FOOD ADDITIVES & CONTAMINANTS: PART B, 2018
https://doi.org/10.1080/19393210.2018.1440638

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ARTICLE

Polycyclic aromatic hydrocarbons in teas using QuEChERS and HPLC-FLD

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are food-processing contaminants considered to be carcinogenic and genotoxic. Due to its drying process stage, teas may be contaminated with PAHs. The aim of the study was to validate an analytical method involving QuEChERS and HPLC-FLD for the determination of PAH4 in teas and evaluate the contamination levels in 10 different types of teas from Brazil. Recoveries varied from 54% to 99% and relative standard deviations from 1% to 21%. Limits of detection and quantification were from 0.03 to 0.3 µg/kg and 0.1 to 0.5 µg/kg, respectively. Mate tea presented the highest PAH levels, with PAH4 varying from 194 to 1795 µg/kg; followed by black (1.8–186 µg/kg), white (24–119 µg/kg), and green teas (3.1–92 µg/kg). Teas with lowest PAH4 were strawberry, lemongrass, peppermint, and boldo. Only trace levels of PAHs were detected in tea infusions, so apparently it would not affect PAH intake by Brazilian population.

ARTICLE HISTORY
Received 31 October 2017
Accepted 10 February 2018

KEYWORDS
Polycyclic aromatic hydrocarbons; QuEChERS; tea; mate; *Camellia sinensis*

Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic compounds and consist of two or more condensed aromatic carbon rings. It is a food contaminant, and some of them have carcinogenic and genotoxic potentials. Several of individual PAHs are formed by pyrolysis or incomplete combustion of organic materials, and these contaminants are distributed in the air, water, soils, and sediments, usually at minimum concentrations. Humans are exposed to PAHs mainly through digestive tract, air inhalation, and skin. Food can be contaminated by PAHs that are present in the environment, through industrial processing, and through home food preparation (EFSA 2008; IARC 2010).

The most known and studied PAH, benzo[*a*]pyrene, was categorised by the International Agency for Research on Cancer – IARC (2010) as a human carcinogen in group 1. The European Food Safety Authority panel reviewed the available data on the occurrence and toxicity of PAHs and concluded that benzo[*a*]pyrene, which was used individually as a marker for the presence of PAHs in food, is not indicated for this purpose and suggested as an indicator the combined presence of four PAHs (PAH4: benzo[*a*]pyrene, chrysene, benz[*a*]anthracene, and benzo[*b*]fluoranthene) or of eight PAHs (PAH8: the previous four plus benzo[*k*]fluoranthene, benzo[*ghi*]perylene, dibenz[*a,h*]anthracene, and indeno[1,2,3-*cd*]pyrene) (EFSA 2008).

PAHs have been detected in various types of food including tea, coffee, oils and fats, smoked meat and fish, fruit and vegetables, cereals, cereal products, seafood, and alcoholic beverages (Duedahl-Olesen et al. 2015; WHO 2005; EFSA 2008; Ziegenhals et al. 2008; Tfouni et al. 2014; Garcia et al. 2017; Molle et al. 2017).

In recent years, the consumption of teas has increased due to the development of new flavours available in the market and the rise of health consciousness (De Godoy et al. 2013). Tea is one of the oldest beverages in the world, traditionally consumed because of its biological properties and health benefits such as antioxidant activity conferred by polyphenols and free radical scavenging activity of the high levels of flavonoids (Serafini et al. 2011). However, studies have reported (Adisa et al. 2015; Garcia-Londoño et al. 2015; Pincemaille et al. 2014; Sadowska-Rociek et al. 2014) the presence of potentially toxic substances in teas, such as PAHs.

Tea leaves have a high surface area that may be environmentally contaminated by PAHs. During tea preparation and production stages such as roasting and drying, PAHs may be formed due to high-temperature processes. Consequently, PAHs can be released into infusions and be harmful to human health (Lin et al. 2005; Ziegenhals et al. 2008; Adisa et al. 2015). There is little or no information regarding PAH levels in teas commercialised in Brazil.

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QuEChERS sample preparation, originally developed as a method for the determination of pesticide residues in fruits and vegetables, has been widely used for the determination of pesticides and other compounds in different food matrices (Anastassiades et al. 2003; Lesueur et al. 2008; Cunha and Fernandes 2010; Sadowska-Rociek et al. 2014; Furlani et al. 2015).

Therefore, the objective of the present study was to validate an analytical method involving Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) sample preparation and High performance liquid chromatography with fluorescence detector (HPLC-FLD) for the determination of four PAHs (PAH4) in teas and teas infusions and evaluate for the first time the contamination levels in 10 different types of teas available in the Brazilian market.

Materials and methods

Samples

Samples from 10 different types of tea leaves were collected from the Brazilian market: black tea; green tea; white tea (*Camellia sinensis*); boldo (*Peumus boldus Molina*); chamomile (*Matricaria recutita*); lemongrass (*Cymbopogon citratus*); mate (*Ilex paraguariensis*); peppermint (*Mentha piperita* L.); strawberry (*Fragaria* spp. and *Pyrus malus* L. fruits, and *Hibiscus sabdariffa* L. flowers); and flowers and fruits (*H. sabdariffa* L. flowers; *Pyrus malus* L. fruits; *Rosa canina* L. flowers, and fruits; *Ribes nigrum* fruits; *Cichorium intybus* L. fruits; and *Vaccinium myrtillus* L. fruits).

For each type of tea, three batches from three brands were acquired. Tea was homogenised by crushing leaves in a mill. Infusions were prepared using a proportion of 1.5 g of tea for 200 mL of boiling water and a 3 min steep time. A total of 180 samples, 90 samples of tea leaves and their respective brews, were analysed for the presence of PAH4: benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), and benzo[*a*]pyrene (BaP).

Standards and reagents

BaA, Chr, BbF, and BaP analytical standards were purchased from Supelco Inc. (St. Louis, MO, USA). HPLC grade ethyl acetate and acetonitrile (ACN) were purchased from J.T. Baker (USA), reagent grade anhydrous $MgSO_4$ and NaCl were purchased from Synth (Diadema, SP, Brazil), primary secondary amine sorbent (PSA) (40 µm particle size) was purchased from Varian (USA), and silica gel (70–230 mesh, ASTM) was purchased from Merck (Darmstadt, Germany). Magnesium sulphate was heated in a muffle furnace at 500°C for 5 h. Water was obtained from a Millipore Milli-Q water purification system (Bedford, MA, USA) and Agilent RC 0.45 µm filters (Santa Clara, CA, USA) were used for the filtration prior to injection.

Method for PAH determination

The analytical method of extraction and cleanup procedure employed was a modification of the original QuEChERS sample preparation method by Anatassiades et al. (2003) and Lehotay (2007).

Extraction and cleanup

Samples (1 g for leaves and 10 mL for brew) were transferred to a 50 mL polypropylene centrifuge tube where 10 mL of water (only for tea leaves) and 10 mL of ethyl acetate were added. This solution was mixed in vortex for 1 min, and 4 g of anhydrous $MgSO_4$ and 1 g of NaCl were added, and then tube was set in vortex for 1 min and centrifuged for 3 min at 2000 rpm (Eppendorf 5804R Centrifuge, Hamburg, Germany). A 5 mL aliquot of the upper layer was transferred to a centrifuge tube containing 300 mg of silica gel, 100 mg of PSA, and 300 mg of anhydrous $MgSO_4$. Extract was mixed in a vortex for 1 min and centrifuged (2000 rpm for 3 min). A 3 mL aliquot of the upper layer was dried under a flow of nitrogen (TurboVap LV, Caliper Life Science, Hopkinton, MA, USA), suspended in 1 mL of ACN, filtered through a 0.45-µm filter, and analysed by HPLC with fluorescence detection. Samples were analysed in triplicate.

HPLC-FLD

The analyses were carried out using a Shimadzu (Kyoto, Japan) HPLC chromatographic system with an LC-20AT quaternary pump, on-line degasser, an SIL-20A autosampler (30 µL injection volume), CTO-20A column oven (stabilised at 30°C), RF-10A xl fluorescence detector and LCsolution software, for data acquisition and processing. A C18 column (Vydac 201 TP54, 250 × 4.6 mm, 5 µm particle size; Vydac, Hesperia, CA, USA) and a gradient mobile phase of ACN and water at a flow rate of 1 mL/min were used for separation. The gradient was programmed as follows: 8% ACN (from 0 to 22 min), increase to 75% ACN (22–23 min), 75% ACN (23–38 min), increase to 100% ACN (38–39 min), 100% ACN (39–46 min), and decrease to 65% ACN (46–47 min). An excitation and emission wavelength programme was used for detection: 0.01 min (274/414 nm) for BaA and Chr and

23.00 min (290/430 nm) for BbF and BaP. External standard plot method was used for quantification.

Statistical analysis

Data were processed using one-way analysis of variance with mean comparison (Tukey test) with 95% confidence using software Statistica (Statistica 5.5, Stat Soft Inc.). Measurement of uncertainty data in the additional excel file was based on type A calculations.

Results and discussion

Method optimisation

Initially, the aim of the present study was to make use of original QuEChERS method for analysis of some PAHs in tea by HPLC-FLD, as it would consume less time than traditional PAHs extraction methods for food. Therefore, tests were performed using ACN as extraction solvent and PSA as cleanup sorbent. However, the method's performance was not satisfactory, showing low recovery and insufficient cleanup of the extracts, with interfering peaks in the chromatogram. So, an alternate option was initiated with some modifications to the original method.

Sadowska-Rociek et al. (2014) tested different modifications on QuEChERS method for tea analysis by gas chromatography–mass spectrometry (GC–MS). Different solvents and sorbents were tested, and the conditions that authors considered more successful involved extraction with ACN, cleanup with PSA, and SAX (anion exchange) followed by a liquid–liquid extraction with hexane. Pincemaille et al. (2014) also used a modified QuEChERS for PAH analysis in teas by GC–MS. ACN/acetone was used for extraction and cleanup was by SPE with C18 and fluorisil cartridges. In both studies, an extra step was added to the original method.

As the purpose of QuEChERS is, among others, to be a fast and easy extraction method, with low consumption of reagents and organic solvents, tests were performed in an attempt to maintain the method as close to the original as possible. For this, ethyl acetate was tested as extraction solvent and PSA was tested in combination with carbon black, C18, and silica gel as cleanup sorbents. As a result, higher recovery rates were obtained using ethyl acetate and a more efficient cleanup was achieved when using PSA and silica gel combined. These modifications resulted in the best combination for analysing these PAHs in tea by HPLC-FLD without the need of an additional cleaning step.

As shown in Figure 1, chromatographic conditions were adequate for the separation of four PAHs peaks, and the addition of silica gel, combined with PSA, during the cleanup step of QuEChERS method was shown to be effective and provided clean chromatograms, free from co-eluting peaks.

In-house validation

Method validation was performed in accordance to the Brazilian Institute of Metrology, Standardization and Industrial Quality (INMETRO) guidelines (INMETRO 2011) considering the following parameters: linearity, accuracy, precision, limit of detection (LOD), and limit of quantification (LOQ).

Linearity was evaluated by constructing linear regression lines (peak area ratios vs. PAH concentration) from duplicate injections of six concentration levels of PAH standard solutions, in ACN (0.10–25.0 ng/mL). Analytical curves obtained for the PAHs studied were shown to be linear, with correlation coefficients between 0.9997 and 0.9999.

Accuracy and precision data were obtained through recovery studies carried out by spiking a blank sample with PAH standard solutions at three concentration levels (0.5, 2, and 10 µg/kg for leaves, and 0.1, 1, and 5 µg/L for brews) in five replicates. Precision (repeatability) of the method was evaluated through the relative standard deviation (RSD) associated with the recovery studies. Reproducibility was evaluated from RSDs under within-laboratory reproducibility conditions using recovery tests performed in different days. Results obtained are presented in Table 1. Recoveries obtained varied from 67% to 99% for leaves and from 54% to 99% for brews, showing adequate transfer of the compounds to the extracting solvent (ethyl acetate). RSDs for repeatability (five replicate analyses in the same day) varied from 3% to 21% and 1% to 20%, for leaves and brews, respectively, while RSDs under within-laboratory reproducibility conditions (analysis performed in different days) were from 4% to 9% and 4% to 7%, for leaves and brews, respectively.

For LOD determination, seven independent analyses of the blank sample spiked with PAHs at a level of 0.5 µg/kg (leaves) and 0.1 µg/L (brews) were performed. The LODs were calculated from the standard deviation of these determinations. LOQs were established as the lower concentrations used in the calibration curves and the recovery tests. As shown in Table 1, LODs ranged from 0.2 to 0.3 µg/kg for leaves and from 0.03 to 0.05 µg/L for brews, while LOQs were established as 0.5 µg/kg and 0.1 µg/L,

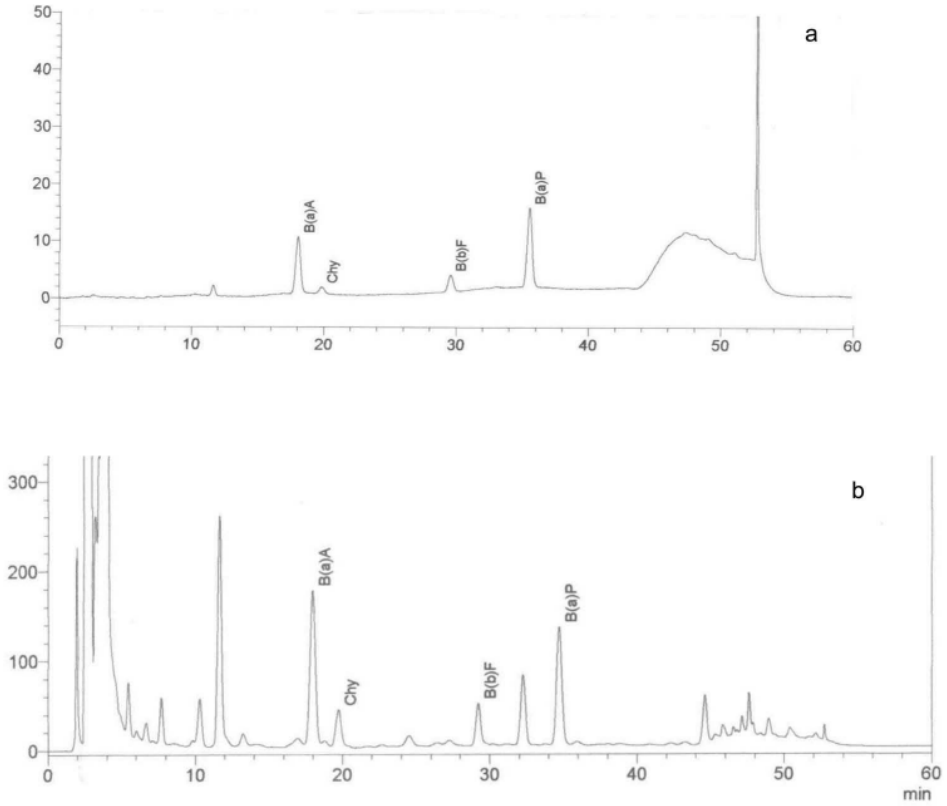

Figure 1. HPLC-FLD chromatograms of (A) PAH standard solution and (B) black tea sample (leaves). Conditions: Vydac 201 TP54 (25 cm × 4.6 mm d.i., 5 µm). Detection by fluorescence (wavelength program). Gradient mobile phase acetonitrile:water, flow rate 1 mL/min. B(a)A: benz[*a*]anthracene; Chr: chrysene; B(b)F: benzo[*b*]fluoranthene; B(a)P: benzo[*a*]pyrene.

respectively. The limits obtained allow the quantification of these compounds below the limits established by European Union for BaP in different foodstuffs (CEC 2011).

The in-house validation results are considered satisfactory for determinations at µg/kg levels and fulfil the performance criteria proposed by European Union for BaP methods of analysis, where LOD should be lower than 0.3 µg/kg and recovery should be in the range of 50–120% (CEC 2007).

PAHs in teas

Ten different types of tea were analysed: black tea, green tea, white tea, boldo, chamomile, lemongrass, mate, peppermint, strawberry, and flowers and fruits.

Results obtained for PAHs in tea leaf samples are presented in Table 2. PAH individual levels varied from not detected to 434 µg/kg (BaA), 555 µg/kg (Chy), 383 µg/kg (BbF), 423 µg/kg (BaP), and 1795 µg/kg (PAH4). BaA was the PAH more frequently

Table 1. Validation parameters [accuracy, precision (RSD), limit of detection (LOD), and limit of quantification (LOQ)] for PAH analysis in teas and infusions.

PAH	LOD (µg/kg)	LOQ (µg/kg)	Recovery (%) (RSD) (%) (n = 5)			RSD (%) (n = 10)
Tea			**0.5 µg/kg**	**2 µg/kg**	**10 µg/kg**	
BaA	0.3	0.5	75 (15)	92 (9)	70 (7)	8
Chr	0.3	0.5	99 (21)	71 (25)	76 (11)	9
BbF	0.3	0.5	73 (11)	82 (6)	81 (14)	4
BaP	0.2	0.5	97 (10)	72 (8)	67 (3)	9
Infusion			**0.1 µg/L**	**1 µg/L**	**5 µg/L**	
BaA	0.04	0.1	93 (12)	95 (3)	97 (2)	5
Chr	0.05	0.1	54 (20)	93 (3)	97 (1)	7
BbF	0.04	0.1	78 (10)	99 (3)	98 (4)	4
BaP	0.03	0.1	90 (5)	92 (1)	97 (3)	5

BaA: benz[*a*]anthracene, Chr: chrysene, BbF: benzo[*b*]fluoranthene, BaP: benzo[*a*]pyrene.

Table 2. Mean PAH levels in different types, brands, and batches of teas.

		Mean (range) (μg/kg)[a]				
	Brand	BaA	Chr	BbF	BaP	PAH4
Black	A	27 (3.9–44)	54 (8.7–84)	21 (4.1–35)	14 (2.3–54)	115 (19–186)
	B	0.7 (0.6–0.9)	0.9 (<LOD–1.5)	0.9 (0.8–1.1)	<LOD	2.5 (1.8–3.1)
	C	1.5 (1.6–3.1)	3.2 (1.5–6.5)	1.2 (0.6–2.3)	0.3 (<LOD–0.8)	6.2 (2,9–13)
Green	A	22 (21–24)	27 (26–29)	18 (17–20)	17 (16–19)	84 (79–92)
	B	0.6 (0.6–0.6)	1.8 (1.6–1.9)	0.7 (0.6–0.8)	0.2 (0.2–0.3)	3.4 (3.1–3.5)
	C	2.5 (2.2–3.0)	4.1 (3.6–4.6)	1.3 (0.8–2.0)	1.1 (0.7–1.4)	9.0 (7.9–11)
White	A	28 (26–30)	32 (31–33)	25 (24–26)	30 (28–32)	115 (108–119)
	B	21 (17–24)	22 (17–26)	17 (16–18)	12 (8.4–14)	72 (58–82)
	C	13 (5.5–19)	18 (8.9–25)	12 (6.3–16)	8.5 (3.2–13)	52 (24–73)
Boldo	A	0.8 (0.6–1.0)	<LOD	1.3 (<LOD–3.2)	3.5 (2.4–5.5)	5.7 (3.6–9.6)
	B	0.3 (<LOD–1.0)	<LOD	0.5 (<LOD–1.0)	3.9 (2.8–5.7)	4.7 (2.8–7.7)
	C	1.5 (0.7–1.9)	<LOD	0.8 (<LOD–1.5)	4.3 (4.0–4.6)	6.5 (4.8–8.0)
Chamomile	A	0.8 (0.7–0.8)	2.9 (2.7–3.2)	0.7 (0.5–0.8)	<LOD	4.4 (3.9–4.8)
	B	4.7 (3.1–8.8)	5.6 (3.2–8.8)	3.5 (1.4–6.6)	3.2 (1.3–6.3)	17 (8–30)
	C	6.9 (2.5–10)	11.5 (5.0–17.5)	4.7 (1.9–6.1)	2.9 (1.2–4.2)	26 (11–37)
Lemon grass	A	2.0 (0.7–3.1)	2.9 (2.0–3.5)	1.4 (0.9–1.8)	0.6 (<LOD–1.2)	6.9 (4.7–9.5)
	B	0.2 (<LOD–0.5)	0.5 (<LOD–0.9)	<LOD	<LOD	0.7 (<LOD–1.2)
	C	0.9 (<LOD–1.4)	1.5 (<LOD–2.9)	0.9 (<LOD–1.4)	0.3 (<LOD–0.8)	3.5 (<LOD–5.7)
Mate	A	214 (122–270)	309 (187–391)	158 (106–200)	190 (114–252)	871 (529–1071)
	B	337 (244–434)	481 (413–555)	286 (205–383)	322 (223–423)	1426 (1085–1795)
	C	143 (41–305)	197 (84–370)	88 (30–175)	113 (39–252)	542 (194–1128)
Peppermint	A	0.8 (0.7–0.9)	1.5 (1.0–1.7)	1.1 (0.9–1.4)	0.2 (<LOD–0.3)	3.5 (2.9–4.0)
	B	1.2 (0.5–1.1)	1.9 (1.5–2.4)	1.2 (1.0–1.3)	0.7 (0.5–1.0)	5.0 (3.9–6.1)
	C	0.9 (0.6–1.1)	5.1 (3.7–6.0)	1.6 (0.8–2.5)	0.1 (<LOD–0.2)	7.7 (5.5–10)
Strawberry	A	1.1 (0.7–1.4)	1.7 (1.2–2.3)	0.7 (0.7–0.8)	<LOD	3.6 (2.6–4.5)
	B	0.8 (0.5–1.1)	0.7 (<LOD–1.5)	0.2 (<LOD–0.6)	<LOD	1.7 (0.7–2.6)
	C	1.1 (0.9–1.4)	1.7 (1.3–2.3)	0.8 (0.5–1.3)	<LOD	3.6 (2.7–5.1)
Flowers and fruits	A	0.8 (<LOD–1.5)	2.0 (<LOD–3.4)	0.6 (<LOD–0.9)	<LOD	3.4 (<LOD–5.8)
	B	2.4 (1.5–4.3)	4.8 (3.6–4.2)	1.5 (0.8–2.6)	1.0 (<LOD–2.5)	9.6 (6.4–16)
	C	0.7 (<LOD–1.2)	4.6 (1.6–9.3)	1.1 (0.7–1.6)	0.4 (<LOD–0.7)	7.0 (3.6–13)

[a]Mean of three batches in triplicate (n = 9). BaA: benz[*a*]anthracene, Chr: chrysene, BbF: benzo[*b*]fluoranthene, BaP: benzo[*a*]pyrene.

detected, being present in 92% of the tea samples studied, while BaP was detected in 60 samples (67%). Mate tea had highest levels of the compounds analysed, with PAH4 varying from 194 to 1795 μg/kg, followed by teas from *Camellia sinensis*, where PAH4 levels were from 1.8 to 186 μg/kg (black tea), 24 to 119 μg/kg (white tea), and 3.1 to 92 μg/kg (green tea). Teas with lowest PAH4 content were as follows: strawberry (0.7–5.1 μg/kg), lemongrass (not detected–9.5 μg/kg), peppermint (2.9–9.6 μg/kg), and boldo (2.8–9.6 μg/kg).

Statistical analysis showed that PAH levels in mate tea are different ($p > 0.05$) from the other teas. The high amount of PAH detected in mate tea can be explained by the fact that leaves come into contact with flames and smoke from burning wood during drying process. In order to obtain mate tea, the leaves go through two consecutive drying steps, the first one (called "sapeco") involves direct contact with flames generated from wood, as well as contact with the smoke, which is intended to inhibit enzymatic activity and reduce water content; the second one uses rotating cylinders or belt dryers that are heated by burning wood (Maccari Junior 2005; Vieira et al. 2010).

The results obtained in the present study agree with the results from previous studies. Garcia-Londoño et al. (2015) detected PAH4 (4.1–355.9 μg/kg) in teas from *Camellia sinensis* commercialised in Argentina. Pincemaille et al. (2014) detected higher PAH4 levels in smoked black tea (27.4–218.0 μg/kg), while in non-smoked samples the levels were between 1.5 and 35.0 μg/kg.

When taking into account the same type of tea, a large variation in PAHs levels was noticed between different brands analysed and between different batches of a same brand. Four types of tea (green, white, lemongrass, and peppermint) presented statistically significant difference ($p > 0.05$) in PAH4 levels between different brands evaluated, while 17 brands of tea from different types showed difference ($p > 0.05$) between batches. In some cases, such as different brands of black tea, there was apparently a large variation between brands (2.5–115 μg/kg for PAH4); however, the wide difference among batches lead brands not to show statistical difference. Chamomile and mate teas were the only ones that showed no statistical difference between brands and batches analysed.

These differences can be due to variations in the drying process among different producers and different types of tea, and also to variations in environmental contamination levels (when leaves are exposed to PAH contamination by deposition while still in the field, which may vary according

to geographical location of the plantation). Another factor that can influence these variations is the fact that during processing and/or packaging, producers commonly mix teas from different origins and suppliers.

There are no maximum limits for PAHs in tea in both Brazilian and European regulation. In Brazil, there are only limits set for BaP in olive pomace oil, smoke flavourings, and drinkable water, which range between 0.03 and 2 µg/kg (Brasil 2003; Brasil 2004, 2007). In Europe, limits are established for some foods and vary from 1.0 to 6.0 µg/kg (for BaP) and 1.0 to 35.0 µg/kg (PAH4) (CEC 2011). When comparing the maximum levels set (6.0 for BaP and 35.0 µg/kg for PAH4), 23 samples (26%) would surpass the allowed amount for both parameters, being 1 sample of chamomile, 2 black, 3 green, 8 white, and 9 mate teas.

As for tea infusions, only trace levels of PAHs were detected (below LOQ). This is probably due to the lipophilic nature of these compounds, which would decrease their transference to the infusion. Also, PAHs with high molecular weight, as the ones analysed in the present study, show lower water solubility than the ones with low molecular weight. Duedahl-Olesen et al. (2015) observed a maximum PAH transference rate of 2.3% from teas to the infusion, which agrees with the present study findings. Another fact that could affect the transference is the preparation mode. Lin et al. (2005) studied different tea steep times and obtained different PAH rates of transference; however, among the PAHs with high molecular weight, only BaA was detected in the infusions.

Conclusion

The analytical method was shown to be suitable for analysing BaA, Chr, BbF, and BaP in tea after slight modifications made to the original QuEChERS sample preparation method.

Considering the values of BaP and PAH4 detected in the present study, PAH levels may be considered high in some types of tea, as 26% of the samples would be in discordance to the legislation when considering the maximum levels set by European regulation in foodstuff. As for PAH4 presence in the infusions, only traces were detected, so apparently it would not affect PAH intake by the Brazilian population. However, it is possible that different tea preparation modes result in different transference rates to the infusion.

Acknowledgements

This work was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (Fapesp) under Grant 2012/19142-7. R.M.R. (Instituto de Química, UNICAMP, Campinas, SP, Brazil) thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), Brazil for PIBIC/CNPq undergraduate student fellowship program.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo [2012/19142-7].

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