mate extracts, the aqueous infusions were stored at -20°C and one vial was analyzed per experiment. The concentrations of caffeine, 5-CQA and theobromine were determined 20 times (in different days) over the course of 69 days. A normal distribution of the residues was observed for the proposed model (linear regression), and appropriate values of the quantitative attribute (concentration) were obtained (Table S2). The samples were stable for the analysis of caffeine for 51 days, for theobromine for 47 days and 5-CQA for 55 days.

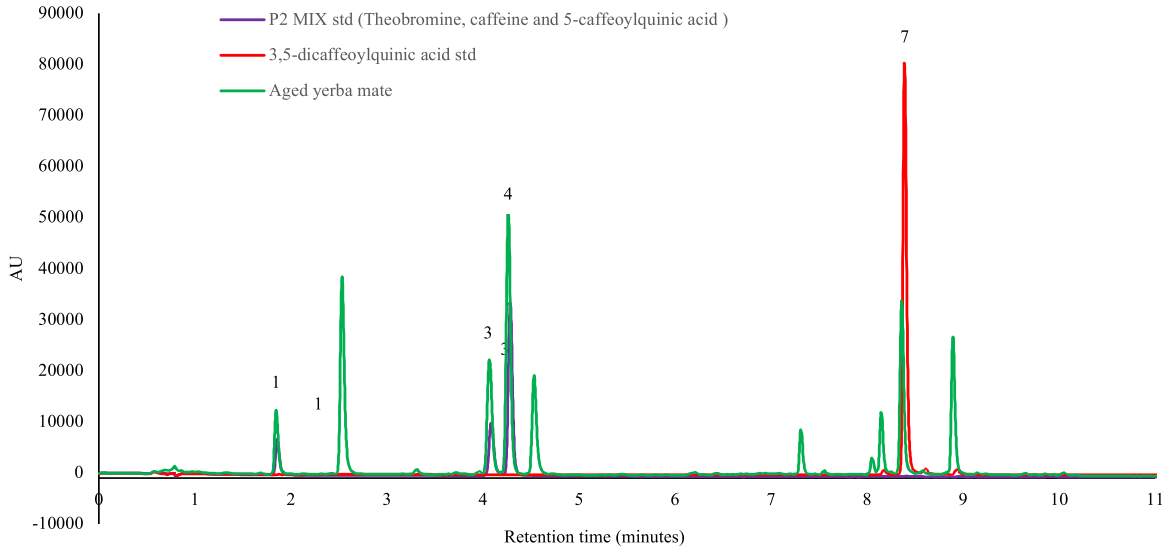

Fig. 4. UHPLC-DAD profile of standards and *Ilex paraguariensis* by high-pressure extraction (YM 15). Chromatogram monitored at 272 nm and 325 nm wavelengths of standard solution. P2 Mixture of theobromine (1) RT = 1.8 min, 5-caffeoylquinic acid (3) RT = 4.0 min, caffeine (4) RT = 4.2 min and 3,5-dicaffeoylquinic acid (7) RT = 8.2 min.

The content of the analytes in the aqueous infusions of different types of commercial yerba mate samples are shown in Table 4, where values are presented in mg g^{-1} of yerba mate used for the infusion. Aged yerba mate infusions contained 7.6 to 13.5 mg g^{-1} of caffeine, green yerba mate 7.4 to 13.7 mg g^{-1}, aged yerba mate with herbs 9.1 to 11.8 mg g^{-1} and roasted yerba mate 5.7 mg g^{-1}. The estimated total sum of caffeoylquinic and di-caffeoylquinic acids contents were 79.2 to 97.8 mg g^{-1} for aged yerba mate, 77.5 to 95.8 mg g^{-1} for green yerba mate, 74.6 to 92.6 mg g^{-1} for yerba mate with herbs and 12.4 mg g^{-1} for roasted yerba mate. Caffeoylquinic acids isomers were quantified with 5-CQA as surrogate standard (Clifford & Madala, 2017), and dicaffeoylquinic acids isomers concentrations were estimated using 3,5 DCQ.

3-CQA was the isomer of caffeoylquinic acids present in higher concentration in the 26 samples, in agreement with previous reports (Colpo et al., 2016), and in contrast with the chemical profile of coffee, where 5-CQA is the prevalent caffeoylquinic isomer (Farah & Donangelo, 2006) .

Chromatograms of yerba mate aqueous extractions are depicted in Fig. 3 for each type of product and the xanthines profile (caffeine and theobromine) and main chlorogenic acids (5-CQA and 3,5-DCQ) are shown in Fig. 4. The chemical profiles of different types of yerba mate infusions have a typical relative distribution among the main caffeoyl and dicaffeoylquinic acid isomers, except for roasted yerba mate (Lima et al., 2016; Marques & Farah, 2009). Due to the roasting process, the composition changes, as reflected in the lower content of all the analytes and in the relative proportion of the isomers. The ratio of 3-CQA to 5-CQA is < 1 and the 4,5-DCQ/3,5-DCQ ratio is > 1 for roasted yerba mate, whereas for green and aged yerba mate, inverse ratios are found (Table 4).

The ratio of caffeine to caffeoylquinic acids correlates with the degree of coffee roasting (Farah et al., 2005; Ludwig et al., 2014), with higher values corresponding to darker roasts. In the case of yerba mate, the only product that undergoes a similar process is roasted yerba mate. Thus, the ratio of caffeine to the sum of caffeoylquinic acids is about 0.6 for roasted yerba mate, and between 0.15 and 0.27 for other types of yerba mate products. Consumers may use this ratio as a quality parameter to evaluate their intake of polyphenols relative to caffeine, as reported in studies of coffee drinks with values of 0.4 to 4.6 for ground coffee and values of 0.6 to 5.9 for ready-to-drink coffees (Jeon et al., 2019). Yerba mate provides a high amount of CGAs relative to the caffeine intake as reflected by low ratios of this parameter and may be considered a good source of CGAs in the diet.

The diversity of consumption practices and analytical extraction methods adds complexity to the interpretation of results of the potential dietary intake of bioactive compounds from yerba mate. Laboratory adaptations of the “mateada” infusions have been employed, as well as other infusion methods, and data obtained in the present study are presented along with values reported by several authors in Table 5 . In order to make comparisons among the reported data, all results were recalculated and expressed as amount of analyte in dry extracted material. The ratios of yerba mate to water used in the extractions were also calculated for the reviewed literature, with ratios ranging from 1:4 to 1:200 under several methodological procedures. Chemical profiles of yerba mate extracts may vary according to the type of product analyzed and analytical extraction methodology employed, but general trends are consistent among most authors. Higher amounts of xanthines and polyphenols are generally observed in aged and green yerba mate compared to tereré (Bastos et al., 2006; da Silveira et al., 2016; Peres et al., 2013), probably due to a higher content of twigs/stems in tereré. Roasted yerba mate, the only product that undergoes a roasting process, contains lower amounts of all analytes, and is also consumed as a tea-like infusion, involving the use of smaller amounts of product per serving (about 2.5 grams according to manufacturer instructions). The variation in the level of the analytes in yerba mate samples from different manufacturing processes or production regions can be determined using the fast and simple espresso machine method, which offers the same end point of extraction for comparison of the infusions. The chemical profiles obtained with the validated analytical method add to the experimental data related to the determination of dietary polyphenols and xanthines in commercial yerba mate products.

When considering the consumption of the different yerba mate products (roasted yerba mate for tea infusions using 2.5 grams per serving, and green, aged and with herbs with 25 grams per serving), the intake of the bioactive compounds was estimated, and results are shown in Table S3. These infusions provide a good intake of CGAs depending on the form of consumption. For the equivalent to the traditional drinking manner (25 g per serving), the intake of caffeine is between 172 and 342 mg, whereas the sum of caffeoylquinic acids is between 803 to 1404 mg. The ratio of caffeine to the sum of caffeoylquinic acids (CQAs) is between 0.15 to 0.27, values that are comparable to green or lightly roasted coffee and indicate that yerba mate is a good source of CQAs with a lower intake of caffeine. For mate tea (2.5 g per serving), the intake of caf-

Table 4
Mean concentration ± SD (n=3, mg g^{-1}) of xanthines, caffeoylquinic acids and dicaffeoylquinic acids in yerba mate aqueous infusions.

N° YM	Theobromine (mg g^{-1})	Caffeine (mg g^{-1})	3-CQ [d] (mg g^{-1})	5-CQA (mg g^{-1})	4-CQA [d] (mg g^{-1})	3,4-DCQ [e] (mg g^{-1})	3,5-DCQ (mg g^{-1})	4,5-DCQ [e] (mg g^{-1})	Caffeine / ΣCQA ratio	3-CQA/5-CQA ratio	4,5-diCQA/3,5-diCQA ratio
1 [a]	2.11 ± 0.03	11.41 ± 0.26	24.05 ± 0.26	13.44 ± 0.23	13.20 ± 0.59	6.77 ± 0.28	22.35 ± 0.19	15.13 ± 0.68	0.23	1.79	0.68
2 [a]	1.98 ± 0.03	10.94 ± 0.16	18.86 ± 0.53	12.86 ± 0.08	10.13 ± 0.18	4.43 ± 0.24	19.16 ± 0.77	12.09 ± 0.26	0.26	1.47	0.63
3 [b]	1.04 ± 0.06	9.72 ± 0.53	19.98 ± 1.27	14.82 ± 0.82	12.21 ± 0.84	2.71 ± 0.22	17.95 ± 1.16	11.53 ± 0.89	0.21	1.35	0.64
4 [c]	2.00 ± 0.04	12.07 ± 0.09	22.91 ± 0.25	15.66 ± 0.06	13.22 ± 0.15	5.49 ± 0.03	20.85 ± 0.20	13.89 ± 0.15	0.23	1.46	0.67
5 [a]	2.01 ± 0.06	13.67 ± 0.35	24.99 ± 0.69	14.28 ± 0.32	12.64 ± 0.43	5.21 ± 0.29	23.56 ± 0.58	14.47 ± 0.67	0.26	1.75	0.61
6 [a]	1.37 ± 0.11	8.82 ± 0.88	15.17 ± 1.48	8.88 ± 0.57	8.07 ± 0.75	2.63 ± 1.04	16.50 ± 1.61	9.39 ± 0.90	0.27	1.71	0.57
7 [a]	1.75 ± 0.10	9.48 ± 0.60	19.14 ± 1.29	13.05 ± 0.39	11.08 ± 0.45	5.49 ± 0.22	19.23 ± 1.50	13.49 ± 0.49	0.22	1.47	0.70
8 [a]	2.17 ± 0.04	13.44 ± 0.24	23.82 ± 0.40	13.22 ± 0.25	12.34 ± 0.25	5.96 ± 0.15	24.29 ± 0.16	16.21 ± 0.26	0.27	1.80	0.67
9 [a]	2.19 ± 0.07	7.38 ± 0.13	22.21 ± 0.31	14.86 ± 0.20	12.20 ± 0.53	5.31 ± 0.11	18.77 ± 0.35	12.73 ± 0.42	0.15	1.49	0.68
10 [c]	1.23 ± 0.01	10.44 ± 0.03	22.59 ± 0.20	15.05 ± 0.10	13.04 ± 0.18	3.39 ± 0.10	20.66 ± 0.08	14.48 ± 0.19	0.21	1.50	0.70
11 [c]	2.15 ± 0.01	13.49 ± 0.13	25.81 ± 0.10	15.91 ± 0.15	14.42 ± 0.06	5.83 ± 0.05	21.47 ± 0.18	14.36 ± 0.15	0.24	1.62	0.67
12 [a]	0.92 ± 0.03	5.65 ± 0.15	2.57 ± 0.05	3.98 ± 0.13	2.94 ± 0.08	0.55 ± 0.02	0.91 ± 0.02	1.45 ± 0.11	0.60	0.65	1.59
13 [b]	0.97 ± 0.07	6.88 ± 0.46	15.77 ± 1.38	14.40 ± 0.68	10.53 ± 0.59	4.06 ± 0.21	13.83 ± 1.28	11.26 ± 0.70	0.17	1.10	0.81
14 [b]	1.61 ± 0.10	10.96 ± 0.53	20.71 ± 0.90	15.45 ± 0.61	11.39 ± 0.51	3.97 ± 0.22	16.91 ± 0.89	12.76 ± 0.80	0.23	1.34	0.75
15 [c]	2.14 ± 0.05	10.51 ± 0.30	21.60 ± 0.20	14.77 ± 0.47	12.32 ± 0.05	4.76 ± 0.02	17.32 ± 0.74	12.32 ± 0.14	0.22	1.46	0.71
16 [c]	1.50 ± 0.05	9.56 ± 0.07	19.22 ± 0.13	13.77 ± 0.15	11.49 ± 0.17	3.85 ± 0.08	15.79 ± 0.18	11.78 ± 0.39	0.21	1.40	0.75
17 [c]	2.50 ± 0.09	12.32 ± 0.39	22.27 ± 0.63	15.87 ± 0.47	12.88 ± 0.24	5.50 ± 0.03	18.45 ± 0.48	13.16 ± 0.23	0.24	1.40	0.71
18 [c]	2.37 ± 0.06	13.10 ± 0.15	23.44 ± 0.17	17.21 ± 0.36	13.84 ± 0.48	5.57 ± 0.14	19.03 ± 0.31	13.90 ± 0.66	0.24	1.36	0.73
19 [c]	1.21 ± 0.03	7.57 ± 0.22	18.11 ± 0.67	15.54 ± 0.47	12.02 ± 0.25	5.04 ± 0.14	18.82 ± 0.68	15.15 ± 0.34	0.17	1.17	0.80
20 [c]	1.58 ± 0.02	9.06 ± 0.03	18.54 ± 0.13	13.92 ± 0.09	11.62 ± 0.34	4.50 ± 0.11	14.37 ± 0.31	11.69 ± 0.34	0.21	1.33	0.81
21 [c]	2.63 ± 0.02	11.39 ± 0.18	21.66 ± 0.20	15.58 ± 0.12	12.82 ± 0.13	5.71 ± 0.11	18.30 ± 0.22	13.31 ± 0.36	0.23	1.39	0.73
22 [c]	2.09 ± 0.04	11.84 ± 0.42	22.72 ± 0.94	13.94 ± 0.41	12.55 ± 0.41	6.09 ± 0.17	21.81 ± 1.25	15.48 ± 0.71	0.24	1.63	0.71
23 [c]	1.01 ± 0.04	7.85 ± 0.08	18.93 ± 1.48	13.87 ± 0.57	11.05 ± 0.75	5.33 ± 0.11	17.46 ± 0.17	12.54 ± 0.33	0.18	1.36	0.72
24 [c]	1.09 ± 0.02	7.55 ± 0.10	17.95 ± 0.25	13.37 ± 0.18	10.53 ± 0.44	5.00 ± 0.46	16.60 ± 0.52	12.26 ± 0.49	0.18	1.34	0.74
25 [c]	1.66 ± 0.02	10.28 ± 0.10	22.58 ± 0.77	16.00 ± 0.34	13.59 ± 0.16	6.17 ± 0.13	19.30 ± 0.87	14.51 ± 0.26	0.20	1.41	0.75
26 [c]	1.56 ± 0.06	9.12 ± 0.32	21.21 ± 0.70	14.21 ± 0.63	15.33 ± 0.78	5.70 ± 0.22	20.13 ± 0.61	14.84 ± 0.75	0.18	1.49	0.74

Compounds: 3-CQA - 3-caffeoylquinic acid, 4-CQA - 4-caffeoylquinic acid, 5-CQA - 5-caffeoylquinic acid, 3,4-DCQ - 3,4 dicaffeoylquinic acid, 3,5-DCQ - 3,5 dicaffeoylquinic acid, 4,5-DCQ - 4,5 dicaffeoylquinic acid.
ΣCQA = sum of 3-CQA+ 4-CQA+ 5-CQA.

[a] Produced and consumed in Brazil.
[b] Produced and consumed in Argentina.
[c] Produced in Brazil and consumed only in Uruguay.
[d] Expressed as 5-CQA.
[e] Expressed as 3,5-DCQ.

Table 5
Quantification of xanthines and polyphenols in infusions of yerba mate (*Ilex paraguariensis*).

Extraction and analysis	Sample	Analytes (Range, mg g^{-1})								Ref.
		Caffeine	Theobromine	3-CQA	5-CQA	4-CQA	3,5 DCQ	3,4 DCQ	4,5 DCQ	
Aqueous extraction: 5g with 70 mL of boiling water during 20 min. HPLC-DAD. Ratio yerba mate: water 1:14.	Leaves collected in its original habitat from Argentina	19.22	4.84	Not reported	29.0	Not reported	30.4	8.5	28.9	(Filip et al., 2001; Rosana Filip et al., 1998)
Aqueous extraction: 10 g with 100 mL of water at 75°C. Capillary Electrophoresis – DAD. Ratio yerba mate: water 1:10.	Milled aged yerba mate from Argentina	7.8-17.2	1.1-6.7	Not reported						(Pomilio et al., 2002)
Two serial extractions: Chimarrão 1.5 g with 30 mL of boiling water. Tererê was prepared in a similar procedure, with cold water at 10°C HPLC-DAD. Ratio yerba mate: water 1:20.	Chimarrão from Brazil (Brand 1 to 3)	8.1-13.2	Not reported		13.2-18.5	Not reported				(Bastos et al., 2005)
	Tererê yerba mate (Brand 1 to 3)	4.5-8.2	Not reported		10.6-14.8	Not reported				
Aqueous extraction 2.7 g dried leaves with 250 mL of boiling water at 98°C. HPLC-DAD. Ratio yerba mate: water 1:93.	Native-Planted Forest-Plantation, dry in wood or air from Argentina, Brazil and Paraguay	3.9-16.7	1.5-7.3	4.8-24.9	6.9-33.0	4.6-41.3	Not reported			(Heck et al., 2008)
Aqueous extraction 1 g with 190 mL of water at 95°C.	Green yerba mate from Brazil	Not reported		21-24.7	14.3-15.0	9.5-10.7	18.5-29.2	3.6-5.4	10.2-15.2	(Marques & Farah, 2009)
HPLC-DAD/MS. Ratio yerba mate: water 1:190.	Roasted yerba mate from Brazil	Not reported		1.9-4.3	3.8-7.5	2.4-5.6	0.6-2.1	0.4-1.5	0.9-3.3	
Thirty serial extractions: Chimarrão 85 g with 110 mL of water at 75°C and Tererê, 50 g of yerba mate with 100 mL of water at 11°C. Capillary Electrophoresis. Ratio 1:40/1:61.	Chimarrão (native, traditional, smooth and course ground) from Brazil	6.1-8.3	1.6-2.0	Not reported						(Meinhart et al., 2010)
	Tererê yerba mate from Brazil	10.2	2.12	Not reported						
Aqueous extraction 100 g with 500 mL (x3) of boiling water (100°C).	Young green leaves processed (1 month old) from Brazil	9.5-11.1	2.6-3.4	8.4-12.3	9.3-11.4	11.6-12.5	Not reported			(Dartora et al., 2011)
UHPLC-QqQ. Ratio yerba mate: water 1:15.	Matured green leaves processed (6 month old) from Brazil	12.4-13.9	3.2-4.6	10.6-14.4	11.8-15.0	13.8-17.0	Not reported			
Aqueous extraction: Chimarrão 5 g with 250 mL of water at 70°C. Tererê was prepared in a similar procedure, except that cold water at 5°C was used.	Chimarrão from Brazil	6.2-13.4	3.2-6.3	7.6-12.1	9.2-13.2	6.2-9.4	5.6-8.4	Not reported	7.2-14.5	(Peres et al., 2013)
HPLC-DAD. Ratio 1:50.	Tererê yerba mate from Brazil	5.7-12.3	2.7-5.7	6.1-10.9	8.2-10.5	5.1-8.5	5.2-7.3	Not reported	6.9-12.8	
Aqueous extraction 500 mg with 50 mL of boiling water at 98°C.	Leaves processed yerba mate- Plan A from Argentina	Not reported		20.8	27.3	15.4	Not reported			(Butiuk et al., 2016)
HPLC-DAD. Ratio yerba mate: water 1:100.	Leaves processed yerba mate-Plant B from Argentina	Not reported		16.9	21.8	12.6	Not reported			

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Table 5 (*continued*)

Thirty serial extractions: Chimarrão 85 g with 110 mL of water at 75°C and Tererê, 50 g of yerba mate with 100 mL of water at 11°C.	Chimarrão from Brazil	Not reported			9.7-11	Not reported	8.6-15.1	1.7-2.5	2.8-7.3	(da Silveira et al., 2016)
HPLC-DAD. Ratio yerba mate: water 1:4.	Tererê yerba mate from Brazil	Not reported			2.5		2.8	0.5	0.7	
Aqueous extraction 70 g with 1000 mL at 80°C and stirring at 400 rpm. Ratio yerba mate: water 1:14.	Commercial yerba mate-Paraná from Brazil	12 1.7			Not reported	8.5	Not reported			(Boger et al., 2018)
Aqueous extraction 2.5 g with 240 mL of boiling water. HPLC-DAD/MS. Ratio yerba mate: water 1:96.	Mate C from Spain	Not reported		22.1	17.2	10.9	7.3	1.7	3.9	(Baeza et al., 2018)
Aqueous extraction: 2 g with 100 mL of water at 80°C for 8 min.	Paraná commercial yerba mate from Brazil	27.2	6.4	14.2	23.2	9.5	Not reported			(Zielinksi et al., 2020)
HPLC-DAD.	Santa catarina commercial yerba mate from Brazil	27.3	7.2	13.5	22	8.7				
Ratio yerba mate: water 1:50.	Rio Grande commercial yerba mate from Brazil	29.9	7.2	13.6	25.3	7.1				
Exhaustive aqueous extraction (EAE) with 1 g with 200 mL of water at 100°C.	Uruguay commercial yerba mate (typical standard and fine)	9.8-10.6	1.9-2.3	32.2-34.5	19.9-22.5	Not reported	25.1-29.4			(Kaltbach et al., 2020)
	Argentina commercial yerba mate (typical standard and mild)	10.6-11.1	1.5-1.9	30.9-32.1	19.9-22.1		26.6-28.5			
HPTLC-MS.	Brazil commercial yerba mate (typical standard and coarse)	7.4-11.5	1.6-2.4	26.2-32.9	17.2-21.7		24.7-27.8			
	Brazil commercial yerba mate (craft)	5.6-13.9	1.3-2.4	25.4-36.7	14.9-19.4		19.8-24.6			
Ratio yerba mate: water 1:200.	Roasted yerba mate from Brazil	5.8	1.1	6.9	6.7		4.6			
Aqueous extraction: 1 g beans or leaves with 100 mL of water at 94°C for 10 min. HPLC-MS. Ratio yerba mate: water 1:100.	YM A	11.4	2.3	Not reported						(Jeszka-Skowron et al., 2020)
	YM B	9.8	1.2							
Exhaustive aqueous extraction (EAE) with 1 g with 200 mL of water at 100°C. HPTLC-MS. Ratio yerba mate: water 1:200.	Σ 3 samples de yerba mate (fine, medium and coarse ground)	8.4	1.6	18.9	27.2	Not reported	23.9	Not reported	13.4	(Kaltbach et al., 2022)
Serial extraction (3) in espresso machine extraction: 3 g with 480 mL of water at 95-97°C.	Aged yerba mate from Argentina and Uruguay	7.6-13.5	1.0-2.5	18.1-25.8	14.0-17.0	11.0-14.4	17.0-21.0	3.0-6.0	12.0-15.0	This study

(*continued on next page*)

Table 5 (*continued*)

	Aged with herbs from Uruguay	7.6-12.0	1.0-2.6	17.9-22.7	13.0-16.0	10.5-15.3	14.0-22.0	4.0-6.0	12.0-15.5
UHPLC-DAD.	Aged with stems from Argentina	6.8-9.7	1.0	15.7-19.9	14.4-14.8	10.5-12.2	14.0-18.0	3.0-4.0	11.0-12.0
	Tererê from Brazil	8.8-9.5	1.4-1.8	15.1-19.1	9.0-13.0	8.0-11.0	17.0-19.0	3.0-5.0	9.0-13.0
Ratio yerba mate: water 1:170.	Green yerba mate from Brazil	7.4-14.0	2.0-2.2	18.8-24.9	13.0-15.0	10.1-13.2	19.0-24.0	5.0-7.0	13.0-16.0
	Roasted yerba mate from Brazil	5.6	0.9	2.6	4.0	2.9	0.9	0.6	1.5

feine is about 14 mg and 24 mg for the sum of caffeoylquinic acids, with a ratio of 0.58, like other roasted products. The reported amounts of caffeine in coffee and tea present variations according to the type of product and amount of serving (Center for Science in the Public Interest, n.d.). For coffee shops brews, the amount of caffeine ranges from 150 mg in an expresso (1.5oz) to 410 mg in a 20oz serving of coffee. Brewed bags of black tea provide 55 to 60 mg of caffeine and green teas 35-58 mg. Thus, yerba mate (25 mg serving) provides an amount of caffeine comparable to coffee brews, and roasted yerba mate (2.5g serving) a small amount of caffeine which is less of that of a serving of black tea.

4. Conclusions

The use of an *espresso* machine system is a valuable tool for the aqueous extraction of bioactive compounds, such as theobromine, caffeine, caffeoylquinic acids and dicaffeoylquinic acids from different products of yerba mate (*Ilex paraguariensis)*. Target compounds were quantitatively extracted in three simple and fast steps using a small amount of sample, and the analysis was performed by UHPLC-DAD in a chromatographic method with a rapid separation of the analytes. The validated analytical method is fit-for-purpose for the evaluation of the chemical profiles of yerba mate infusions, with the advantages of small consumption of samples and chromatographic solvents and short extraction and analysis times. The new method that resulted from this work has a potential application to be used as a simple and efficient quality control method in the evaluation of yerba mate tea products. Chemical profiles of twenty-six commercial samples of yerba mate are reported using the validated method. Variations of the chemical profiles and total content of xanthines and polyphenols can be observed among different types of yerba mate products (green, aged, with herbs, roasted), with a typical relative distribution among the main caffeoyl and dicaffeoylquinic acid isomers, except for roasted yerba mate due to the roasting process it undergoes. Yerba mate products have a low caffeine/CGAs ratio, which can be an attractive quality parameter for consumers. The results of this study increment experimental databases of food polyphenols, thus contributing to further research on the consumption of yerba mate products in different populations required to evaluate their potential health-promoting effects. The analysis of other tea matrices and the relevant analytes they require (herbal teas, *Camellia sinensis*, green coffee, and others), as well as the study of sample modification (through grinding) for the use of the method as a routine quality control are suggested topics for future investigations.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

María Victoria Panzl: Conceptualization, Investigation, Methodology, Formal analysis, Writing – original draft, Funding acquisition. **David Menchaca:** Formal analysis, Validation, Software. **Alejandra Rodríguez-Haralambides:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – review & editing.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.afres.2022.100192.

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