Received: 29/05/2024 Revised: 07/12/2024 Accepted: 13/02/2025 Published: 31/03/2025

Journal of the Institute of Brewing
EST 1895

ORIGINAL ARTICLE

DOI 10.58430/jib.v131i1.68

Polycyclic aromatic hydrocarbons and physicochemical analysis of cachaça packaged in polyethylene terephthalate (PET)

- Ana Paula Abrantes[1]
- Maria das Graças Cardoso[1]
- Pamela Aparecida dos Santos[1]
- Richard Bispo Barbosa[1]
- Vanuzia Rodrigues Fernandes Ferreira[2]
- Gabriela Fontes Alvarenga[3]
- Antonia Isadora Fernandes[1]
- Carolina Salles Freire[1]
- Wilder Douglas Santiago[1]
- Guilherme Max Dias Ferreira[1]

[1]Department of Chemistry, Federal University of Lavras, Lavras, MG, Brazil.

[2]Department of Forest Science, Federal University of Lavras, Lavras, MG, Brazil.

[3]Department of Food Sciences, Federal University of Lavras, Lavras, MG, Brazil.

✉ cardoso@ufla.br

Abstract

Why was the work done: The Brazilian distilled spirit cachaça has a complex composition. Numerous reactions occur throughout the production chain from fermentation, to distillation and then packaging. During these processes secondary compounds, together with organic and inorganic contaminants, are formed. Among the organic contaminants, carcinogenic and genotoxic polycyclic aromatic hydrocarbons (PAHs) can be introduced into the distillate from packaging such as polyethylene terephthalate (PET).
What are the main findings: This study analysed physicochemical properties and quantified PAHs in cachaça packaged in PET stored under different conditions. These included storage in the cold (refrigerator) and ambient under artificial light, continuous sunlight, and protected from light. Physicochemical analyses of cachaça, was performed before and after packaging in PET for a period of twelve months. The methodology was as established by MAPA (Ministry of Agriculture and Livestock), with the quantification of PAHs by HPLC. PET was characterised by thermogravimetric analysis, and changes in its surface were evaluated by Fourier-Transform Infrared Spectroscopy.
Why is the work important: Cachaça stored in glass packaging complied with the Normative Instructions for Identity and Quality from MAPA. Cachaça was affected by packaging and storage in PET due to mass transfer, migration of substances, oxidation, and loss of aroma. Storage of cachaça under both laboratory light and sunlight resulted in higher concentrations of benzo[a]pyrene and benzo[a]anthracene compared to storage in glass. The quality of cachaça was also affected by storage conditions, mainly due to the loss of the water-ethanol fraction and the oxidation of some compounds.
Why is the work important: The findings highlight that PET packaging, when combined with exposure to light, can facilitate the transfer of PAHs to cachaça. This suggests that packaging of cachaça in PET may be unsuitable in certain situations.

Keywords

cachaça; quality; polycyclic aromatic hydrocarbons; organic contaminants; polyethylene terephthalate (PET), packaging.

Introduction

The beverage sector in Brazil is in rapid development with distilled alcoholic beverages such as cachaça playing a prominent role. In 2021, exported cachaça (7.2 million litres) generated US$ 13.2 million representing a 38% increase in revenue compared to the previous year. Cachaça has an alcohol content of 38-48% (v/v) at 20°C (Brazil 2005). A standard production supply chain together with quality control are important in providing a consistent product without affecting the attributes of beverages from different producers. To ensure quality control, regulations such as Normative Instructions (Ministry of Agriculture and Livestock 13/2005, 28/2014) establish the identity and quality standards of sugarcane spirit and cachaça according to Brazilian legislation (Brazil 2005, 2014).

Polycyclic aromatic hydrocarbons (PAHs) are compounds with carcinogenic characteristics. Their formation occurs in both natural and anthropogenic sources, through the burning of organic matter at high temperatures, via incomplete combustion or pyrolysis of materials containing carbon and hydrogen atoms. Contamination via PAHs can occur through food processes such as baking, smoking and drying. In sugarcane products and distilled beverages, PAHs can occur across production, from the raw material to bottling (Galinaro and Franco 2009; Bortolotto et al. 2024; Su and Penning 2024).

A major source of PAH contamination is food intake, raising concerns about the need for monitoring in the food industry. In recent years, increasing levels of PAH have been reported in developing and developed countries due to their presence in food and beverages (Dennis et al. 1983; Bettin and Franco 2005; Bansal and Kim 2015; Paris et al. 2018; Peng and Lim 2022; Agus et al. 2023; Azari et al. 2023; Bortolotto et al. 2024). PAHs have been identified in whiskey (Kleinjans et al. 1996; Da Porto et al. 2006; Da Porto and Moret 2007; Chinnici et al. 2007; Peng and Lim 2022). To date, there is no universal limit for PAH in beverages. In the European Community, the maximum concentration of PAHs in foods are 1-50 µg/Kg (including naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and chrysene (EFSA 2008: EC 2006: EC2011: EC 2014). Souza et al (2022) identified PAHs in cachaça packaged in PET. Although there is no Brazilian legislation governing the maximum concentration of PAHs in cachaça, this is of concern as PAHs are classified as carcinogenic by the International Agency for Research on Cancer (IARC 2012). In the case of cachaça, areas of concern include (i) contamination from lubricants and greases, (ii) addition of sugar to correct product colour, (iii) burnt raw material or sugarcane fields near highways, (iv) tanks lined with asphalt resins or thermally treated wooden barrels for aging and (v) use of inappropriate containers for storage of the beverages.

Food packaging made of polymeric materials must meet criteria compatible with their use and without interaction with the food. Polyethylene terephthalate (PET) is widely used in the packaging of beverages due to its low gas permeability and resistance to mechanical impact (Nisticò 2020). Although this polymer is not commonly used to package high ABV products, it has been used in Brazil by some producers due to its low cost and greater durability during transport. However, this polymer may contain small amounts of low molecular weight oligomers that can migrate from the packaging material to the beverage. Migration depends on factors such as the physicochemical properties of the migrating compound, the type of polymer in the package, the contact time and the storage temperature (Alamri et al. 2021).

With the growing market acceptance of cachaça and the need to standardise quality, the qualitative parameters of distillates need to be analysed to ensure that consumption is safe. In terms of food safety, the quantification of PAHs in cachaça has become important in enabling regulators to identify and reduce sources of contamination.

This study quantified the PAHs in cachaça packed in PET under different storage conditions and evaluated the effect of these conditions on the content of PAHs. The chemical structure of the PET packaging was analysed to determine the contribution to PAH content in the cachaça and identify changes in the structure of PET subject to different storage environments for twelve months.

Materials and methods

Cachaça

Freshly distilled cachaça was from Engarrafadora Estiva in Alto Rio Doce, Minas Gerais. Cachaça was stored in a glass bottle (GLASS) under ambient conditions with samples in sterile, virgin PET packaging stored (i) at ambient conditions with artificial light (LIGHT), (ii) in a refrigerator (REFRI), (iii) with continuous exposure to solar radiation (SOLAR) and (iv) in the dark (DARK). The storage conditions were designed to reflect the conditions that cachaça is stored in local markets. All samples were stored for a period of twelve months.

Physicochemical analyses and chromatography

The physicochemical and chromatographic analyses were performed according to IN No. 13 of 06/29/2005 and IN No. 28 of 08/11/2014 established by MAPA (Brazil 2005, 2014).

Analysis of PAHs were performed using high-performance liquid chromatography (HPLC) with a Shimadzu chromatograph and a diode array detector (DAD) (Souza et al. 2022). Identification and quantification of PAHs was performed by comparing the retention times of each compound with internal standards of analytical purity (from Merck/Sigma-Aldrich). The following PAHs were analysed: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, acenaphthene, and benzo[a] pyrene. Calibration curves were created between 10 to 500 µg/L.

Statistical analysis

Analysis of variance, and means were compared by Tukey's test at the 95% confidence level using SISVAR software in the STATISTICA program (Ferreira 2011: Statsoft 2011).

Thermal characterisation of PET - thermogravimetry, differential scanning calorimetry and attenuated total reflectance Fourier transform infrared spectroscopy

Samples (ca. 2 cm^2) of PET were taken from bottles that had contained cachaça stored under different conditions for thermal and spectroscopic analyses. A control sample (C) – a virgin PET bottle - was kept under ambient conditions for twelve months.

Thermogravimetry analysis (TGA), required a scale, an oven, sample support, temperature sensor and oven temperature programmer (DTG-60A/60AH), and a recording system (TA-60 WS) with flow and atmosphere control of the oven (FC-60A). The analyses were performed as described by Silva and Wiebeck (2022) with modifications. The LIGHT, REFRI, SOLAR, DARK and C samples, weighing ca. 10 mg, were heated in an alumina crucible from 25 to 600°C with a heating rate of 10°C/min under a continuous flow of nitrogen at 50 mL/min.

Differential scanning calorimetry (DSC) required an oven, sample support, temperature sensor and oven temperature programmer (DSC-60A), recording system (TA-60 WS) with oven flow and atmosphere control (FC-60A). The analyses were performed using the modified method of Sorolla-Rosário et al (2022). Samples of the LIGHT (4.1 mg), REFRI (4.7 mg), SOLAR (5.3 mg), DARK (4.5 mg) and C (4.6 mg) were subject to two cycles of heating/cooling with temperatures between 25 and 300°C and a heating rate of 10°C/min under an atmosphere of nitrogen. The thermograms were integrated to determine the enthalpy changes for the phase transitions of the polymers.

To obtain IR spectra, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTI) was performed using a Varian 600-IR FT-IR spectrometer, with a GladiATR accessory (Pike Technologies) for attenuated total reflectance (ATR) measurements at 45°C with a zinc selenide crystal. The analyses were performed using the modified methodology by Silva and Wiebeck (2022). The spectral range was 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, with 32 scans collected at room temperature.

Results and discussion

Physicochemical and chromatographic analyses

The physicochemical analysis of cachaça stored under different conditions in glass and PET packaging are reported in Table 1. All samples maintained their alcohol level between 38-48% ABV (alcohol by volume). The ABV of the SOLAR sample was 43.9 ± 0.1%, marginally lower than the LIGHT (44.6 ± 0.1%) and DARK (44.5 ± 0.1%) samples. Zhu et al (2019) reported a theoretical study of the shelf life of beverages stored in plastic packaging by analysing mass transfer of ethanol and water in a water-ethanol mixture as a solvent. It was observed that different water-ethanol proportions influence the transfer of both substances, resulting in a shorter or longer shelf life. The shelf life of beverages stored in PET packaging was altered by mass transfer, change of water-ethanol content, migration problems, oxidation and loss of aroma. This was confirmed by Santiago et al (2020) who reported that ABV was affected by nonconformities in sealing of the containers used, suggesting that evaporation may have decreased the alcohol content of the SOLAR relative to the LIGHT and DARK samples.

Aldehydes have sensory importance in cachaça, and all samples were within the specification recommended by Brazilian legislation, corresponding to 30 mg per 100 mL of anhydrous alcohol (99.5% purity) (Brazil 2005). The SOLAR sample had the highest concentration with 27.6 ± 0.1 mg/100 mL anhydrous alcohol. This may relate to the decomposition of polymers in the PET packaging. The most prevalent migrant carbonyl compounds found in the PET bottles were acetaldehyde and formaldehyde. These compounds can be formed as by-products of thermal degradation in the polycondensation phase and melt processing of PET. Exposure to UV radiation affects the migration of aldehydes which increased significantly at temperatures above 40°C (Gerassimidou et al. 2022).

Demirel et al (2021) noted that an increase in temperature had a marked effect on PET due to the degradation of isophthalic acid, acetaldehyde and ethylene glycol, which generated volatile compounds. Cardoso et al (2022) reported that aldehydes are oxidized to acids. Thus, the low concentrations of aldehydes in cachaça stored cold in PET (REFRI) sample may reflect their oxidation. This was consistent with volatile acidity, as the REFRI sample had the highest concentration with 225.9 ± 0.4 mg per 100 mL of anhydrous alcohol.

The furfural concentration allowed by Brazilian legislation is 5 mg/100 mL of anhydrous alcohol (Brazil 2005). In Table 1, furfural was < 0.4 mg/100 mL anhydrous ethanol and was not detected in GLASS and SOLAR samples. Fragmentation of the furfural forms acetic acid, perhaps contributing to

Table 1.

Physicochemical parameters of cachaça under different storage conditions.

Samples	LIGHT	REFRI	SOLAR	DARK	GLASS
ABV[1]	44.6 ± 0.1^{a}	44.3 ± 0.1^{ab}	43.9 ± 0.1^{b}	44.5 ± 0.1^{a}	44.2 ± 0.1^{ab}
Aldehyde[2]	24.8 ± 0.1^{b}	23.7 ± 0.2^{c}	27.6 ± 0.1^{a}	25.6 ± 0.2^{b}	25.5 ± 0.2^{b}
Furfural[2]	0.2 ± 0.1^{b}	0.4 ± 0.1^{a}	ND	0.4 ± 0.1^{a}	ND
Volatile acid[2]	164.9 ± 0.1^{c}	225.9 ± 0.4^{a}	194.2 ± 0.4^{b}	195.1 ± 0.1^{b}	126.6 ± 0.2^{d}
Esters[2]	107.4 ± 0.8^{a}	95.5 ± 0.2^{b}	75.6 ± 0.8^{d}	105.73 ± 1.0^{a}	86.3 ± 0.2^{c}
Higher alcohols (propanol, isobutyl and Isoamyl)[2]	261.7 ± 0.1^{b}	264.2 ± 0.1^{b}	262.8 ± 0.1^{b}	282.8 ± 0.1^{a}	289.6 ± 0.1^{a}
Copper[3]	0.6 ± 0.1^{a}	0.6 ± 0.1^{a}	0.6 ± 0.1^{a}	0.6 ± 0.1^{a}	0.7 ± 0.0^{a}
Methanol[2]	ND	ND	ND	ND	ND
Butyl alcohol[2]	1.0 ± 0.1^{a}	1.1 ± 0.1^{a}	1.1 ± 0.1^{a}	0.6 ± 0.1^{b}	1.1 ± 0.1^{a}
***sec*-Butyl alcohol[2]**	7.1 ± 0.5^{a}	7.4 ± 0.2^{a}	5.3 ± 0.1^{a}	5.7 ± 1.0^{a}	8.2 ± 0.7^{a}
Ethyl carbamate[4]	ND	ND	ND	ND	ND

Units: [1](% v/v at 20°C); [2](mg/100mL anhydrous alcohol.); [3](mg/L); [4](µg/L). LIGHT – PET stored in ambient conditions. REFRI – PET stored in a refrigerator. SOLAR – PET stored with continuous solar radiation. DARK – PET protected from light. GLASS – glass stored in ambient conditions. ND = not detected. $^{a,\ b,\ c}$ and ^{c} = 95% confidence level.

the volatile acidity of the REFRI sample, which may in turn be be related to alcohol oxidation (Bortoletto and Alcarde 2013; Cardoso et al. 2022).

Ferreira et al (2020) showed that some components of a passion fruit (maracujá-do-mato) beverage can change due to temperature, packaging, light, enzymatic and nonenzymatic factors. In addition, gas exchange occurs enabling entry of oxygen and increasing the volatile acidity. Safaei et al (2022) reported that oxygen within PET pouches affected the absorption of moisture and accelerated oxidation reactions in Ghavoot (an Iranian traditional food).

The concentration of esters after twelve months of storage ranged from 75 (SOLAR) to 107 (LIGHT) mg/100 mL anhydrous alcohol. Interestingly, Arena et al (2021) reported that the aromas and flavours of *Malvasia delle Lipari* sweet wine deteriorate through photolytic autoxidation reactions. Matias-Guiu et al (2020) reported that extended storage times and high temperatures (45°C) reduced the content of ethyl esters, alcohols and acids in fruit spirits. According to Cardoso et al (2022), the alcohol content in the beverage should be proportional to the ester levels. This proportionality was observed for the DARK sample, which showed higher concentrations of esters and higher alcohols than the other samples.

Butyl alcohol ranged from 0.6 to 1 mg/100 mL anhydrous alcohol, with legislation allowing a maximum of 3 mg/100 mL) (Brazil 2005). With sec-butyl alcohol, the concentration ranged from 5 to 8 (legislation allows a maximum of 10) mg/100 mL anhydrous alcohol (Brazil 2005) (Table 1). Methanol and ethyl carbamate were not detected in the samples. Copper was present at < 1 mg/L in accord with Brazilian legislation (limit of 5 mg/L) and meets international standards for distilled beverages that limit the copper content to 2 mg/L.

Analysis of polycyclic aromatic hydrocarbons (PAH) in cachaça stored in glass and PET under different conditions (LIGHT, REFRI, SOLAR, DARK) are reported in Table 2.

Identification and quantification of the polycyclic aromatic hydrocarbons

Analysis of polycyclic aromatic hydrocarbons (PAH) in cachaça stored in glass and PET under different conditions (LIGHT, REFRI, SOLAR, DARK) are reported in Table 2.

In agreement with Barbosa et al (2022), anthracene was not detectable in any samples of cachaça. Naphthalene and phenanthrene were detected in cachaça packaged in glass (GLASS) but not in PET.

Table 2.

Polycyclic aromatic hydrocarbons in cachaça stored in PET or glass.

						Polycyclic aromatic hydrocarbons (μg/L)					
Samples	**Nap**	**Ace**	**Flu**	**Phe**	**Ant**	**Fluo**	**Py**	**Benza**	**Acef**	**Benzo**	**Total**
LIGHT	<LQ	0.3 ± 0.1^{b}	1.7 ± 0.1^{ab}	<LD	<LD	0.9 ± 0.1^{c}	0.3 ± 0.1^{b}	1.6 ± 0.1^{a}	3.0 ± 0.1^{a}	$1.3 \pm 0.^{b}$	9.1
REFRI	<LD	0.3 ± 0.1^{b}	1.8 ± 0.1^{ab}	<LQ	<LD	9.9 ± 0.1^{a}	<LD	<LD	1.7 ± 0.1^{d}	<LD	13.8
SOLAR	<LD	0.5 ± 0.1^{a}	1.6 ± 0.1^{b}	<LD	<LD	0.5 ± 0.1^{d}	<LD	<LQ	2.2 ± 0.1^{c}	2.0 ± 0.1^{a}	7.0
DARK	<LQ	<LQ	1.2 ± 0.1^{c}	<LD	<LD	1.2 ± 0.1^{b}	<LD	<LD	1.6 ± 0.1^{e}	<LD	4.2
GLASS	0.4 ± 0.1^{a}	0.6 ± 0.1^{a}	1.9 ± 0.1^{a}	0.6 ± 0.1^{a}	<LD	0.8 ± 0.1^{c}	1.5 ± 0.2^{a}	<LD	2.3 ± 0.1^{b}	<LD	8.3
LD	0.1	0.1	0.2	0.11	0.2	0.1	0.1	0.1	0.1	0.2	
LQ	0.2	0.3	0.6	0.36	0.5	0.2	0.3	0.4	0.3	0.6	

Nap (naphthalene); Ace (acenaphthylene); Flu (fluorene); Phe (phenanthrene); Ant (anthracene); Fluo (fluoranthene); Py (pyrene); Benza (benz[a]anthracene); Acef (acephenanthrene); Benzo (benzo[a]pyrene). LIGHT – stored in ambient conditions. REFRI – stored in a refrigerator. SOLAR – stored with continuous solar radiation. DARK – protected from light. GLASS – glass stored in ambient conditions. LD - Limit of detection. LQ - Limit of quantification. $^{a, b, c, d, e}$ = 95% confidence level

Machado et al (2014) also reported phenanthrene in cachaça packaged in glass, with lower concentration found in the less gas permeable HDPE (high-density polyethylene). Pyrene was detected at 0.3 (LIGHT) and 1.5 µg/L (GLASS), well below 25 µg/L, the limit allowed by European Community (EFSA 2008: EC 2006: EC 2011: EC 2014). Pyrene was detectable in the LIGHT sample (0.3 µg/L) but undetectable in the other PET samples suggesting the pyrene may be removed by adsorption or absorption it into the polymer matrix.

Acenaphthylene was detected but complied with limits of the European Community. The level in the DARK sample, could not be quantified as it was below the limit of quantification. Fluorene was found in all samples, with those in PET (1.2-1.7 µg/L) lower than that packaged in glass (1.9. µg/L). All samples were below the acceptable limit of the European Union (EFSA 2008; EC 2006; EC2011; EC 2014). However, in contrast, Souza et al (2022) reported that fluorene levels were above the legal limit in PET packaging after four months of storage.

Fluoranthene was detected and quantified in all samples. With the exception of the REFRI sample, the concentration of fluoranthene in cachaça was about 1 µg/L in broad agreement with the report of Galinaro and Franco (2009). The concentration in the REFRI sample was 9.9 ± 0.1 µg/L suggesting that cachaça packaged in PET and stored at low temperatures but in the absence of light has a higher content of fluoranthene.

Acephenanthrene was highest in the LIGHT sample at 3 ± 0.1 µg/L, followed by GLASS with 2.3 ± 0.1 µg/L and SOLAR with 2.2 ± 0.1 µg/L. The content of acephenanthrene in REFRI and LIGHT was lower at 1.6 and 1.7 µg/L. This suggests that the availability of light increased the content of acephenanthrene in cachaça. Li et al (2017) found that in polystyrene packaging, the contact time and storage temperature reduced the migration of contaminants. Further, Alamri et al (2021) reported that the equilibrium time of a migrating compound is inversely correlated with temperature.

Benzo[a]pyrene was quantified at 1.3 ± 0.1 µg/L in LIGHT and 2 ± 0.1 µg/L in SOLAR but was below the limit of detection in REFRI, DARK and GLASS. It is noteworthy that the level of benzo[a]pyrene in the LIGHT and SOLAR samples was greater than the limit from Brazilian legislation of 0.7 µg/L for bottled waters. Alemu and Getahun (2020) reported that the exposure of mineral water in PET bottles to prolonged solar radiation led to the generation of genotoxic substances due to leaching of the photoproducts from the packaging material. Similarly, Orodu (2021) reported that water packaged in plastic bottles and exposed to heat above room temperature may contain carcinogenic substances, and that the conditions may accelerate migration of the substances.

Barbosa et al (2023) evaluated 15 commercial cachaça samples packaged in PET, focusing on their physicochemical profiles and polycyclic aromatic hydrocarbons (PAHs). The study revealed that 60% of the samples contained components exceeding the quality standards established by MAPA, with only five samples meeting the legal level for ABV. Analysis of PAHs showed that all samples had higher concentrations than those reported for cachaça stored in other types of packaging. The authors suggested that PAH contamination may be linked to the thermal processes involved in producing the packaging. Additionally, the high alcohol content in cachaça could increase PAH solubility, facilitating the migration of these compounds from the packaging into the beverage.

The work reported here does not show a correlation between high alcohol content and elevated PAHs, suggesting that migration depends on the balance between beverage properties and the thermodynamic conditions to which the bottle is exposed. This suggests that cachaça stored in PET packaging may be unsuitable for consumption and commercialisation due to high contaminant levels.

Characterisation of polymers stored under different conditions

Thermogravimetry analysis (TGA) in Figure 1 show the mass changes of the polymer samples induced by increases in temperature.

PET was stable up to approximately 350°C with all storage conditions, suggesting that the different storage conditions did not affect the thermal stability of the polymer. Between 400 and 480°C, a substantial loss in mass was observed, which was attributed to scission of the PET polymer chains. Mass varied between storage conditions with losses (as %) of 65.8 (C), 73.5 (SOLAR), 76.4 (REFRI), 74.5 (LIGHT) and 76.4 (DARK).

The degradation of PET has been reported for temperatures above 400°C, with rupture of the weak bonds in the polymer chain that generate short chain and aromatic hydrocarbons (Palmay et al. 2021; Sorolla-Rosario et al. 2022). Under pyrolytic conditions with PET, mass losses of almost 70%, with the formation of semi-volatile compounds and low molar weight hydrocarbons. About 11% of weight loss was due to compounds such as benzene, together with aromatic and polyaromatic compounds, such as PAHs (Martín-Gullón et al. 2001).

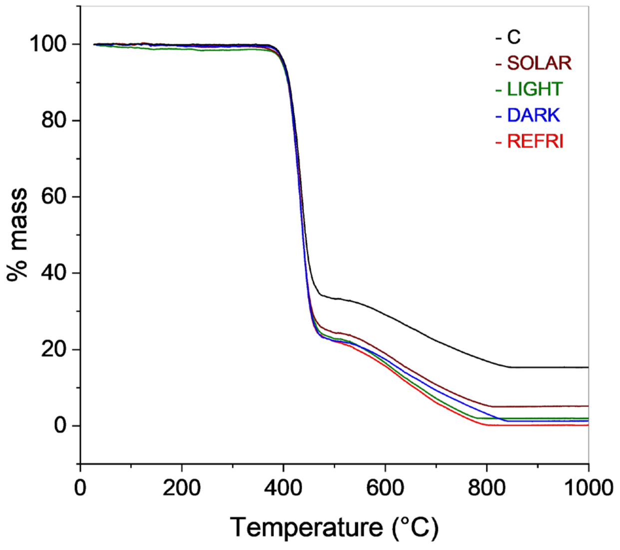
A second thermal event in the TGA curve (Figure 1) was observed between 500 and 800°C and was associated with secondary reactions between radicals in the system. Products such as carbon monoxide, carbon dioxide, acetaldehyde, benzene, benzoic acid, acetophenone, vinyl benzoate and dimethyl terephthalate were formed at 700°C via pyrolysis of PET (Das and Tiwari 2019; Palmay et al. 2021).

Figure 2 shows the differential scanning calorimetry (DSC) curves for PET stored under the different conditions and the phase transition parameters obtained from thermograms. In all the thermograms (Table 3), subtle variations in the baseline were observed at approximately 74.5 to 75.6°C, which corresponded to the glass transition temperature (T_g). This is a property of the amorphous phases of polymers related to the mobilities of polymer chains in the amorphous state. Pacheco et al. (2021) reported that the glass transition of PET is 70°C whereas, in agreement with this study, Dhaka et al (2022) noted that the T_g of semicrystalline PET varies between 67 and 80°C.

Heat induced PET crystallisation was indicated by a small exothermic peak between 135 and 150°C, which was less apparent in the control PET (Figure 2). The crystallisation temperatures (T_c) were about 148°C and varied little with the different storage conditions. Wang and Wen (2022) reported that the crystallisation peak for untreated PET was weak

Figure 1.

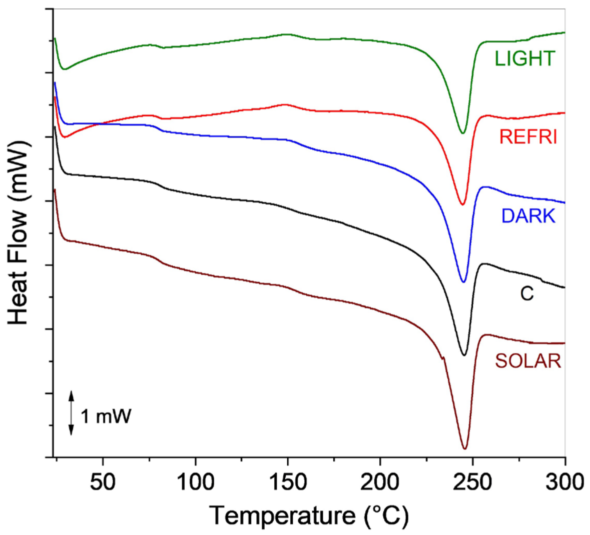
TGA curves for PET subject to different storage conditions.



LIGHT - laboratory ambient. REFRI - domestic refrigerator. SOLAR - continuous solar radiation. DARK - protected from light. Control (C), no treatment.

Figure 2.

DSC curves for PET bottles stored with different light and temperature.



LIGHT - laboratory ambient. REFRI - domestic refrigerator. SOLAR - continuous solar radiation. DARK - protected from light. Control (C), no treatment. The curves were shifted relative to each other for better visualisation. The recording was from the second heating cycle.

because of the time of the crystallisation process. They also noted that the higher the crystallisation temperature, the slower the crystallisation. This reflects the thermal movement of the chains, which increased at higher crystallisation temperatures.

Fitaroni et al (2020) noted that samples that suffered the most severe degradative processes had shorter crystallisation times, which was attributed to lower molar masses. However, the presence of contaminants can induce changes in this process, as they hinder packing of the polymer chains and influence crystallisation of polyethylene samples (Veroneze et al. 2022).

The third thermal event in PET (Figure 2), with the highest endothermic peak in the thermogram, was attributed to melting of the polymer. The peak melting temperatures (M_p) of the polymer for the different storage conditions were in the range of 244.4 to 245.5°C (Table 3). These values did not differ with different storage conditions. The range over which PET crystals melt may depend on cooling of the polymer from its molten state, when the polymer chains reorganise themselves in a regular manner to form the crystalline structure (Girard et al. 2021; Thomsen et al. 2022). Mammo et al (2020) and Wang et al (2021) reported that a high energy crystallisation process destabilised the crystalline region of a semicrystalline polymeric material and enabled sorption of compounds, depending on the crystallinity. Decreased crystallinity in polyethylene can lead to increased sorption of compounds such as phenanthrene, lindane and naphthalene.

The crystallinity of a polymer can be calculated from the total latent heat of fusion (ΔH_f) (Table 3) relative to the maximum latent heat of fusion for the polymer. If PET were 100% crystalline, the latent heat of fusion would be 140 J/g (Seif and Challita 2022). The degrees of crystallinity of the PET samples calculated for the different conditions evaluated were 7.6% (LIGHT), 5.8% (REFRI), 7.2% (SOLAR), 7.2% (DARK) and 6.3% (control). Dhaka et al (2022) and Beltran-Sanahuja et al (2020) reported that large changes in crystallisation and variations in the enthalpy of melting occurred when amorphous regions of the polymer were degraded, and oligomers were formed due to photodegradation and chain scission.

The lower crystallinities for polymers stored under the REFRI and DARK conditions may have reduced the sorption properties of the PET and enabled the migration of compounds into the cachaça. Table 2 shows high fluoranthene concentrations for samples subjected to the REFRI and DARK conditions, with values of 9.9 ± 0.1 µg/L and 1.2 ± 0.1 µg/L, respectively.

The ATR-FTIR technique provides information on functional groups, and the spectra obtained for the different samples of cachaça are shown in Figure 3. The spectra obtained were similar for PET irrespective of storage conditions. An intense band was observed at 1700 cm^{-1} for stretching of the C=O

Table 3.

Phase transition parameters from differential scanning calorimetry of PET.

Samples	M (mg)	T_g (°C)	T_c (°C)	ΔH_c (J g^{-1})	M_p (°C)	ΔH_f (J g^{-1})
LIGHT	4.1	75.6	149.2	1.5	244.9	10.7
REFRI	4.7	74.5	148.7	1.0	244.4	8.1
SOLAR	5.3	75.1	148.5	0.1	245.5	10.1
DARK	4.5	75.6	148.3	0.4	244.9	10.1
Control	4.6	75.6	-	-	245.0	8.8

LIGHT – stored in ambient conditions. REFRI – stored in a refrigerator. SOLAR – stored with continuous solar radiation. DARK – protected from light. Control (C), virgin, empty PET. M – PET mass. T_g - glass transition temperature. Tc - crystallisation temperature. ΔH_c – enthalpy of crystallisation variation. M_p - Melting temperature. ΔH_f – enthalpy change for melting.

bonds. Absorption bands between 1000 and 1100 cm^{-1} (vibrations of the aromatic rings) may represent a group of mononuclear aromatic hydrocarbons in the polymer. The bands between 2800 and 2900 cm^{-1} corresponded to the C-H stretching vibrations (Palmay et al. 2021).

Analysis of the region between 2000–1500 cm^{-1} (inset of Figure 3), showed that a band at approximately 1700 cm^{-1} for SOLAR storage had a higher relative intensity compared to the other samples with absorption at 1715 cm^{-1}. Silva and Wiebeck (2022) observed an intense peak at 1715 cm^{-1} for the C=O stretching vibrations of carboxylic acid groups with various plastics such as polystyrene, polypropylene, polyvinyl chloride and PET.

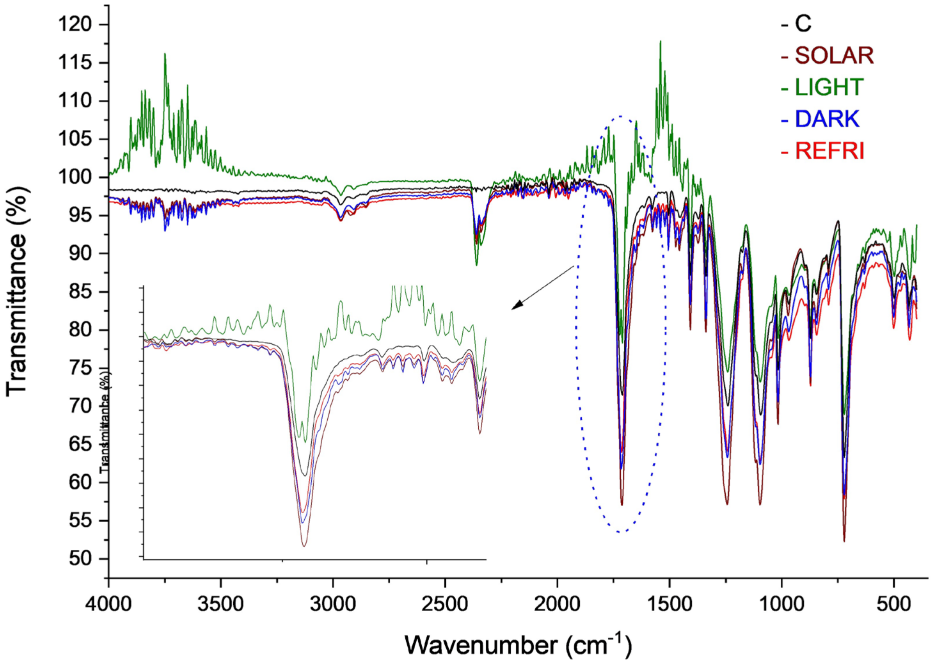
The relative vibrational peak in the SOLAR spectrum indicated degradation of the polymeric material. The LIGHT sample, unlike those subjected to the other storage conditions, exhibited two bands at 1722 cm^{-1} and 1711 cm^{-1}. This suggests the bands were from the carboxylic acid and an ester (Barbosa 2007). Data in Table 1 reported volatile acidity values of 164.9 ± 0.6 mg/100 mL anhydrous alcohol. and an ester content of 107.4 ± 0.9 mg/100 mL anhydrous alcohol.

In thermo-oxidative degradation, PET undergoes polymer chain scission. This forms carboxylic acids and vinyl esters, which undergo secondary reactions and generate carbon monoxide, carbon dioxide, acetaldehyde, aromatic acid and vinyl esters as by-products (Das and Tiwari 2019; Nisticò 2020).

In the analysis of PAHs (Table 2), higher concentrations of benzo[a]anthracene, benzo[a]pyrene and acephenanthrene were found in the LIGHT cachaça compared to that stored in glass containers under ambient conditions. For the SOLAR sample, the highest concentrations were of acephenanthrene and benzo[a]pyrene, while benzo[a]anthracene was detected but not quantified. In conclusion, the Scientific Committee for Food (SCF) of the European Commission and the European Food Safety Authority (EFSA) reported that benzo[a]pyrene and benzo[a]anthracene can be carcinogenic markers (Caruso and Alaburda 2008; Riachi et al. 2014). These data were correlated with those observed in quantification of PAHs for storage conditions exposed to light (LIGHT and SOLAR).

Figure 3.

ATR-FTIR spectra of PET subject to different storage conditions.



LIGHT - laboratory ambient. REFRI - domestic refrigerator. SOLAR - continuous solar. DARK - protected from light. Control (C) - no treatment.

Conclusions

Cachaça stored in glass met the identity and quality standards for the spirit. However, the quality of cachaça was affected when stored in PET packaging for twelve months, due to mass transfer, migration of compounds, oxidation and loss of aroma. The LIGHT and SOLAR samples showed elevated concentrations of carcinogenic and genotoxic substances, including benzo[a]pyrene and benzo[a] anthracene. The characterisation of PET subjected to different storage conditions showed few changes in the thermal and spectroscopic properties of the material, but the data indicated reductions in the crystallinity for PET stored in the cold (REFRI) or DARK. Accordingly, the temperature, time and storage conditions can influence the migration of PAHs from PET packaging to cachaça.

Author contributions

Ana Paula Abrantes: Conceptualisation, formal analysis, writing (original draft).
Maria das Graças Cardoso: Resources, project administration, writing (review and editing), funding acquisition, supervision.
Pamela Aparecida dos Santos: Conceptualisation, investigation.
Richard Bispo Barbosa: Methodology, validation, investigation, data curation.
Vanuzia Rodrigues Fernandes Ferreira: Methodology, validation, investigation, data curation.
Gabriela Fontes Alvarenga: Formal analysis, validation, investigation, supervision.
Carolina Salles Freire: Conceptualisation, investigation.
Antonia Isadora Fernandes: Conceptualisation, investigation.
Wilder Douglas Santiago: Conceptualisation, investigation, supervision, data curation.
Guilherme Max Dias Ferreira: Conceptualisation, methodology, data curation, writing (review and editing).

Acknowledgements

This work was supported by the Fundação de Amparo à Pesquisa de Minas Gerais (FAPEMIG – ProjectCAG/APQ 02390/2018), the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq – Project CNPQ 311183/2022-0), and the Coordenação do Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES – Finance code 001). The authors thank the funding agencies for the scholarships and financial support and the Central of Analysis and Chemical Prospecting of the Federal University of Lavras (CAPQ) for supplying the equipment for chromatographic analyses.

Conflict of interest

The authors declare that there were no conflict of interests.

References

Agus BAP, Rajentran K, Selamat J, Lestari SD, Umar NB, Hussain N. 2023. Determination of 16 EPA PAHs in food using gas and liquid chromatography. *J Food Compos Anal* 116:105038. https://doi.org/10.1016/j.jfca.2022.105038

Alamri MS, Quasem AAA, Mohamed AA, Hussain S, Ibraheem MA, Shamlan G, Alqah HA, Qasha AS. 2021. Food packaging's materials: A food safety perspective. *Saudi J Biol Sci* 28:4490–4499. https://doi.org/10.1016/j.sjbs.2021.04.047

Alemu A, Getahun AH. 2020. Evaluation of the genotoxicity of mineral water in polyethylene terephthalate bottles exposed to solar radiation and temperature at variable timescale. *Water Environ J* 34:906-915. https://doi.org/10.1111/wej.12600

Arena E, Rizzo V, Licciardello F, Fallico B, Muratore G. 2021. Effects of light exposure, bottle colour and storage temperature on the quality of *Malvasia delle Lipari* sweet wine. *Foods* 10:1881. https://doi.org/10.3390/foods10081881

Azari A, Abtahi M, Dobaradaran S, Saeedi R, Yari AR, Vaziri MH, Razavinasab SA, Malakoutian M, Yaghmaeain K, Jaafarzadeh N. 2023. Polycyclic aromatic hydrocarbons in high-consumption soft drinks and non-alcoholic beers in Iran: Monitoring, Monte Carlo simulations and human health risk assessment. *Microchemical Journal* 191:108791. https://doi.org/10.1016/j.microc.2023.108791

Bansal V, Kim KH. 2015. Review of PAH contamination in food products and their health hazards. *Environ Int* 84:26–38. https://doi.org/10.1016/j.envint.2015.06.016

Barbosa LCA. 2007. *Espectroscopia no Infravermelho na Caracterização de Compostos Orgânicos*. UFV Viçosa (ed), Brazil.

Barbosa RB, Santiago WD, Alvarenga GF, Oliveira RES, Ferreira VRF, Nelson DL, Cardoso MG. 2022. Physical–chemical profile and quantification of phenolic compounds and polycyclic aromatic hydrocarbons in cachaça samples aged in oak (*Quercus sp.*) barrels with different heat treatments. *Food Bioprocess Technol* 15:1977-1987. https://doi.org/10.1007/s11947-022-02853-w

Barbosa RB, Alvarenga GF, Ferreira VRF, Santiago WD, Nelson DL, Cardoso MG. 2023. Cachaça sold in polyethylene terephthalate packaging: Determination of the physical-chemical profile, polycyclic aromatic hydrocarbons and ethyl carbamate. *Science and Agrotechnology* 47:e007522. https://doi.org/10.1590/1413-7054202347007522

Beltrán-Sanahuja A, Casado-Coy N, Simó-Cabrera L, Sanz-Lázaro C. 2020. Monitoring polymer degradation under different conditions in the marine environment. *Environ Pollut* 259:113836. https://doi.org/10.1016/j.envpol.2019.113836

Bettin SM, Franco DW. 2005. PHAs in spirits. *Food Sci Techno* 252:234-238. https://doi.org/10.1590/S0101-20612005000200008

Bortoletto AM, Alcarde AR. 2013. Congeners in sugar cane spirits aged in casks of different woods. *Food Chem* 139:695–701. https://doi.org/10.1016/j.foodchem.2012.12.053

Bortolotto A, Will C, Huelsmann RD, Carasek E. 2024. Lab-made automated parallel-dispersive pipette extraction device for the determination of polycyclic aromatic hydrocarbons in distilled beverages (sugarcane spirits) using HPLC-DAD. *J Chromatogr A* 1733:465257. https://doi.org/10.1016/j.chroma.2024.465257

Brazil. Ministry of Agriculture, Livestock and Supply (MAPA). Normative Instruction No. 13, of June 6, 2005. Official Gazette of the Union, Section I, p 3-3.

Brazil. Ministry of Agriculture, Livestock and Supply (MAPA). Normative Instruction No. 28, of August 8, 2014. https://www.gov.br/agricultura/pt-br/assuntos/inspecao/produtos-vegetal/legislacao-1/biblioteca-de-normas-vinhos-e-bebidas/instrucao-normativa-no-28-de-8-de-agosto-de-2014.pdf/view.

Cardoso MG, Machado AMR, Caetano ARS, Campolina GA, Nelson DL. 2022. Volatile compounds formation in cachaça, p 15-31. In Reis FR, Santos CME (eds), *Volatile Compounds Formation in Specialty Beverages*, CRC Press – Taylor & Francis Group, London, UK.

Caruso MSF, Alaburda J. 2008. Polycyclic aromatic hydrocarbons – benzo(a)pyrene: a review. *Rev Inst Adolfo Lutz (RIAL)* 671:1-27. https://doi.org/10.53393/rial.2008.67.32785

Chinnici F, Natali N, Spinabelli U, Riponi C. 2007. Presence of polycyclic aromatic hydrocarbons in woody chips used as adjuvant in wines, vinegars and distillates. LWT 40:1587–1592. https://doi.org/10.1016/j.lwt.2006.11.005

Das P, Tiwari P. 2019. Thermal degradation study of waste polyethylene terephthalate (PET) under inert and oxidative environments. *Thermochim Acta* 679:178340. https://doi.org/10.1016/j.tca.2019.178340

Da Porto C, Moret S, Soldera S. 2006. A study on the composition of distillates obtained from smoked marc. *Analytica Chimica Acta* 563:396–400. https://doi.org/10.1016/j.aca.2005.11.026

Da Porto C, Moret S. 2007. Comparison of polycyclic aromatic hydrocarbons (PAHs) between smoked marc spirits and whiskies. *Food and Chemical Toxicology* 45:2069–2071. https://doi.org/10.1016/j.fct.2007.04.022

Demirel B, Inaner NB, Gezer DU, Daver F, Yaras A, Akkurt F. 2021. Chemical, thermal, and mechanical properties and ultraviolet transmittance of novel nano-hydroxyapatite/ polyethylene terephthalate milk bottles. *Polym Eng Sci* 61:2043–2054. https://doi.org/10.1002/pen.25720

Dennis MJ, Massey RC, Mcweeny DJ, Knowles ME. 1983. Analysis of polycyclic aromatic hydrocarbons in UK total diets. *Food Chem Toxicol* 21:569-574. https://doi.org/10.1016/0278-6915(83)90142-4

Dhaka V, Singh S, Anil AG, Naik TSSK, Garg S, Samuel J, Kumar M, Ramamurthy PC, Singh J. 2022. Occurrence, toxicity and remediation of polyethylene terephthalate plastics. A review. *Environ Chem Lett* 20:1777–1800. https://doi.org/10.1007/s10311-021-01384-8

EC. 2006. Commission of the European Regulation No 1881/2006 of Commission of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. *Official J Eur Union* L364:5-24.

EC. 2011. Commission of the European Communities. Regulation No 835/2011 of Commission of 19 August 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in foodstuffs. *Official J Eur Union* L215:4-8.

EC. 2014. Commission of the European Communities. Regulation No 1327/2014 of Commission of 12 December 2014 amending Regulation (EC) No 1881/2006 s regards maximum levels of polycyclic aromatic hydrocarbons (PAHs) in traditionally smoked meat and meat products and traditionally smoked fish and fishery products. *Official J Eur Union* L358:13-4.

EFSA. 2008. European Food Safety Authority. Scientific opinion of the panel on contaminants in the food chain on a request from the European commission on PAHs in food. *Eur Food Safety Authority J* 724:1-114.

Ferreira LG, Fonseca AAO, Novais Júnior MM, Lima JGF, Jesus RS, Hansen DS, Silva SMPC. 2020. Development, evaluation of physico-chemical and sensory stability of maracujá-do-mato (Passiflora cincinnata Mast.) alcoholic fermented beverage during storage. *Brazil J Dev* 6:58064-58078. https://doi.org/10.34117/bjdv6n8-280

Ferreira, DF. 2011. Sisvar: A computer statistical analysis system. *Ciênc Agrotec* 35:1039-1042. https://doi.org/10.1590/S1413-70542011000600001

Fitaroni LB, Oliveira EC, Marcomini AL, Paranhos CM, Freitas FL, Cruz SA. 2020. Reprocessing and solid state polymerization on contaminated post consumer PET: Thermal and crystallization behavior. *J Polym Environ* 28:91–99. https://doi.org/10.1007/s10924-019-01579-9

Gerassimidou S, Lanska P, Hahladakis JN, Lovat E, Vanzetto S, Geueke B, Muncke KJGJ, Maffini M, Martin OV, Lacovidou E. 2022. Unpacking the complexity of the PET drink bottles value chain: A chemicals perspective. *J Hazard Mater* 430:128410. https://doi.org/10.1016/j.jhazmat.2022.128410

Girard M, Combeaud C, Billon N. 2021. Effects of annealing prior to stretching on strain induced crystallization of polyethylene terephthalate. *Polymer*, 230:124078. https://doi.org/10.1016/j.polymer.2021.124078

IARC. 2012. International Agency for Research on Cancer. Chemical agents and related occupations: a review of human carcinogens. Lyon, France IARC, p 111-114. https://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Chemical-Agents-And-Related-Occupations-2012

Kleinjans, JCS, Moonen, EJC, Dallinga, JW, Albering, HJ, Vanden Bogaard, AEJM, Van Schooten, FJ. 1996. Polycyclic aromatic hydrocarbons in whiskies. *The Lancet* 348:1731.

Li SQ, Ni HG, Zeng H. 2017. PAHs in polystyrene food contact materials: An unintended consequence. *Sci Total Environ* 609:1126-1131. https://doi.org/10.1016/j.scitotenv.2017.07.262

Machado AMR, Cardoso MG, Dórea HS, Emídio ES, Silva MMS, Anjos JP, Saczk AA, Nelson DL. 2014. Contamination of cachaça by PAHs from storage containers. *Food Chem* 146:65-70. https://doi.org/10.1016/j.foodchem.2013.08.113

Mammo FK, Amoah ID, Gani KM, Pillay L, Ratha SK, Bux F, Kumari S. 2020. Microplastics in the environment: Interactions with microbes and chemical contaminants. *Sci Total Environ*. 743:140518. https://doi.org/10.1016/j.scitotenv.2020.140518

Martín-Gullón I, Esperanza M, Font R. 2001. Kinetic model for the pyrolysis and combustion of poly-(ethylene terephthalate) (PET). *J Anal Appl Pyrolysis* 58–59:635–650. https://doi.org/10.1016/S0165-2370(00)00141-8

Matias-Guiu P, Rodríguez-Bencomo JJ, Pérez-Correa JR, López F. 2020. Aroma compounds evolution in fruit spirits under different storage conditions analyzed with multiway anova and artificial neural networks. *J Food Process Preserv* 44:e14410. https://doi.org/10.1111/jfpp.14410

Nisticò R. 2020. Polyethylene terephthalate (PET) in the packaging industry. *Polymer Testing*. 90:106707. https://doi.org/10.1016/j.polymertesting.2020.106707

Orodu VE. 2021. Migration and degradation by volatile compounds from scent leaf (*Ocimum gratissimum*) on polyethylene terephthalate packaged water. *Chem Phys Polym* 1:1-11. https://10.23977/chepp.2021.010101

Pacheco JAL, Farias RM, Pacheco GF, Pacheco APL. 2021. Accelerated thermo-oxidation in PET bottles discarded in the environment. *Braz J Dev* 7:18957-11972. https://doi.org/10.34117/bjdv7n2-509

Palmay P, Puente C, Barzallo D, Bruno JC. 2021. Determination of the thermodynamic parameters of the pyrolysis process of post-consumption thermoplastics by non-isothermal thermogravimetric analysis. *Polymers* 13:4379. https://doi.org/10.3390/polym13244379

Paris A, Ledauphin J, Poinot P, Gaillard JL. 2018. Polycyclic aromatic hydrocarbons in fruits and vegetables: origin, analysis, and occurrence. *Environ Pollut* 234:96–106. https://doi.org/10.1016/j.envpol.2017.11.028

Peng PL, Lim LH. (2007). Polycyclic aromatic hydrocarbons (PAHs) sample preparation and analysis in beverages: a review, *Food Anal. Methods* 15:1042–1061. https://doi.org/10.1007/s12161-021-02178-y

Riachi LG, Santos A, Moreira RFA, De Maria CAB. 2014. A review of ethyl carbamate and polycyclic aromatic hydrocarbon contamination risk in cachaça and other Brazilian sugarcane spirits. *Food Chem* 149:159-169. https://doi.org/10.1016/j.foodchem.2013.10.088

Safaei FS, Sedaghat N, Sharif A. 2022. Effect of packaging material and oxygen concentration on quality of Ghavoot during the storage. *J Food Sci Technol* 59:879–889. https://doi.org/10.1007/s13197-021-05083-8

Santiago WD, Borges, CN, Barbosa RB, Mendonça HA, Nelson DL, Cardoso MG. 2020. Investigation of Brazilian cachaças regarding their standardization and quality. *Res Soc Dev* 9:1-21. https://doi.org/10.33448/rsd-v9i7.4117

Silva DJ, Wiebeck H. 2022. ATR-FTIR spectroscopy combined with chemometric methods for the classification of polyethylene residues containing different contaminants. *J Polym Environ* 20:3031-3044. https://doi.org/10.1007/s10924-022-02396-3

Sorolla-Rosário D, Llorca-Porcel J, Pérez-Martínez M, Lozabo-Castelló D, Bueno-López A. 2022. Study of microplastics with semicrystalline and amorphous structure identification by TGA and DSC. *J Environ Chem Eng* 10:106886. https://doi.org/10.1016/j.jece.2021.106886

Souza RHZ, Cardoso MG, Machado AMR, Santiago WD, Pedroso MP, Brandão RM, Oliveira RES, Barbosa RB, Alvarenga GF, Caetano ARS, Nelson DL. 2022. Polycyclic aromatic hydrocarbons in cachaças packed in bottles of polyethylene terephthalate. *J Food Sci* 87:1906-1915. https://doi.org/10.1111/1750-3841.16095

Statsoft, Inc. Statistica (Data Analysis Software System). Version 10. 2011.

Su AL, Penning TM. 2024. Polycyclic aromatic hydrocarbons: updates on occurrence and mitigation in foods, detection methods, determinants of toxicity, biomonitoring, and legislation. *Encyclopaedia of Food Safety* (second edition) 343-355. https://doi.org/10.1016/B978-0-12-822521-9.00095-2

Thomsen TB, Hunt CJ, Meyer AS. 2022. Influence of substrate crystallinity and glass transition temperature on enzymatic degradation of polyethylene terephthalate (PET). *N Biotechnol* 69:28–35. https://doi.org/10.1016/j.nbt.2022.02.006

Veroneze IB, Onoue LA, Cruz SA. 2022. Thermal stability and crystallization behavior of contaminated recycled polypropylene for food contact. *J Polym Environ* 30:3474–3482. https://doi.org/10.1007/s10924-022-02447-9

Wang B, Mathew A, Napolitano S. 2021. Temperature and thickness dependence of the time scale of crystallization of polymers under 1D confinement. *ACS Macro Lett* 10:476−480. https://doi.org/10.1021/acsmacrolett.1c00123

Wang B, Wen B. 2022. Effect of functional filler morphology on the crystallization behavior and thermal conductivity of PET resin: A comparative study of three different shapes of BN as heterogeneous nucleating agents. *Compos Sci Technol* 222:109346. https://doi.org/10.1016/j.compscitech.2022.109346

Zhu Y, Guillemat B, Vitrac O. 2019. Rational design of packaging: Toward safer and ecodesigned food packaging systems. *Front Chem* 7:1-20. https://doi.org/10.3389/fchem.2019.00349