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Improvement of the Chemical Quality of *Cachaça*

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Highlights:

- Previous studies have addressed the difficulty of complying with the Good Manufacturing Practices of *Cachaça* producers based on the high number of samples that fall outside the parameters required by legislation;
- Improving the chemical and sensory quality of *Cachaça* is a crucial factor in increasing exports of this distillate;
- The current study demonstrates the levels of contaminants found in 531 samples of *Cachaça* between the years 2021 and 2023.

Abstract: The objective of this study was to determine the chemical composition of sugarcane spirits and commercial *Cachaças*, comparing them with the limits established by national legislation and with studies conducted in previous periods. Previous studies have shown that 50% of the samples of this distillate were above the contaminant limits allowed by national legislation, constituting one of the main factors responsible for the low volume of exports. In this research, 531 *Cachaça* samples were analyzed in order to verify whether they complied with the limits of contaminants and volatile compounds required by Brazilian legislation. The results obtained indicate that Brazilian producers have adapted to the use of good manufacturing practices during the production process, ensuring the standardization of this distilled beverage and consequent compliance with legislation.

Keywords: chemical analysis; quality; contaminants; food security; *Cachaça*

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1. Introduction

The definition of the nomenclature *Cachaça* is exclusive to the sugarcane distillate produced in Brazil, which is obtained from fermented sugarcane must and has a minimum alcohol content of 38% and a maximum of 48% v/v at 20 °C. The maximum limit of added sugars is 6 g/L [1].

At the end of the twentieth century, the Brazilian Government created incentive programs such as "Pró-Cachaça" to allow *Cachaça* producers to invest on a large scale in this sector in 1992 [2]. Also, in 2002, Decree No. 4.072 reserved the term 'Cachaça' for sugarcane brandy made within Brazilian territory [3], and, in 2005, the technical regulation that defines the Standards of Identity and Quality for *Cachaça* was approved [4]. Finally, in 2013, *Cachaça* was recognized as a distillate typically produced in the Brazilian territory [5].

The history of *Cachaça* and that of Brazil are closely intertwined since this distillate was the first to be produced in Latin America between the years 1534 and 1549 in the captaincy of São Vicente in the state of Sao Paulo, Brazil. The broth, "forgotten" in pots by the slaves and fermented overnight, was later distilled and gave rise to the "cagaça", the early name for *Cachaça* [5].

Currently, 1.7 billion liters of *Cachaça* are produced in Brazil, 75% of which stems from industrial production, and 25% is produced by artisanal manufacturers [6]. *Cachaça* is the fourth most produced distilled beverage in the world, falling behind baijiu, vodka, and soju [7].

The distinctions between *Cachaça* and rum, both produced from sugarcane, are defined primarily by the production process and legislation. Rum holds significant historical and gastronomic value in the Caribbean, much like *Cachaça* does in Brazil. Unlike *Cachaça*, which is produced exclusively from fresh sugarcane must [1], rum can be produced entirely from molasses, sugarcane syrup, or sugarcane juice. Rhum Agricole, like *Cachaça*, is also produced entirely from sugarcane juice.

Rum and Rhum Agricole are subject to different regulations in each producing country, leading to variations across different regions. In contrast, *Cachaça* is recognized as a distillate typically produced in Brazil, and its producers must adhere to specific Identity and Quality Standards established by Brazilian law [8].

The production of *Cachaça* includes both field processes, such as planting, harvesting, and transporting sugarcane, as well as industrial practices such as receiving and sanitizing the sugarcane, milling, fermentation, distillation, optional aging, standardization, and packaging [9].

The chemical and sensory quality of *Cachaça* are closely related to every stage of its manufacturing process. Most chemical hazards arise during fermentation and/or distillation, making their removal from the final product difficult or even impossible after these steps [10]. Adherence to good manufacturing practices in national distilleries is a crucial tool for achieving safety levels that comply with the legislation.

The Identity and Quality Standards for Brazilian distilled spirits were established by the Ministry of Agriculture, Livestock, and Food Supply (MAPA), to ensure that *Cachaça* does not pose risks to the health of consumers when consumed in moderation [1]. The quality standards address, for example, low concentrations of acetic acid and volatile contaminants, which are responsible for the decline in the chemical and sensory quality of *Cachaça* [11].

The most common contaminants in *Cachaça* are methanol, sec-butanol, copper, n-butanol, and ethyl carbamate. *Ethyl carbamate* ($NH_2COOCH_2CH_3$) is formed mainly by the reaction of cyanogenic precursors with ethanol during fermentation and can be controlled through correct distillation practices [12].

Copper, for example, is used in the construction of stills due to its malleability, good thermal conduction, and corrosion resistance and because it improves the sensory aspects of *Cachaça* through reactions of wine compounds it catalyzes [13]. Thus, the copper concentrations in *Cachaça* are regulated by Brazilian legislation, with the maximum limit set at 5 mg/L [1].

The final quality of *Cachaça*, both chemical and sensory, is closely associated with all stages of production, particularly fermentation and distillation, as these stages present the highest risks for chemical contamination.

The purpose of this research was to determine the chemical composition of sugarcane spirits and commercial *Cachaças*, comparing them with the limits established by national legislation and with studies conducted in previous periods.

2. Materials and Methods

2.1. Sample Collection

In this research, we analyzed 531 samples of commercial *Cachaça* produced between 2021 and 2023. The number of samples of each brand varied between two and three units, depending on viability and availability.

2.2. Obtaining Samples

The technological scheme below (Figure 1) summarizes all the stages of the alembic *Cachaça* production process.

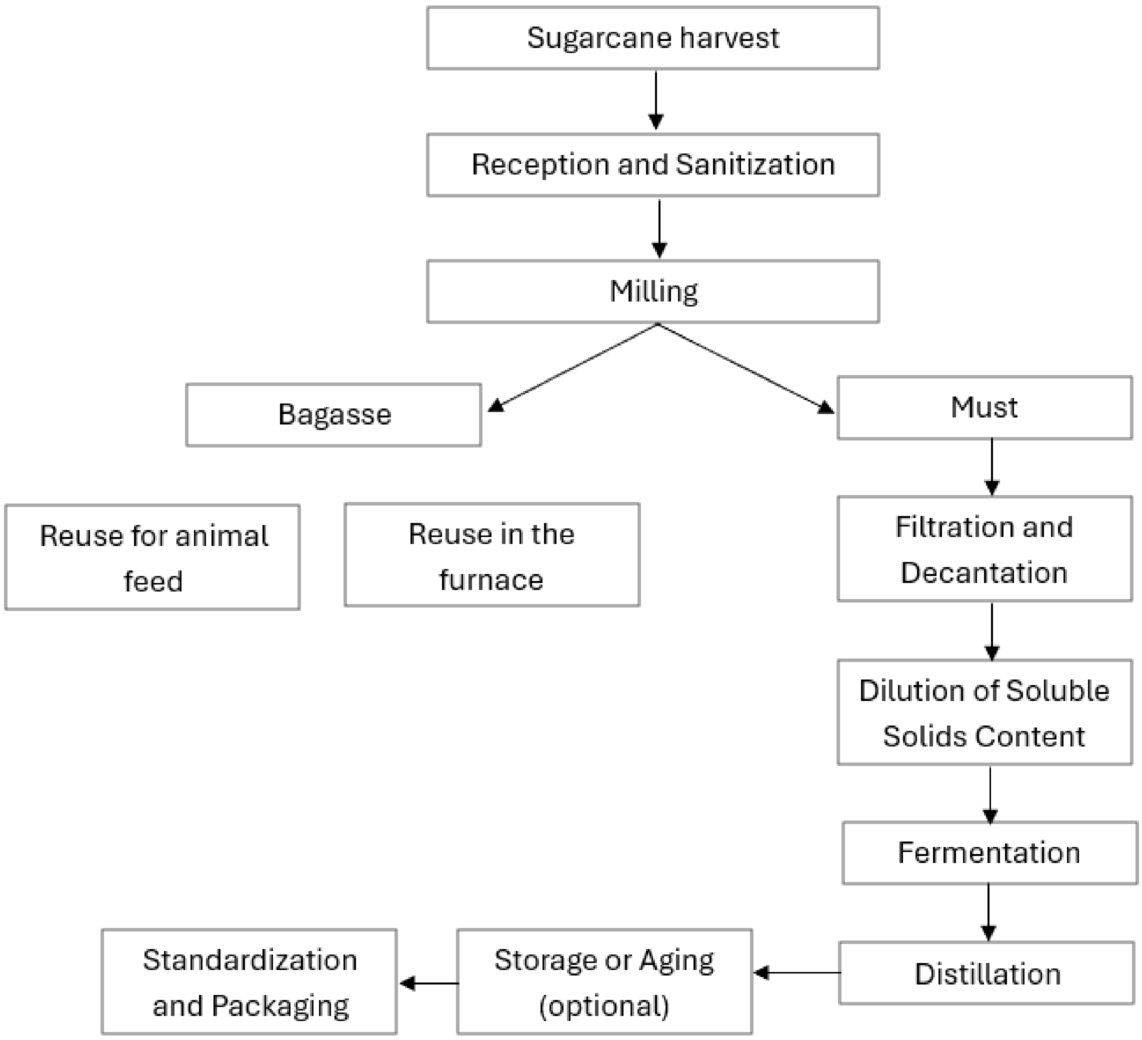

Figure 1. Flow chart of the production of *Cachaça* in an alembic. Source: Developed by the authors.

2.3. Analytical Methods

2.3.1. Gas Chromatography with Flame Ionization Detection (FID)

A Shimadzu GC 2010 Plus (Shimadzu Co., Kyoto, Japan) with automatic injection (1.0 µL) was used for gas chromatography with flame ionization detection (FID), together with a Stabilwax-DA column (polyethylene glycol carbowax crossbond, film thickness: 30 m × 0.18 mm × 0.18 µm). The carrier gas employed was N_2 released at 31.8 cm/s. Regarding the temperatures used, the injector was set to 220 °C and the column temperature to 35 °C (5 min); then, the temperature was increased to 220 °C (4 °C/minute) and maintained for 10 min. In turn, the detector temperature was set to 220 °C (FID). The compounds analyzed through this methodology were methanol, acetic acid, ethyl acetate, higher alcohols (iso-butanol, n-propanol, and isoamyl), acetic aldehyde, n-butanol, and 2-butanol. All analyses were performed in triplicate in a ratio of 1:25 [14]. An example of chromatograms for GC-FID analysis can be found in the Supplementary Materials of the present work (Figure S1).

2.3.2. Gas Chromatography with Mass Spectrophotometer (GC-MS)

An analysis of the compound ethyl carbamate was performed using the methodology developed by Alcarde et al. [15] in a gas chromatograph coupled to a mass spectrophotometer, model GCMS-QP2010 Plus from Shimadzu (Shimadzu, Kyoto, Japan), using monitoring acquisition of selected ions (m/z = 62) and a capillary chromatographic column with a polar phase (esterified polyethylene glycol-HP-FFAP; stationary phase film thickness: 49 m × 0.2 mm × 0.33 µm). The detector and injector interface temperatures were 240 °C and 230 °C, respectively. An example of chromatograms for GC-MS analysis can be found in the Supplementary Materials of the present work (Figure S2).

The temperature program used in the oven of the equipment is defined in Table 1.

Table 1. Temperature program according to the methodology designed and used in GC-MS.

Temperature	Length of Stay or Gradual Increase
90 °C	Permanence time for the first 2 min
150 °C	Increase at a rate of 10 °C/min until it reaches 150 °C
220 °C	Increase at a rate of 40 °C/min until it reaches 220 °C
220 °C	Permanence time over 2 min

Source: Prepared by the author based on the work by Alcarde et al. [15].

Helium gas released at 30.0 cm/s was used as carrier gas, and a 2.0 µL aliquot was injected using a splitless injection method [12]. Based on external analytical curves constructed from six standard concentration points, the quantification of the compounds analyzed using GC-MS and FID was performed. Both the detection limit and the quantification limit were calculated in accordance with Currie's work [16] based on the signal-to-noise ratio of the chromatograms (Table 2).

Table 2. Mean retention indices (RI), limit of detection (LD), limit of quantification (LQ) of volatile compounds and contaminant congeners, and concentration range and correlation coefficients (a, b, r^2) of the analytical curves in alcoholic solutions (40% alcohol by volume) for quantification of the compounds.

Compound	RI (min)	LD *	QL *	Concentration Range *	a	b	r^2
Volatile Congeners							
Acetic aldehyde	0.29	0.070	0.220	7.5–37.5	5.5900	−1.0200	0.9957
Ethyl acetate	1.41	0.057	0.171	12.5–62.5	2.8792	0.9075	0.9996
n-Propanol	4.43	0.038	0.114	37.5–187.5	2.0471	−0.2444	0.9999
Isobutanol	5.22	0.014	0.042	12.5–62.5	1.7260	−0.1724	0.9998
Isoamyl alcohol	6.72	0.016	0.048	50–250	1.6748	9.1053	0.9999
Acetic acid	19.15	0.530	1.590	37.5–187.5	5.4259	4.1160	0.9997
Contaminant congeners							
Metanol	1.62	0.092	0.276	5–25	4.1394	−0.1620	0.9997
sec-Butanol	4.02	0.049	0.180	2.5–12.5	1.9168	−5.1082	0.9998
n-Butanol	5.99	0.072	0.216	0.75–3.75	1.1168	−1.8596	0.9997
Ethyl carbamate	10.15	0.180	0.550	50–500	64.714	1241.67	0.9984

* Milligrams per 100 mL of anhydrous ethanol. Source: Adapted by the author based on the work of Bortoletto et al. [17].

2.3.3. Copper

The copper concentration of the samples was determined using a Pocket Colorimeter™ II, Copper (Hach Lange GmbH, Dusseldorf, Germany). This equipment allows the identification of the copper concentration in *Cachaça* by using a 10 mL aliquot of the distillate and adding the CuVer® reagent. This equipment is able to read copper concentrations up to 5 mg/L, the maximum level allowed by Brazilian legislation. If the concentration of the sample exceeds this value, the manufacturer's recommended dilution procedure is performed.

2.3.4. Alcohol Content

To determine the ethanol concentration, the samples were subjected to steam distillation using laboratory microdistillation equipment, followed by measurement with a digital hydrometer (DMA-4500, Anton-Paar GmbH, Graz, Austria) [1].

3. Results and Discussion

The chemical and sensory quality of *Cachaça* and sugarcane brandy are closely related to all stages of these products' manufacturing processes. Most chemical hazards arise during fermentation and/or distillation, making it difficult or impossible to remove hazardous contaminants from the final product after these steps [11]. However, it is possible to avoid the formation of these compounds with the implementation of good manufacturing practices (GMPs) and Hazard Analysis and Critical Control Points (HACCP) [11]. The use of good manufacturing practices in national distilleries is a fundamental tool for achieving safety levels appropriate for legislation.

Fermentation can be considered the most critical point in the production chain of sugarcane *Cachaça* and brandy since the composition of the must is vulnerable to microbiological contamination that directly affects the quality of the final product [18]. Thus, good practices that ensure proper hygiene and asepsis are essential to avoid contamination.

Fermentation is any process that decomposes and transforms a substrate through the action of living metabolisms, such as yeasts, bacteria, or fungi. In the case of alcoholic fermentation, yeasts are responsible for converting the sugar in the broth into ethanol, CO_2, and secondary compounds (congeners) [19].

In this case, the yeasts are inoculated after they are ground and the °Brix of the sugarcane juice [20] is adjusted, and they tolerate fermentation and microbial growth through their sugars (glucose, fructose, and sucrose) and nitrogenous material (peptides, amino acids, proteins, nucleic acids, and nitrogenous ions), as well as vitamins, organic acids, lipids, and inorganic elements (magnesium, phosphorus, potassium, magnesium, copper, manganese, zinc, and iron) [21].

Despite the predominance of the yeast Saccharomyces cerevisiae, bacteria and other yeast species naturally present in the environment and broth can also develop in the prepared yeast. Thus, due to the diversity of these microorganisms, this type of fermentation can be inconstant and impair the quality of *Cachaça* since this process is difficult to control [7].

Such microorganisms do not have good fermentative development for ethanol production and, in turn, can produce compounds such as acetic acid, esters, acetaldehyde, sec-butanol, n-butanol, and higher alcohols. High concentrations of these compounds can negatively influence the sensory characteristics of *Cachaça* and affect the safety of the final product, resulting in a failure to meet the Brazilian Standards of Identity and Quality [1].

Commercial yeasts are the most suitable option when it comes to better controlling fermentation [22,23], although some *Cachaça* producers prefer to use yeasts from the microbiota of sugarcane juice [9]. The commercial yeast strains for distillate production are isolated according to particular characteristics such as their fermentation rate, sugar consumption, flocculation, low acetic acid content, stress tolerance, high ethanol production, and content of desired aromatic compounds [23–25].

However, some studies show that the mixture of commercial yeasts and native yeasts can positively influence the sensory quality of *Cachaça*. Mixtures of *Saccharomyces cerevisiae* and non-*Saccharomyces* yeasts were evaluated with respect to their effects on fermentation performance and flavor and aroma regarding *Cachaça*. It was found that the mixture of *Pichia caribbica* and *Saccharomyces cerevisiae* improved fermentation and the product's sensory profile, in addition to increasing ethanol production [18,26]. In turn, *Saccharomyces cerevisiae* and *Meyerozyma caribbica* have been shown to increase the content of esters and higher alcohols [27].

The fermentation of *Cachaça* is carried out over several fermentation cycles in a process called "batches". The yeast *Saccharomyces cerevisiae* is predominant during this process;

however, such fermentations are easily contaminated by natural organisms in the environment. The very composition of sugarcane juice is also reflected in the different types of environmental yeast cells that play a key role in fermentation. The main environmental yeasts include *Saccharomyces*, *Schizosaccharomyces*, *Pichia*, *Debaryomyces*, *Kloeckera*, *Zygosaccharomyces*, and *Candida* [22].

The presence of bacteria in sugarcane juice is also responsible for the conversion of sugar and ethanol into acetic acid and lactic acid [18]. These acids may be associated with the formation of volatile compounds, although there is still no concrete evidence for this [22].

After fermentation is complete, the wine is produced and immediately sent for distillation to prevent contamination by bacteria and secondary fermentations that consume the ethanol and form undesirable byproducts. The purpose of this stage is to separate, concentrate, and select compounds from the previous stages based on their different boiling and solubility temperatures.

Distillation consists of heating a liquid until it vaporizes, followed by the selective collection of its condensed vapors through cooling. This process results in the separation of volatile components, increasing the alcohol concentration and allowing purification by the reducing congeners and contaminating components of the distillate [13,28].

Quality *Cachaça* can be produced in both stills and distillation columns. However, due to the inherent characteristics of the production process, the chemical composition of each distillate will vary according to the process used. Usually, distillates produced in copper stills have a higher congener content compared to those produced through continuous distillation [7].

During distillation in copper stills, the distillate is separated into three different fractions. The first fraction, known as the "head", is collected at the beginning of distillation and corresponds to 1 to 2% of the boiler's useful volume. This fraction contains the most volatile and ethanol-soluble compounds with low boiling points, such as methanol, ethyl acetate, and acetaldehydes. The second fraction, called the "heart", is collected after the separation of the "head" and until the alcohol content of the liquid at the condenser outlet reaches 38 to 40% v/v, resulting in a final alcohol content of the heart fraction between 42 and 48%. The "heart" fraction is used to produce *Cachaça*. The final fraction, known as the "tail", is collected until the distillate at the condenser outlet is free of ethanol. In this fraction, the least volatile and most-water-soluble compounds are concentrated, such as acetic acid and 5-hydroxymethylfurfural [7,18,29,30].

Column distillation is the most common type of distillation in medium and large distilleries. In this case, there is no separation of distillate fractions, and therefore the process is called continuous. The column is fed with wine, and the distillate is released simultaneously throughout the process [31].

In order to chemically differentiate *Cachaças* produced in stills from those produced in columns and contribute to the classification of the national distillate, the authors of [32] carried out a study with samples collected at the time of distillation, which were analyzed using chemometric techniques. In this study, it was found that the *Cachaça* samples distilled in columns presented higher concentrations of ethyl carbamate (EC) and benzaldehyde (BenzH). In contrast, the samples distilled in stills presented mainly higher median values of copper (Cu) and acetic acid (HOAc).

According to the literature, one of the factors that can influence the low concentration of ethyl carbamate in *Cachaças* distilled in stills is the effect of the geometry of the equipment used, combined with the temperature control and reflux rate, since this equipment is often operated with high reflux rates, low distillation temperatures (<80 °C), and low yields, conditions with a tendency to reduce the levels of this contaminant [33].

In turn, the higher levels of benzaldehyde in *Cachaças* distilled in columns are directly related to the fact that the distillate is not separated into the head, heart, and tail fractions, as occurs in still production. Studies show that benzaldehyde is found in higher concentrations in the tail fraction, suggesting that it should be transported via steam distillation in column distillation [32].

Consistent with the material used to produce stills, the samples with the highest concentration of copper came from distillation in this type of equipment [32].

The volatile components of wine (ethanol, higher alcohols, acetic acid, aldehydes, esters, and methanol) have different boiling temperatures and can be totally or partially separated during distillation. Intuitively, the lower the boiling temperature of the compound, the greater the tendency for it to be distilled at the beginning of the process [7]. Another factor influencing wine distillation, besides the boiling temperature of the components in their pure state, is the preferential solubility of a substance in ethanol within alcoholic vapor [7].

Since the publication of Ordinance No. 539 of 26 December 2022, which refers to the Standard of Identity and Quality of Sugarcane Spirit and *Cachaça* as set by the Ministry of Agriculture, Livestock, and Supply (MAPA), the Government recognizes and classifies the production of still *Cachaça* as a traditional practice and part of traditional culture and, consequently, its chemical and sensory differentiation from column *Cachaça*. Thus, the ordinance establishes that *Cachaça* must be produced exclusively in a copper still and obtained from the distillation of the fermented must of raw sugarcane juice [1].

In order to determine the distribution pattern of the concentration ranges of each sample, each analyzed compound was assorted into four concentration ranges (Table 3). In Table 3, it can be observed that the levels of the majority (>90%) of volatile compounds and contaminants not only comply with the current Brazilian legislation but also fall well below the established limits.

Regarding volatile compounds, 90.97% of the samples are present in a range below 100 mg/100 mL of anhydrous ethanol, 95.93% of the aldehydes in acetic acid are present below 20 mg/100 mL of anhydrous ethanol, 99.52% of esters are present at levels below 100 mg/100 mL of anhydrous ethanol, 81.57% of furfural is below 1 mg/100 mL of anhydrous ethanol, 88.05% of upper alcohols are present at levels below 300 mg/100 mL of anhydrous ethanol, and 90.6% of the samples are within the allowable range for the congener coefficient.

For the contaminants analyzed in the present study, we also found satisfactory results for at least 90% of the samples. In relation to copper, 96.07% of the samples were in accordance with the limits (5 mg/L), with the contaminant levels for 75.62% of the samples being below 2 mg/L. Regarding ethyl carbamate, 94.64% of the samples presented levels complying with the legislation (210 µg/L), with 83.14% exhibiting levels below 150 µg/L. Regarding N-butyl alcohol, sec-butanol alcohol, and methyl alcohol, 99.8%, 91.4%, and 99% of the samples, respectively, presented levels complying with the maximum limit of the legislation.

Based on the data collected from the 531 samples analyzed between January 2021 and October 2023, it is possible to observe the percentage of each sample that is within or outside the limits established by the legislation (Figure 2).

Figure 2 shows that 100% of the samples analyzed met the Standards of Identity and Quality of *Cachaça* and Sugarcane Brandy concerning esters and n-butyl alcohol. For furfural, aldehydes in acetic acid, and ethyl alcohol, 99% of the samples were compliant with the established standards.

It is also possible to observe (Figure 2) that the other analyzed compounds were, in the vast majority, within the limits established: volatile acidity (97%), copper (96%), higher alcohols (96%), ethyl carbamate (95%), alcohol grade (94%), sec-butanol (91%), and congener coefficient (91%).

The volatile congeners (acetic acid, esters, acetaldehyde, sec-butanol, n-butanol, and higher alcohols) produced during fermentation can only be measured in the final product. Therefore, preventive measures must be implemented during this process and, if necessary, corrective measures during the distillation process.

Table 3. Samples of *Cachaça* that were within the concentration range regarding each compound analyzed and the total number of samples of each compound.

Compound	Percentage of Samples within Concentration Ranges				Samples in Non-Compliance with Brazilian Legislation	Total Number of Samples
Alcohol content at 20 °C [a]	<38	38–<42	42–<48	>49	<38 or >48	527
	5.88	17.49	76.66	0	5.88	
Volatile congeners						
Volatile acidity (acetic acid) [b]	<100	100–<150	150–<200	>200	>150	527
	90.97	5.73	1.19	2.11	3.3	
Aldehydes (acetic aldehyde) [b]	<20	20–<30	30–<40	>40	>30	521
	95.93	3.07	0.58	0.42	1	
Esters (ethyl acetate) [b]	<100	100–<200	200–<300	>300	>200	521
	99.52	0.38	0.1	0	0.1	
Furfural [b]	<1	1–<5	5–<10	>10	>5	521
	81.57	17.43	0.62	0.38	1	
Higher alcohols [b]	<300	300–<360	360–<420	>420	>360	522
	88.05	7.85	2.18	1.92	4.1	
Coefficient of congeners [b]	<200	200–<650	650–<700	>700	<200 or >650	521
	8.44	90.6	0.19	0.77	9.4	
Contaminants						
Copper [c]	<2	2–<5	5–<7	>7	>5	484
	75.62	20.45	1.24	2.69	3.93	
Ethyl-Carbamate [d]	<150	150–<210	210–<300	>300	>210	391
	83.14	11.5	2.04	3.32	5.37	
N-butyl alcohol [b]	<1	1–<3	3–<5	>5	<3	521
	98.46	1.34	0.2	0	0.2	
Alcohol sec-butanol [b]	<5	5–<10	10–<20	>20	<10	521
	86.41	4.99	1.7	6.9	8.6	
Methyl alcohol [b]	<10	10–<20	20–<30	>30	<20	521
	96.7	2.3	0.81	0.19	1	

[a]:% ethanol (v/v) a 20 °C. [b]: mg/100 mL of anhydrous ethanol. [c]: mg/L. [d]: µg/L. Source: Developed by the authors.

Methanol is also produced during the fermentation process, making it a highly toxic and undesirable substance. According to Moreira et al. [34], this compound is generated by the action of pectic yeasts, present in the juice due to sugarcane bagasse particles.

The “head” fraction of *Cachaça* has the highest concentration of this highly volatile compound and can be controlled with the correct “cutting” and separation of this fraction from the final product or by using double distillation (bidistilled *Cachaça*) [10].

The volatile acidity of *Cachaça* is measured according to the concentration of acetic acid in the final product and comes from the presence of acetic bacteria competing with fermentative yeasts, increasing the sensory acidity of the product [10]. High levels of acidity are one of the main reasons for consumers’ rejection of the sensory quality of the distillate.

The main preventive measures used for the containment of acetic bacteria during fermentation consist of the correct cleaning of the grinding and fermentation utensils before and after use, in addition to the correct cutting of the “tail” fraction. As a remedial measure for excessive acidity, bidistillation is also a good alternative for removing the excess acetic acid from *Cachaça*.

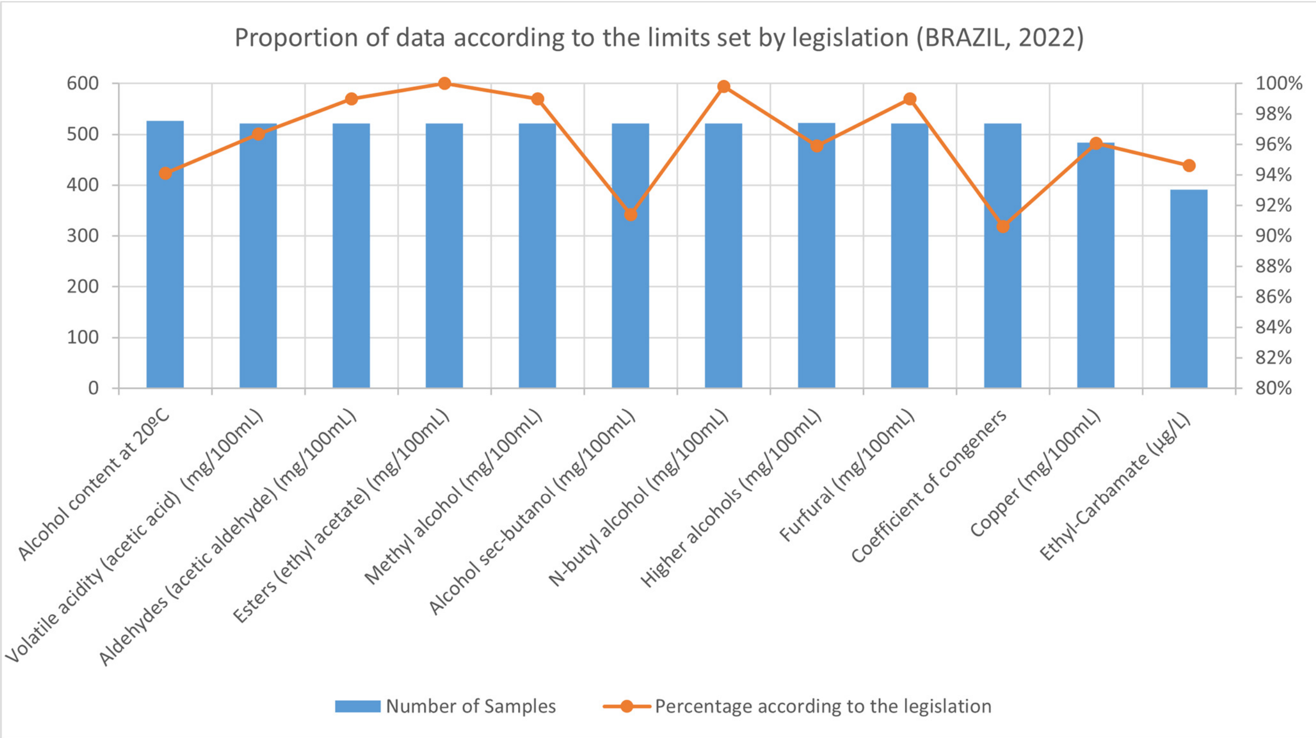

Figure 2. Graph of data proportions according to the limits established by the legislation. Source: Developed by the authors.

The higher alcohols n-propyl, isobutyl, and isoamyl are also produced by yeasts during fermentation. They are responsible for the sensory characterization of *Cachaça* and can also impart negative characteristics when present in excess. Control measures include maintaining the fermentation temperature within appropriate parameters, using suitable yeasts, maintaining a pH $\geq$ 4.0, avoiding excessive oxygenation in the fermentation vats, and reducing the wait time between the end of fermentation and the beginning of distillation. These compounds are impossible to remove, and in extreme cases, batch disposal is highly recommended [10].

Regarding the distillation process, when distilled in stainless steel, *Cachaças* can present sensory defects due to the absence of copper in the distiller. These defects are related to the presence of sulfur compounds in the beverage, particularly dimethylsulfide (DMS), which is often responsible for the unpleasant sulfide odor in food and beverages. The Cu^{2+} ion catalyzes the conversion of sulfides to sulfates, reducing the pungency of the unpleasant odor [7].

However, if good manufacturing practices are not adopted, copper can contaminate distilled spirits during distillation. The dissolution of holm oak, present in the internal parts of the equipment, and its subsequent loading by alcohol and acid vapor lead to the contamination of the final product. High levels of copper are harmful to human health, and therefore the limit of this compound is established by law at a maximum of 5 mg/L^{-1} [1,35].

As mentioned, sugarcane contains 0.06 mg of copper/L in its juice, used by the yeast during the fermentation process. This cation acts as an essential cofactor for enzymes, being fundamental for the metabolism of yeasts during iron homeostasis [36]. However, this copper does not interfere with the copper content of *Cachaça* since it remains in the "tail" fraction after distillation [9].

As a preventive measure, it is recommended that when the equipment is not in use, it should be kept with the coils full of water, as the water reduces the oxidation of copper, the formation of holm oak, and the consequent contamination of *Cachaça*. The first distillation, after an interval in the dry season, should be carried out with a solution of 2% acetic acid, as this acidity promotes the removal of the holm oak in the equipment. As an option for producers who do not have access to commercial solutions, a solution with vinegar or citric acid can also be used for the first distillation.

Thus, there was a significant increase in the number of samples within the limits established by the legislation compared to previous studies [17,37,38], as can be observed in Table 4.

Table 4. Comparison between samples that do not comply with current legislation [1].

Compounds	Non-Conforming Samples Present Study	Non-Conforming Samples	Non-Conforming Samples	Non-Conforming Simples
Esters	0%	1.5%	6,4%	-
N-Butil alcohol	0.2%	7.7%	-	-
Furfural	1%	2.1%	-	-
Aldehydes	1%	6.3%	17%	-
Volatile acidity	3.3%	16,4%	8.5%	-
Higher alcohols	4.1%	25.7%	4.3%	-
Copper	3.9%	26.2%	14.9%	7%
Ethyl carbamate	5.4%	39.1%	-	-
Sec-butanol alcohol	8.6%	12.5%	-	-
Coefficient of congeners	9.4%	6.1%	8.5%	-
Alcohol content	5.8%	4.9%	9.6%	21%

Source: Prepared by the author based on Bortoletto and Alcarde [17], Labanca et al. [38], and Miranda et al. [37].

Specifically in relation to the contaminant ethyl carbamate, it is also possible to observe advances regarding legal compliance over the years (Figure 3). In 2002, about 80% of the *Cachaças* and spirits analyzed did not meet the Standards of Identity and Quality for this beverage. Halfway through the period, in 2016, 27.8% of the samples analyzed exceeded the permitted limits. In the present study, another significant reduction was observed, with only 5% of the samples analyzed having ethyl carbamate concentrations above 210 μg/L.

Ohe et al. [39] observed a strong correlation between the presence of urea in the fermentation juice and the concentrations of ethyl carbamate in the resulting sugarcane brandy. It is possible that the supplementation of sugarcane juice with urea increases the concentration of this contaminant in *Cachaça* [11,40–43].

The formation of ethyl carbamate is also associated with the raw material and the fermentation and distillation processes [41,44,45].

Brazilian legislation stipulates a limit of 210 μg for the ethyl carbamate content in *Cachaça* [1]. At the international level, several countries do not have this threshold parameter in their respective food and distilled beverage legislations [46]. The European Union, in 2007, carried out a risk assessment of the limit concentration of ethyl carbamate in distilled beverages and subsequently approved a limit of up to 1000 μg in distilled stone-fruit beverages, which are more susceptible to containing high concentrations of this compound, with redistillation being recommended in case of higher levels [47,48].

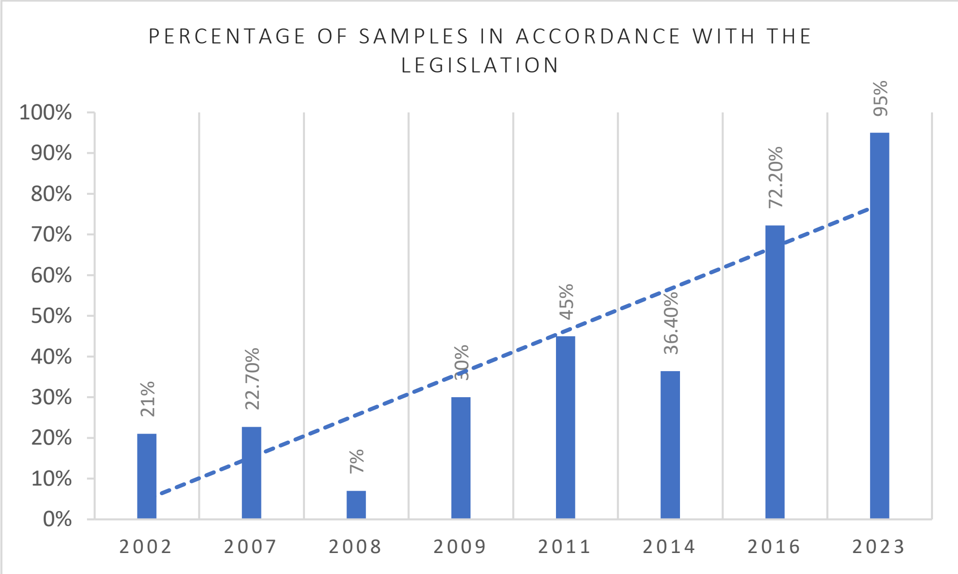

Figure 3. Evolution of the percentage of *Cachaças* and sugarcane spirits that fail to meet the Brazilian legislation in relation to ethyl carbamate over the years. Source: This material was prepared by the authors based on the work conducted by Andrade-Sobrinho et al. [49], Baffa Júnior et al. [50], Labanca et al. [51], Nóbrega et al. [52], Nóbrega et al. [53], Masson et al. [54], and Bortoletto and Alcarde [55].

Ethyl carbamate ($H_2NCOOC_2H_5$) belongs to the group of organic compounds classified as ethyl esters of carbamic acid ($H_2NCOOCH$) and has been the subject of constant research aimed at its quantification, characterization, and application due to its toxicity [30,56].

This contaminant can be found in fermented foods and beverages, such as yogurts, cherries in syrup, bread, tequila, beer, whiskey, rum, brandy, and *Cachaça*. *Ethyl carbamate* can be present in *Cachaça* due to several factors or processes, ranging from the raw materials used in the distillate to the storage methods employed.

The presence of these chemical contaminants in *Cachaça* and other distillates raises safety concerns related to this beverage's consumption, in addition to making it difficult to export *Cachaça* to other countries. The standardization of *Cachaça* is a crucial aspect in terms of allowing it to become a globally recognized and consumed spirit, like rum.

4. Conclusions

The quality of *Cachaça* and sugarcane brandy involves two main factors: ensuring sensory quality, with characteristics that please the consumer, and ensuring chemical quality, so that it does not pose risks to health. Of the 531 samples of commercial *Cachaça* and brandy analyzed between 2021 and 2023, more than 90% met the legal parameters of identity and quality.

Among the compounds analyzed, esters, n-butyl alcohol, furfural, and aldehydes were present within the limits established by Brazilian legislation in 99% of the samples. Volatile acidity, higher alcohols, copper, ethyl carbamate, sec-butanol, congener coefficient, and alcohol content were within the allowed limits in 91 to 97% of the analyzed samples.

The results obtained demonstrate that Brazilian producers understand the importance of implementing good manufacturing practices during the production process and do so satisfactorily, ensuring high standardization of this beverage when compared to previous studies. The increase in consumption of Brazilian distillates and the growth in exports in the coming years depend closely on quality and compliance with legislation, reflecting a positive scenario for the coming years.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/beverages10030079/s1, Figure S1: Examples of chromatograms for GC-FID analysis; Figure S2: Examples of chromatograms for GC-MS analysis.

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