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Simultaneous Extraction of Pesticides and Polycyclic Aromatic Hydrocarbons in Brazilian Cachaça Using a Modified QuEChERS Method Followed by Gas Chromatography Coupled to Tandem Mass Spectrometry Quantification

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Supporting Information

ABSTRACT: A modified QuEChERS method was optimized for simultaneous extraction of 93 pesticides and 6 polycyclic aromatic hydrocarbons (PAHs) in cachaça. The procedure employed 20 mL of sample, 10 mL of dichloromethane, 1 g of NaCl, and 6 g of $MgSO_4$. The methods were validated in accordance with pesticide tolerances set by the National Health Surveillance Agency of Brazil and government guidelines of Brazil and the European Union. The linearity of all curves was adequate, with calculated t_r higher than the critical value, at the 95% confidence level. For pesticides, recoveries ranged between 86.7 and 118.2%, relative standard deviation (RSD) ≤ 20%, at least at two concentration levels, and limit of detection (LOD) and limit of quantitation (LOQ) were 2.5 and 10.0 $\mu g\ L^{-1}$, respectively. For PAHs, recoveries ranged between 84.8 and 111.5%, RSD was between 6.2 and 27.3%, LOD and LOQ were 0.25 and 1.0 $\mu g\ L^{-1}$, respectively. The combined standard uncertainty was lower than 50% of the relative expanded uncertainty value at concentration levels of greater relevance in both methods. Analyses of five commercial samples detected the presence of 9 pesticides (10.0−128.0 $\mu g\ L^{-1}$) and 6 PAHs (2.0−4.0 $\mu g\ L^{-1}$), indicating the need for a specific legislation for Brazilian cachaça.

KEYWORDS: *QuEChERS, pesticides, PAHs, Brazilian cachaça, GC−MS/MS*

INTRODUCTION

Cachaça is a genuine Brazilian beverage, produced from the distillation of sugar cane juice. Through specific legislation in 2005, the Brazilian Ministry of Agriculture, Livestock, and Supply (MAPA) is authorized to determine the quality and identity of the beverage.[1] Cachaça is sometimes confused with rum because they are produced from the same raw material, but there are differences in the production processes. Among them, the most important is the fact that cachaça is produced from fermented sugar cane juice, whereas rum is produced from molasses. This difference modifies the organoleptic properties, flavors, and aromas.[2] Sugar cane is also of great commercial importance in Brazil as the raw ingredient used in the production of ethanol.[3] Maximized production of sugar cane and minimized losses from pest infestations have motivated producers to use pesticides, which, when used incorrectly, can generate residues in sugar cane and its products.[4]

Other environmental and toxicological contaminants that can also be present in cachaça are polycyclic aromatic hydrocarbons (PAHs).[5] This contamination can be caused by various sources: the practice of burning the sugar cane fields, contact with greases, oils, and/or fuel smoke of the vehicle used in the transport of the sugar cane, contact with machinery lubricants, and inadequate storage during beverage processing.[6,7]

Three works were found in the literature involving pesticide analyses in distilled beverages. Han et al. developed a method for sorghum distilled spirit analysis using QuEChERS and gas chromatography coupled to tandem mass spectrometry (GC−MS/MS).[8] Cabras et al. analyzed a distilled spirit of wine through liquid−liquid extraction (LLE) and gas chromatography fitted with an electron capture detector (GC−ECD).[9] Inoue et al. analyzed a distilled spirit of barley shochu, without the extraction step, by ultra performance liquid chromatography coupled to tandem mass spectrometry (UPLC−MS/MS).[10]

PAH quantification in distilled beverage has been described in some papers, using GC or high-performance liquid chromatography (HPLC) with fluorescence or MS/MS detection. In the sample preparation, the solid-phase extraction (SPE) was used by Bettin et al. for sugar cane distilled beverage, Galinaro et al. and Machado et al. for cachaça, and Galinaro et al. for cachaça, rum, and whisky samples.[6,7,11,12] Tfouni et al. used LLE and Menezes et al. used solid-phase microextraction for cachaça analysis.[13,14] Cacho et al. performed the sample preparation of whisky, gin, rum, tequila,

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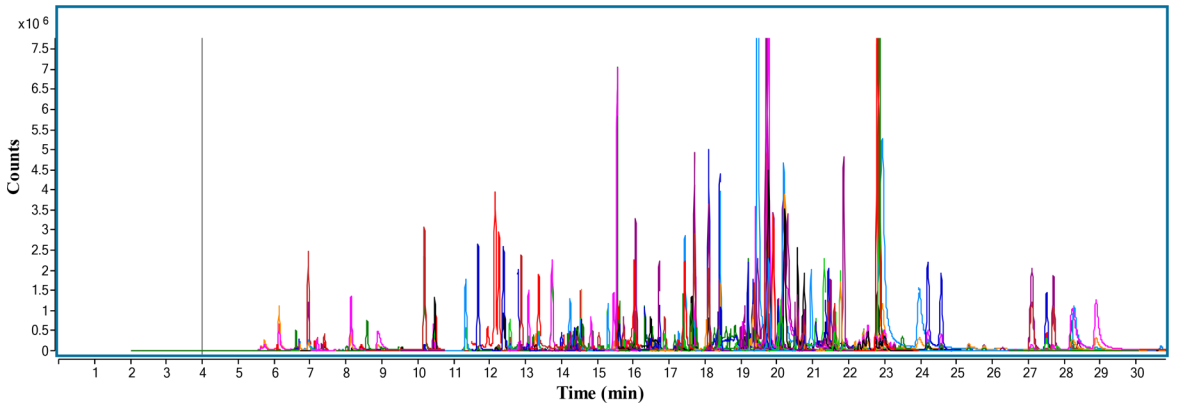

Figure 1. Extracted ion chromatogram obtained from the GC−MS/MS method for the analysis of pesticides in cachaça.

and brandy using ultrasound-assisted emulsification microextraction.[15]

In the present work, a modified QuEChERS method was optimized for simultaneous extraction of 93 pesticides and 16 PAHs in Brazilian cachaça and quantification was performed by two methods of GC−MS/MS, one for pesticides and another for PAHs, as a result of the need of a specific column for PAH isomer separation. The methods were validated in accordance with the recommended criteria for Brazil and the European Union (EU). Finally, commercial cachaça samples were analyzed, and contamination by pesticides and PAHs was verified.

Because there is no national or international regulation for PAHs and pesticides in cachaça, the criteria for the selection of the analytes were, for PAHs, all compounds of the 15 + 1 EU priority PAH list and, for pesticides, the highest number of pesticides available. Thus, in case of future regulation, the method would be viable for determining these compounds.

EXPERIMENTAL SECTION

Reagents and Samples. The pesticide standards were acquired from Dr. Ehrenstorfer (Augsburg, Germany). A solution containing standards of the 16 PAHs monitored by the EU, with each compound at a concentration of 2.5×10^5 $\mu g\ L^{-1}$ in acetone/methylene chloride (80:20, v/v), was acquired from Sigma-Aldrich (St. Louis, MO, U.S.A.). Dichloromethane (99.8%), HPLC grade, was acquired from Scharlau (Barcelona, Spain). Ethyl acetate (99.8%) and acetonitrile (99.9%), both HPLC grade, were acquired from Tedia (Fairfield, OH, U.S.A.). Magnesium sulfate (98%) and sodium chloride (99%), both anhydrous and P.A. grade, were acquired from Sigma-Aldrich (St. Louis, MO, U.S.A.). The blank cachaça samples were produced and acquired from an artisanal alembic in Minas Gerais, Brazil.

Instrumentation. A Thermo Scientific Heraeus Megafuge 40 centrifuge (Waltham, MA, U.S.A.), constant temperature shaking bath (20−110 °C range) model Yamato BT-25 (Tokyo, Japan), and compressed air system were used. Chromatographic separation was performed in Agilent 7000A triple quadrupole GC−MS/MS with electron ionization. Management and treatment of the data were performed by Agilent MassHunter software for 7000 series triple quadrupole GC−MS/MS with unit mass resolution, divided in MassHunter data acquisition, qualitative analysis, and quantitative analysis QQQ (Santa Clara, CA, U.S.A.).

Preparation of Stock and Standard Solutions. The individual pesticide stock solutions were prepared in a range from 1.5×10^6 to 2.0×10^6 $\mu g\ L^{-1}$, in accordance with the value obtained from the weighing and purity of each standard. The mass of each compound was diluted in acetonitrile, and the solutions were stored in amber glass bottles. Pesticide standard mix stock solutions were prepared at 1.0×10^3, 2.0×10^3, 5.0×10^3, and 10.0×10^3 $\mu g\ L^{-1}$ concentrations, using the same solvent. The PAH stock solutions were prepared at 2.5×10^2, 5.0×10^2, and 4.0×10^3 $\mu g\ L^{-1}$ concentrations through dilution of the standard solution 2.5×10^5 $\mu g\ L^{-1}$. Working solutions were prepared through dilution of the stock solutions, as required. All solutions were kept at −20 °C.

GC−MS/MS Method Optimization. The optimized chromatographic method for pesticides consisted of a Rtx-OPPesticides Restek capillary pre-column (2 m × 0.25 mm × 0.25 μm) and capillary column (15 m × 0.25 mm × 0.25 μm) (Bellefonte, PA, U.S.A.), with temperature programming of 40 °C (0.1667 min), 40−50 °C (75 °C min^{-1}), 50−150 °C (50 °C min^{-1}), 150−200 °C (6 °C min^{-1}), 200−280 °C (10 °C min^{-1}), and 280−310 °C (20 °C min^{-1}) and flow programming of 1 mL min^{-1} (0−18.23 min) and 1.2 mL min^{-1} (18.23−30 min). The chromatographic method for PAHs was based on an Agilent J&W DB-EUPAH (30 m × 0.25 mm × 0.25 μm) capillary column (Santa Clara, CA, U.S.A.), with temperature programming of 40 °C (1.8 min), 40−200 °C (70 °C min^{-1}), 200−240 °C (6 °C min^{-1}), 240−280 °C (10 °C min^{-1}), and 280−310 °C (6 °C min^{-1}) and flow programming of 1 mL min^{-1} (0−1.37 min), 3 mL min^{-1} (1.37−2.03 min), 1 mL min^{-1} (2.03−18.23 min), and 1.2 mL min^{-1} (18.23−59 min). For both chromatographic methods, the following conditions were used: helium (He) as the carrier gas, multimode inlet (MMI) in the solvent vent mode, injection volume of 25 μL, injection programming of 45 °C (1.37 min) and 45−350 °C (600 °C min^{-1}), and transfer line temperature of 300 °C.

The optimization of the mass spectrometric conditions was based on precursor ion selection by injection of standard solutions in the full-scan mode. Afterward, the most abundant product ion selection was performed by injection of standard solutions in the full-scan mode (m/z 50−500), applying different collision energies (CEs) (5, 15, 25, and 35 eV). Electron ionization was used with electronic impact of 70 eV, source temperature at 300 °C, and quadrupole temperature at 180 °C. Retention times, selected transitions, and CEs, for each analyte, are shown in Table S1 of the Supporting Information.

Modified QuEChERS Method Optimization. The modified QuEChERS method consisted of (1) adding 10 mL of dichloromethane to 20 mL of spiked sample with 50 $\mu g\ L^{-1}$ pesticides and 5 $\mu g\ L^{-1}$ PAHs and shaking for 1 min in the vortex, (2) adding 1 g of NaCl and 6 g of $MgSO_4$ and shaking again for 1 min, (3) centrifuging for 10 min at 4000 rpm and ambient temperature, (4) collecting 8 mL of the organic phase (high phase) and evaporating the content to dryness in a thermostatic bath at 38 °C under compressed air flow, and (5) dissolving with 1 mL of ethyl acetate and transferring to a vial.

The volume and type of solvent were optimized by the 2^2 factorial design. The solvent volume (factor I) was evaluated at the following levels: (−1) 10 mL and (+1) 20 mL. The type of solvent (factor II) was studied using (−1) dichloromethane and (+1) acetonitrile. Assays were performed in duplicate for estimation of pure error and confidence.

Method Validation. Method validation was performed, on 3 different days, in accordance with the *Analytical Quality Assurance*

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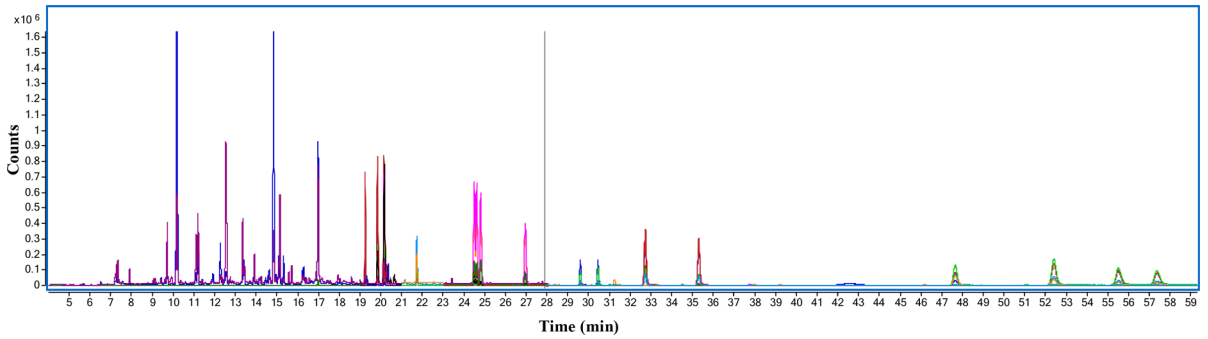

Figure 2. Extracted ion chromatogram obtained from the GC−MS/MS method for the analysis of PAHs in cachaça.

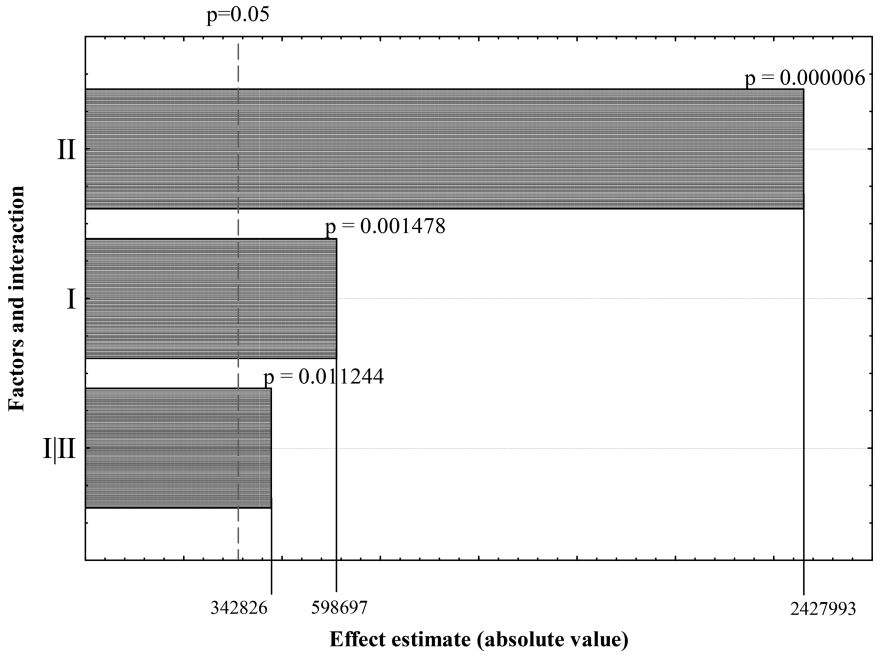

Figure 3. Pareto chart of the estimated effects in the 2^2 factorial design performed in the modified QuEChERS method optimization showing which two factors and the interaction between them were statistically significant (p value of <0.05). I, volume; II, type of extractor solvent.

Manual of MAPA and the guidance document on analytical quality control and method validation procedures for pesticide residues analysis in food and feed of the European Commission (EC), SANTE/11813/2017.[16,17] All validation assays were performed with a blank sample. For the evaluation of linearity, matrix-matched calibration curves were prepared with spiked samples at five concentration levels, ranging from 10 to 100 μg L^{-1} for pesticides and from 1 to 10 μg L^{-1} for PAHs, both in sextuplicate. Recovery and precision were certified through extraction of spiked samples at concentration levels of 10, 50, and 100 μg L^{-1} for pesticides and 1, 5, and 10 μg L^{-1} for PAHs on 3 different days. The limit of quantification (LOQ) was fixed as the lowest concentration level of the calibration curve, which presented adequate recovery and precision. The limit of detection (LOD) was evaluated by injections of spiked samples with 1.0, 2.5, 5.0, and 7.5 μg L^{-1} for pesticides and 10 times more diluted for PAHs. The measurement uncertainty was estimated by top-down methodology, considering the uncertainty from the calibration curve and intermediate precision in the combined uncertainty estimative.

Commercial Cachaça Sample Analyses. Five commercial cachaça samples were extracted according to the optimized modified QuEChERS method. Matrix-matched calibration curves were prepared with spiked samples and employed for quantification of analytes. The injections were carried out at random sequence.

RESULTS AND DISCUSSION

GC−MS/MS Method Optimization. The optimized chromatographic methods allowed for analyte separation in time and/or mass charge ratio (m/z) within 30 min for pesticides (Figure 1) and 59 min for PAHs (Figure 2). Two chromatographic methods were required because the PAHs were nonpolar presented isomers and the pesticides were of intermediate polarity. Chromatographic separation of PAHs was only achieved in the specific column (Agilent J&W DB-EUPAH) for analysis of these compounds. In this column, pesticide separation only occurred at an extremely high temperature (inadequate condition for preservation of the column) and a long run time. The selected reaction monitoring (SRM) mode was used in both methods for analyte detection and quantification. Two transitions for each analyte were monitored. The highest intensity transition was selected for quantification, and the second highest was selected for confirmation. The selected transitions showed a m/z ratio greater than or equal to 3:1, and the variability of the relative intensities between selected ions for each transition met the performance criteria required in both adopted guidelines for the definition of quantification and confirmation transitions.[16,17] The molecular formulas and relevant information

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can be found through the websites of the Pesticide Action Network (PAN) and the National Institute of Standards and Technology (NIST) PAH Structure Index.[18,19]

Modified QuEChERS Method Optimization. In the original QuEChERS method developed by Anastassiades et al. in 2003, the extraction solvent is acetonitrile, the salting out step uses 4 g of $MgSO_4$ and 1 g of NaCl, and the last step of cleanup uses $MgSO_4$ and primary secondary amine. In this work, the QuEChERS method presents modifications concerning type and volume of the extraction solvent and salt mass and eliminates the cleanup step as a result of the nature of the sample.[20] To optimize the modified QuEChERS method, dichloromethane and acetonitrile were evaluated because these are the solvents most employed in PAH and pesticide analyses, respectively. The 10 and 20 mL volumes were evaluated to verify whether the increase in the analyte recoveries justified the employment of the higher solvent volume. The average recoveries of all analytes were used for statistical evaluation of factor influence: volume (factor I) and type of the extractor solvent (factor II). The data statistical analysis showed that both factors and the interaction between them were statistically significant, at the 95% confidence level (p value of <0.05) (Figure 3). Besides, analyte extraction was favored by the use of 20 mL (factor I, +1) of dichloromethane (factor II, −1).

A comparison of the average recoveries of all analytes (Figure 4) shows that the type of solvent was more relevant for

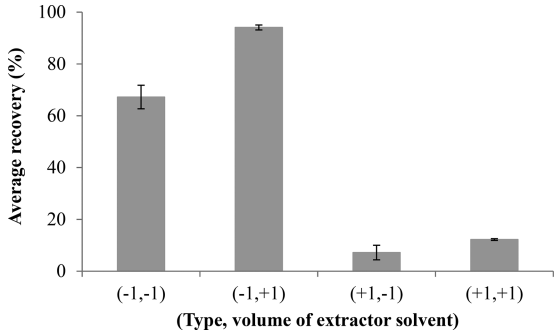

Figure 4. Chart of the average recovery of all analytes obtained for the 2^2 factorial design showing that the type of solvent factor had a greater influence than the volume of the solvent factor.

extraction than for volume. When the dichloromethane solvent was fixed and the volume was doubled, the average recovery showed an increase of 40%, whereas for the acetonitrile solvent, the increase was 71%. However, when the volume was fixed at 10 mL, an increase of 960% was obtained using dichloromethane instead of acetonitrile, and with the volume fixed at 20 mL, the increase was 780%. The high extraction efficiency with dichloromethane can be justified as a result of its immiscibility with the sample, which favored analyte partition for the organic phase. Thus, even with the use of a lower solvent volume, chromatographic peaks with satisfactory symmetry and intensity were obtained. Therefore, 10 mL of dichloromethane solvent was chosen because, in this condition, the extraction presented itself efficient and results were satisfactory to monitor these residues, because the limits established by different legislations are around 1 mg kg^{-1} for pesticides and 1 μg kg^{-1} for PAHs. The influence of NaCl on phase separation and $MgSO_4$ on water removal was evaluated by an experiment in the optimized condition, however, without salt addition. The results of recovery and precision exceeded the recommended acceptability range for a considerable number of analytes. Therefore, salt addition was maintained, and the masses used were based on the previous method developed by the Laboratory of Pesticides of the National Agricultural Laboratory of Minas Gerais (LP-LANAGRO/MG).

At the end of optimization, the modified QuEChERS method consisted of 20 mL of sample, 10 mL of dichloromethane, 1 g of NaCl, and 6 g of $MgSO_4$.

In comparison of the optimized modified QuEChERS to the conditions described in the literature (Table S2 of the Supporting Information), the following was observed: the present method was the sole procedure capable of simultaneously extracting pesticides and PAHs; the analyte number determined was much higher than described in other papers (except that by Inoue et al.);[10] and despite the use of chlorinated solvent, as also observed in several papers involving PAHs,[6,11,12,15] total organic solvent consumption was lower than in most of the referenced works. It is important to emphasize that, for the safety of the analyst, the solvent manipulation must be performed under an exhaust system, using gloves and masks for organic solvents.

Method Validation. Data validation treatment was carried out using the validation spreadsheet of LP-LANAGRO/MG. Selectivity was evaluated during the method optimization process by certifying that signals of possible interferents were lower or equal to 30% of the analyte signal at the lowest concentration level of the calibration curve. As multiresidue methods were employed, the matrix effect was considered present and matrix-matched calibration curves were used.

Linearity was initially verified through the F test and indicated that the area variances were heteroscedastic. Thus, weighted least squares regression was performed using either the inverse of the variance or the concentration, at each level, as the weighting factor. The model fits were evaluated through the t test (eq 1) and analysis of variance (ANOVA). The first test certified the appropriateness of the determination coefficients (R^2), because the calculated t values (t_{cal}) were higher than the t critical values, for all analytes (Table S3 of the Supporting Information). ANOVA considered the regression model statistically significant for all analytes, with estimated model significance ($F_{goodness\ of\ fit}$) 100 times higher than critical F. Statistic models did not show a lack of fit for 79 pesticides and 16 PAHs ($F_{lack\ of\ fit} < F_{critical}$), at the 95% confidence level, on 3 validation days. For 14 pesticides, statistical models showed a lack of fit on some validation days, at the 95% confidence level. However, the other linearity parameters evaluated were satisfactory for these analytes, and method linearity was considered acceptable for all studied analytes.

$$t_{cal} = \sqrt{R^2}\sqrt{(n-2)/(1-R^2)} \quad (1)$$

Recovery was evaluated through spiked blank samples, and all analytes met the criteria recommended (70−120% range). Precision was evaluated by relative standard deviation (RSD) of the recoveries obtained at three concentration levels. For pesticides, RSD was ≤20% at least at two of the three levels evaluated as recommended by the *Analytical Quality Assurance Manual of MAPA*. For PAHs, RSD was ≤30% at the three levels, meeting the acceptability criterion (Table S4 of the Supporting Information).

The LOD was evaluated at four concentration levels, as described in the Experimental Section, and defined as 2.5 μg

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L^{-1} for pesticides and 0.25 $\mu g\ L^{-1}$ for PAHs, because these were the lowest concentrations that provided unequivocal identification of the analyte signals with a m/z ratio higher than 3, for all studied analytes. The LOQ of the method was established as the lowest concentration level of the calibration curve, in which trueness and precision criteria were met, in accordance with both adopted guidelines. In this way, LOQ was defined as 10 $\mu g\ L^{-1}$ for pesticides and 1 $\mu g\ L^{-1}$ for PAHs. The LOQ of the three pesticides, 2,4-DDE, chlorpyrifos, and disulfoton, was defined as 50 $\mu g\ L^{-1}$, because this was the lowest concentration with adequate precision (Table S4 of the Supporting Information).

Combined standard measurement uncertainty (eq 2) was obtained by means of the composition of the analytical curve uncertainties (eq 3) and intermediate precision (eq 4), according to top-down methodology

$$u_{comb} = x_n\sqrt{u_{calib}^{\ 2} + u_{ip}^{\ 2}} \quad (2)$$

$$u_{calib} = \sqrt{(s^2(y_n) + s^2(a) + x_n^{\ 2}s^2(b) + 2x_n\,\mathrm{cov}(a, b))/b^2} \quad (3)$$

$$u_{ip} = s_R/(\bar{R}N) \quad (4)$$

where u_{comb} is combined standard measurement uncertainty, u_{calib} is the uncertainty of the analytical curve, u_{ip} is the uncertainty of the intermediate precision of the analytical method, $s^2(y_n)$ is the instrumental response variance, $s^2(b)$ is the slope variance, $s^2(a)$ is the intercept variance, $\mathrm{cov}(a, b)$ is the covariance between the intercept and the slope from the calibration curve, s_R is the recovery standard deviation obtained on 3 validation days, $\bar{R}$ is the recovery average, and N is the total number of assays performed on 3 validation days, at each concentration level.

The magnitude of the estimated u_{comb} was evaluated by determination of the relative expanded uncertainty (U) (eq 5)[21]

$$U = (ku_{comb}) \times 100 \quad (5)$$

where k is a coverage factor. k = 2, considering the 95% confidence level.[21]

The acceptable criterion used for measurement uncertainty was U lower or equal to 50%, at the 95% confidence level, according to the *Analytical Quality Assurance Manual of MAPA* and SANTE/11813/2017. This criterion was met for all analytes at the second and third concentration levels (Table S5 of the Supporting Information) and for some analytes at the first level (10 $\mu g\ L^{-1}$ for pesticides and 1 $\mu g\ L^{-1}$ for PAHs). Nonetheless, European legislation and Brazilian legislation have established the maximum residue limits (MRLs) of 50 and 100 $\mu g\ L^{-1}$ for a large number of pesticides. At these concentration levels, the method for pesticides met the acceptable criterion.[22−24]

The PAHs, benzo[*a*]pyrene (BaP), benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbFA), and chrysene (CHR), form the system of four specific substances (PAH4) fixed in the EU as indicators of PAH in food.[25] Only BaP presented U higher than 50%, at the first concentration level. The EU legislation establishes MRLs for PAHs in some food groups in terms of the PAH4 sum. In most cases, these MRLs occur at a range from 10 to 35 $\mu g\ L^{-1}$, and at this concentration range, the PAH method met the acceptable criterion for measurement of uncertainty.[25]

Therefore, two GC−MS/MS multiresidue optimized methods were validated following recommendations of the *Analytical Quality Assurance Manual of MAPA* and the guidance document SANTE/11813/2017 of the EC for the determination of 93 pesticides and 16 PAHs in Brazilian cachaça using a sole modified QuEChERS procedure. This extraction procedure has potential to be expanded to analysis of others beverages with higher alcohol content.

Commercial Cachaça Sample Analyses. Five commercial cachaça samples of different brands were acquired in the local commerce and analyzed through optimized methods. The results showed contamination by 9 pesticides and 6 PAHs (Table 1).

Table 1. Pesticide and PAH Concentrations Found in the Commercial Cachaça Samples Analyzed Using Validated Methods[a]

	pesticide		PAH	
sample	contaminant	content/U	contaminant	content/U
S1	carbofuran	17/15	BbFA	2/49
	cinidon-ethyl	13/26	BaP	3/10
	etrimphos	16/43	CPP	4/41
S2	tebuconazole	13/10	BaA	3/9
	fenbuconazole	65/9	BbFA	5/9
			CPP	3/6
S3	4,4-DDT	10/17	BaP	4/8
			BghiP	2/31
			CPP	3/7
S4			CPP	3/6
S5	disulfoton sulfone	12/80	BaP	2/41
	fenbuconazole	128/12	BjFA	2/47
	permethrin	13/40		
	resmethrin	17/63		

[a]S, sample; content/U, ($\mu g\ L^{-1}$/%); and U, relative expanded uncertainty.

Only one among five commercial cachaça samples did not present pesticides. The contaminations by different pesticides were at 10−128 $\mu g\ L^{-1}$. Fenbuconazole was detected in the S2 (65 $\mu g\ L^{-1}$) and S5 (128 $\mu g\ L^{-1}$) samples, with the latter being above of the working range of the curve. In Brazil, its use is not regulated for any culture. In the EU and U.S.A., there are regulations for several cultures; however, only in the EU, there is a MRL (50 $\mu g\ kg^{-1}$) for sugar cane.[22−24]

All commercial cachaça samples verified contamination by PAHs in the 2−4 $\mu g\ L^{-1}$ range. These amounts are higher than the established limits for cultures that present regulations for PAHs, because sugar cane is not regulated by any national or international inspection authority.[25] The most present contaminants were cyclopenta[*c*,*d*]pyrene (CPP) (S1, S2, S3, and S4) and BaP (S1, S3, and S5).[26,27]

The contamination present in the commercial cachaça samples shows the relevance of these methods, which allowed for the quantification of pesticides at 10 $\mu g\ L^{-1}$ (2,4-DDE, chlorpyrifos, and disulfoton in 50 $\mu g\ L^{-1}$) and PAHs at 1 $\mu g\ L^{-1}$, with an analytical frequency of 20 samples/h, and the need for a specific legislation, considering the toxic potential of these compounds. Taking into account the growth and appreciation of the international and national markets of cachaça and the contamination risk by pesticides and PAHs, the present work could be a useful tool for the establishment of a specific legislation by regulatory agencies.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.8b04682.

Retention time, quantification and confirmation transitions, and CEs optimized for pesticides and PAHs (Table S1), description about procedures for pesticides and PAHs reported in the literature (Table S2), values of R^2, t_{cal} for the correlation coefficient, $F_{lack\ of\ fit}$, and F_{sig} on 3 validation days (Table S3), average R and RSD values for pesticides and PAHs on the 3 validation days (Table S4), and u_{comb} and U values for pesticides and PAHs (Table S5) (PDF)

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Notes

The authors declare no competing financial interest.

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