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Avaliação de compostos tóxicos e parâmetros de qualidade em aguardente de cana envelhecida

Evaluation of toxic compounds and quality parameters on the aged Brazilian sugarcane spirit

Evaluación de compuestos tóxicos y parámetros de calidad en aguardiente de caña envejecida

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Resumo

A aguardente de cana típica brasileira, denominada "cachaça", é uma bebida conhecida e comercializada em todo o mundo. Sua popularização mundial se deu por conta da bebida chamada caipirinha, onde a cachaça é utilizada como um de seus principais ingredientes. Surge assim, uma preocupação crescente com a sua qualidade. Dentre os fatores limitantes da qualidade da cachaça, do ponto de vista da segurança alimentar e da adequação ao comércio e exportação, a presença de compostos tóxicos é um dos mais importantes. Alguns compostos tóxicos podem estar presentes na cachaça por contaminação ou formação durante as etapas de produção. Com o objetivo de investigar a presença de alguns desses compostos nas cachaças da Bahia, foram coletadas e analisadas 27 amostras de cachaças envelhecidas e analisadas quanto à sua identidade e padrões de qualidade. Para esse fim, análises de parâmetros de qualidade em relação ao teor de álcool, acidez, cobre, furfural, metanol, carbamato de etila, álcoois superiores, butan-1-ol e butan-2-ol. Em relação aos padrões de qualidade, enquanto 74,1% das amostras não estavam em conformidade com o limite estabelecido por lei no que diz respeito ao conteúdo de compostos tóxicos como cobre, furfural ou carbamato de etila. O conhecimento da qualidade da cachaça brasileira é de grande importância para o seu reconhecimento, uma vez que é comercializado em todo o país com crescente inserção no mercado internacional.

Palavras-chave: Bebida destilada; Contaminates; Carbamato; Cachaça.

Abstract

The typical Brazilian sugarcane spirit, called "cachaça", is a drink known and marketed throughout the world. Its worldwide popularity was due to the drink called caipirinha, where cachaça is used as one of its main ingredients. Thus, there is a growing concern with its quality. Among the limiting factors for the quality of cachaça from the point of view of food security and suitability for trade and export, the presence of toxic compounds is one of the most important. Some toxic compounds may be present in the cachaça through contamination or formation during the production stages. Aiming to investigate the presence of some of these compounds in cachaças from Bahia, twenty-seven samples of aged cachaças were

collected and analyzed regarding their identity and quality standards. For this purpose, analyzes of quality parameters in relation to alcohol content, acidity, copper, furfural, methanol, ethyl carbamate, higher alcohols, butan-1-ol, and butan-2-ol. Regarding the quality standards, while 74.1% of the samples were not in conformity with the limit established by the law concerning the contents of toxic compounds such as copper, furfural, or ethyl carbamate. Knowledge on the quality of Brazilian cachaça is of great importance for its recognition, since it is marketed throughout the country with growing insertion into the international market.
Keywords: Distilled beverage; Contaminants; Carbamate; Cachaça.

Resumen

La aguardiente de caña típica brazileña, llamada "cachaça", es una bebida conocida y comercializada en todo el mundo. Su popularidad mundial se debió a la bebida llamada caipirinha, donde la cachaça se usa como uno de sus ingredientes principales. Por lo tanto, existe una creciente preocupación por su calidad. Entre los factores limitantes de la calidad de la cachaça, desde el punto de vista de la seguridad alimentaria y la idoneidad para el comercio y la exportación, la presencia de compuestos tóxicos es uno de los más importantes. Algunos compuestos tóxicos pueden estar presentes en el espíritu por contaminación o formación durante las etapas de producción. Para investigar la presencia de algunos de estos compuestos en las cachaças en Bahía, se recolectaron 27 muestras de cachaças envejecidas y se analizaron sus estándares de identidad y calidad. Para este propósito, análisis de parámetros de calidad en relación con alcohol, acidez, cobre, furfural, metanol, carbamato de etilo, alcoholes superiores, butan-1-ol y butan-2-ol. En cuanto a los estándares de calidad, mientras que el 74.1% de las muestras no cumplían con el límite establecido por ley con respecto al contenido de compuestos tóxicos como cobre, furfural o carbamato de etilo. El conocimiento de la calidad de la cachaça brasileña es de gran importancia para su reconocimiento, ya que se vende en todo el país con una inserción cada vez mayor en el mercado internacional.
Palabras clave: Bebida destilada; Contaminantes; Carbamato; Cachaza.

1. Introduction

The Brazilian beverage called "cachaça" is a sugarcane spirit, also known as aguardente, pinga, branquinha, and caninha. This is an importante beverage, produced exclusively in Brazil and known internationally (Fernandes et al., 2019). It was popularized around the world, recently, because of its use in the drink, *caipirinha*, which is one of the official cocktails of the International Bartenders Association (IBA, 2015).

It defined that cachaça is the typical and exclusive denomination of the sugarcane spirit produced in Brazil, with an alcohol content between 38 and 48% v/v at 20ºC. Cachaça is obtained from the distillation of the fermented wort of the sugarcane juice with peculiar sensorial characteristics, and it may also include the addition of up to $6g.L^{-1}$ of sugars, expressed as sucrose (Brasil, 2005a). Cachaça is usually aged in wooden barrels to increase its sensory characteristics and add value, just like with other distilled beverages.

The production process of cachaça involves various stages, fermentation (Cardoso, 2013; Vilela et al., 2007; Schwan et al., 2013), destilltion (Cardoso, 2013), to the marketing of the final product, with or without aging (Faria et al., 2003; Santiago et al., 2016). Masson et al. (2007), from the raw material, the sugarcane. Inappropriate production practices, coupled with the complexity of the cachaça matrix compromise the product quality and favor the appearance of organic and inorganic contaminants, which are frequently found in the beverage and demand great attention due to its toxicity, as well as loss of quality. Aging process to improve the characteristics of cachaça can cause the emergence of toxic compounds, as well as in the production of other alcoholic beverages, organic and inorganic contaminants that generate great concern, as they bring many damage to health (García et al., 1999; Roses et al., 1997; Riachi et al., 2014; Milani et al., 2017).

Methanol, furfural and hydroxymethylfurfural, ethyl carbamate, copper, and butan-1-ol and butan-2-ol are the most important contaminants among the toxic compounds found in Brazilian cachaça from the point of view of food security and non-compliance with the minimum values established by current legislation. This is confirmed by the literature (Bortoletto and Alcarde, 2015; Cardoso et al., 2012; Santiago et al., 2016), which points out the large number of samples not in compliance with the legislation and that may affect product acceptance in the internal market and exports, as well as posing a risk to consumer health. These studies point to problems in samples from Minas Gerais and other Brazilian states.

In order to standardize and establish quality criteria for this typical Brazilian drink, it was established on June 29, 2005, the Normative Instruction No. 13 of the Ministry of Agriculture, Livestock and Supply where was approved the "Technical Regulation for the Establishment of Identity and Quality Standards for Sugarcane Spirit and Cachaça” The quality parameters of cachaça according to the Brazilian legislation (Brasil, 2005a). Are sensory characteristics (clear and free of impurities), alcohol content (minimum 38 and maximum 48% v.v^{-1}), volatile acidity ($\leq$ 150 mg.100 mL^{-1}) and higher alcohols ($\leq$ 360 mg.100 mL^{-1}). Limits were established for the contaminants copper ($\leq$ 5 mg.L^{-1}), furfural ($\leq$ 5 mg.100 mL^{-1}), methanol ($\leq$ 20 mg.100 mL^{-1}), ethyl carbamate ($\leq$ 210 µg.L^{-1}), butan-1-ol ($\leq$ 3 mg.100 mL^{-1}) and butan-2-ol ($\leq$ 10 mg.100 mL^{-1}), focusing on copper and ethyl carbamate which, in the case of export products, should comply with the maximum limits of 2 mg.L^{-1} and 210 µg.L^{-1}, respectively, by the Health and Welfare Department (Brasil, 2005a).

However, given the large extent of the Brazilian territory and the large number of producers of this drink in the country, studies that evaluate the quality of cachaças produced in the most diverse regions of Brazil, with a large number of samples, are extremely important.

That said, this study aimed to assess patterns of identity and quality, with emphasis on toxic compounds, of aged cachaças produced in the state of Bahia.

2. Methodology

Sample collection

Twenty-seven samples of different brands of aged cachaça produced and marketed in the state of Bahia/Brazil were evaluated, all of them registered at the Ministry of Livestock and Supply. The samples were purchased from retailers in different cities of the state of Bahia.

Physicochemical analysis

Alcohol content

Alcohol content was determined by densitometry and expressed as % by volume. The samples were redistilled and the alcohol content was measured at 20 °C using a DensiMat Gibertini digital densimeter (Brasil, 2005b).

Volatile acidity

Volatile acidity was determined by volumetric neutralization titration. The volatile acids were extracted from the beverage by steam trapping using an Enochimico Gibertini Electronic

Distiller. The acids were titrated with 0.1 mol.L^{-1} sodium hydroxide in the presence of 1% phenolphthalein. The results were expressed as acetic acid (mg.100 mL^{-1}) (Brasil, 2005b).

Higher alcohols

The total amount of higher alcohols was determined by colorimetric reaction and the quantification was performed in a spectrophotometer (Shimadzu UV-160-1PC) at 540 nm. Concentrations were determined by constructing analytical solution curves of higher alcohols diluted in 1:1 water/ethanol. The total amount of these compounds was expressed as milligrams per 100 mL of anhydrous alcohol (Brasil, 2005b).

Methanol, butan-1-ol and butan-2-ol

Methanol, butan-1-ol and butan-2-ol were determined by gas chromatography (GC) using a Shimadzu (GC-2010) gas chromatograph model C113245 with automatic injector.

The methodology used for the quantification of these compounds in the samples was according to Vilela et al. (2007) with modifications. The conditions of the chromatographic analysis were: DB Wax column (30 m x 0.25 mm, 0.25 μm), Split 1:10, initial oven temperature of 55 °C and column flow of 1.4 mL/min. The temperatures of the injector was 150 °C and the detector was 170 °C. The temperature rate was 1 °C/min from 55 °C to 70 °C, for 16 min. Compounds were identified by comparing the retention time of the samples with the specific standards for determination of methanol, butan -1-ol, butan-2-ol, and higher alcohols, which were represented by the sum of isobutyl, isoamyl, and propyl alcohols.

Copper

Copper quantification was performed by spectrophotometry using a Shimadzu UV - 160-1PC spectrophotometer in the visible region of the spectrum at 546 nm according to the methodology described in the Operational Manual on Drinks and Vinegars of Normative Ruling No. 24 of 08/09, MAPA. The results were compared with absorbance values of a previously constructed analytical curve using copper sulphate as the primary standard. The colorimetric reactions were carried out on the samples of cachaças without redistillation. The results were expressed as mg.L^{-1} of the sample (Brasil, 2005b).

Furfural

Furfural was quantified by spectrophotometry using a Shimadzu UV -160-1PC spectrophotometer in the visible region of the spectrum at 520 nm, by comparing the absorbances observed in the beverage samples with absorbance values of an analytical curve constructed with standard solutions of ethanol/furfural. The results were expressed as mg.100 mL^{-1}. For this analysis, the alcohol content of the distillate was corrected to 50% v v^{-1} (Brasil, 2005b).

Ethyl carbamate

Samples were analyzed for ethyl carbamate in a gas chromatograph coupled with a Shimadzu QP-5050A mass detector, using electron impact (70 eV) as the ionization source. A chromatography capillary column with polar phase of polyethylene glycol DB-WAX (60 m x 0.25 mm x 0.50 µm) was used. The injector and detector interface temperatures were both 220 °C. The following oven temperature program was used: starting with 90 ◦C for 2 min, increasing to 150 ◦C at a rate of 10 ◦C /min followed by heating to 230 ◦C at a rate of 40 ◦C /min, and hold for 10 min. An aliquot of 2.0 µL was injected using the splitless injection mode. Helium (5.0) was used as the carrier gas at a flow of 1.5 mL min^{-1}. SIM acquisition mode was used to monitor the ions m/z 62, 74 and 89 (Baffa-Júnior et al., 2011).

The quantification was performed by comparing the chromatographic results of the cachaça samples with an analytical curve constructed using a stock solution of ethyl carbamate (New Química®), 99%, 2.0 mg mL^{-1} in ethanol:water (40: 60 v/v). Dilutions were performed to cover the concentration range 0.005 - 1.0 mg.L^{-1}. The linear equation was: $y = 1547x + 65205$ and $R^2 = 0.992$, where y is the area of the chromatographic peaks and x the concentration of ethyl carbamate in µg.L^{-1}.

3. Results and Discussion

Table 1 shows the results of the physico-chemical quality standards of aged cachaça. The alcohol content of samples 11 and 20 (37.26 ± 0.02 and 37.86 ± 0.02), respectively, was lower than the minimum limit specified by the current Brazilian legislation and, therefore, these cachaças do not meet the standards required by law (minimum of 38 and maximum of 48% v.v-1). The alcohol content is one of the most important parameters, as it characterizes the spirit. Several cachaça components have their concentrations modified during aging because of the partial evaporation of ethanol and water, with alcohol losses around 3 to 4% per year (Zacaroni et al., 2011). Parazzi et al. (2008) found that the alcohol content varied over a period of two years for aged cachaças stored in wood and glass. Miranda et al. (2007) identifies two causes for the low alcohol content. These are: possible errors and inaccuracies in the equipment used by producers in determining the alcohol content and possible errors in performing the distillation or dilution, which directly affect the amount of alcohol in cachaça.

Table 1. Physico-chemical quality parameters of the Bahian cachaça samples.

Sample	Acohol content[1]	Volatile acid. (acetic ac.)[2]	Higher alcohols*[2]
1	41.50 ± 0.09	45.11 ± 4.40	177.5 ± 1.66
2	40.62 ± 0.01	40.62 ± 1.28	172.28 ± 1.75
3	41.57 ± 0.01	38.79 ± 0.99	178.02 ± 1.53
4	45.82 ± 0.02	33.33 ± 0.48	194.00 ± 1.78
5	43.73 ± 0.02	35.57 ± 0.30	197.23 ± 0.54
6	44.34 ± 0.03	33.98 ± 0.52	191.00 ± 0.85
7	40.67 ± 0.01	53.89 ± 0.91	163.11 ± 1.99
8	41.13 ± 0.02	49.99 ± 0.49	174.53 ± 1.83
9	41.36 ± 0.02	51.85 ± 0.53	167.45 ± 1.77
10	39.40 ± 0.00	161.72 ± 4.30	162.15 ± 1.55
11	37.26 ± 0.02	191.73 ± 6.16	54.32 ± 0.35
12	39.04 ± 0.02	60.54 ± 2.47	189.2 ± 1.30
13	41.07 ± 0.03	27.32 ± 0.66	260.66 ± 1.89
14	41.60 ± 0.04	25.92 ± 2.11	262.03 ± 1.60
15	41.68 ± 0.04	26.13 ± 0.32	259.53 ± 4.79
16	38.60 ± 0.03	142.26 ± 2.61	189.91 ± 1.52
17	38.73 ± 0.01	145.46 ± 0.84	190.81 ± 2.63
18	39.01 ± 0.01	146.84± 1.16	193.44 ± 0.03
19	39.14 ± 0.01	21.91 ± 2.71	237.16 ± 0.82
20	37.86 ± 0.02	19.97 ± 0.17	227.75 ± 3.45
21	38.46 ± 0.06	19.42 ± 0.11	236.96 ± 0.82
22	39.79 ± 0.00	51.39 ± 3.18	166.63 ± 4.52
23	40.33 ± 0.06	53.31 ± 3.98	186.44 ± 3.53
24	41.18 ± 0.02	80.60 ± 0.47	190.51 ± 1.27
25	38.61 ± 0.02	67.21 ± 0.73	216.45 ± 1.19
26	40.36 ± 0.01	59.67 ± 1.82	220.89 ± 1.77
27	38.84 ± 0.02	66.65 ± 0.40	215.87 ± 0.76

[1] (% v/v 20 °C); [2](mg.100 mL^{-1} of anhydrous alcohol); *Higher alcohols = isobutyl + isoamylic + propyl (Gas Chromatography). The results highlighted do not comply with the standards of identity and quality of cachaça regulated by the Normative Instruction No. 13 of June 29, 2005.

Losses along the aging process may also occur due to the storage in wooden barrels and environmental conditions or by acid-ethanol esterification reactions during storage

(Cardoso, 2013; Miranda et al., 2008; Zacaroni et al., 2011). Losses throughout the aging process can be mitigated by storing the spirit at low temperature and higher humidity.

The volatile acidity of samples 10 and 11 was 161.72 ± 4.30 mg.(100 mL a a)$^{-1}$ and 191.73 ± 6.16 mg.(100 mL a a)$^{-1}$ respectively, showing no compliance with the law, which establishes the maximum limit of 150.0 mg of acetic acid.100 mL of anhydrous alcohol^{-1}. Cardoso (2013) and Vilela et al. (2007) argued that high volatile acidity may be related to efficient control of time and temperature of fermentation. Handling of wort and proper sanitation are production factors that, when well controlled, can minimize high acidity values.

The acidity of cachaça depends mainly on the control of the fermentation process, including the strain predominant in the cachaça yeast (*pé-de-cuba*), fermentation purity, time and temperature of fermentation, handling of both the wort and the sugarcane harvested. Wort aeration should be avoided because the increase of oxygen in the medium induces oxidative cell metabolism and carbohydrates are oxidized during yeast respiration leading to cell multiplication and production of acetic acid instead of ethanol, decreasing the spirit yield and consequently increasing acidity (Schwan et al., 2013). It can be inferred that the cachaça samples analyzed are aged, and a significant increase in acidity may also occur in these samples stored in wood barrels, since some wood compounds such as non-volatile organic acids and other secondary matabolites (tannins and phenolic compounds) favor the increase in cachaça acidity during aging. However, this does not disqualify the spirit in the sensory aspect because of the pleasant flavor that forms with other components, therefore, the volatile acidity is an important parameter correlated to the sensorial characteristics of distilled beverages (Alcarde et al., 2010).

As Table 2 shows, samples 4, 16, 17 and 18 (14.81% of the total) had copper content above the maximum allowed limit by law of 5 mg.L^{-1}. In cachaça, the presence of this metal is mainly due to the dissolution of basic copper carbonate [$Cu_2(OH)_2CO_3$] from the inner walls of the alembic (pot still), which is carried by the acidic alcoholic vapors during the distillation. Proper hygiene when removing the patina and filling the alembic and streamers with water to reduce copper oxidation considerably reduce the possibility of cachaça contamination with copper (Cardoso, 2013). The use of ion-exchange resin filters is a good alternative for removing copper from the contaminated spirit without, however, removing secondary components responsible for its sensory quality (Duarte et al., 2012).

Regarding the furfural content, only sample 10 exceeded the maximum allowed limit of 5.0 mg.100 mL^{-1} of anhydrous alcohol, with a content of 6.24 mg.100 mL^{-1}. Furfural and hydroxymethylfurfural are undesirable organic contaminants in the spirit. High temperature

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associated with low pH of the wort leads to dehydration of sugars and hydrolysis of polysaccharides in sugarcane pith (cellulose, hemicellulose, pectin and others) forming 2-furfural (furfural) and 5-hydroxymethyl-2-furfural (hydroxymethylfurfural). Pentoses form furfural as the main degradation product, while the hexoses form hydroxymethylfurfural. Other factors such as aging of cachaça under irregular conditions, addition of caramel, and pyrogenation of organic matter decanted on the bottom of the stills may also contribute to increasing the content of these components (Faria et al., 2003). Masson et al. (2007) studied the formation of furfural and hydriximethylfurfural using raw and burned sugarcane in the production of cachaça and found that burning and reheating sugarcane before grinding influenced the occurrence of these compounds. These factors may have contributed to the contamination of sample 10 by furfural.

Table 2. Analysis of contaminants in the Bahian cachaça samples.

Sample	Copper[1]	Furfural[2]	Methanol[2]	Ethyl carbamate[3]	Butan-1-ol[2]	Butan-2-ol[2]
1	0.64 ± 0.03	0.67 ± 0.02	0.84 ± 0.03	207.61 ± 3.29	0.71 ± 0.02	nd
2	1.28 ± 0.04	0.46 ± 0.01	0.78 ± 0.03	220.56 ± 3.40	0.67 ± 0.01	nd
3	0.62 ± 0.06	0.63 ± 0.01	0.83 ± 0.01	217.79 ± 17.87	0.69 ± 0.01	nd
4	5.10 ± 0.02	0.52 ± 0.01	nd	283.12 ± 18.76	0.81 ± 0.02	1.95± 0.02
5	0.23 ± 0.02	1.15 ± 0.01	0.69 ± 0.04	320.97 ± 20.78	0.82 ± 0.02	nd
6	0.34 ± 0.03	0.65 ± 0.02	0.56 ± 0.02	305.73 ± 17.14	0.82 ± 0.02	nd
7	1.60 ± 0.05	3.23 ± 0.10	nd	102.05 ± 11.57	0.57 ± 0.01	nd
8	1.83 ± 0.03	3.52 ± 0.04	nd	103.68 ± 3.41	0.63 ± 0.02	nd
9	1.72 ± 0.02	3.34 ± 0.04	nd	126.64 ± 1.64	0.56 ± 0.02	nd
10	0.27 ± 0.02	6.24 ± 0.27	0.72 ± 0.00	509.62 ± 6.17	0.79 ± 0.02	nd
11	1.40 ± 0.03	3.54 ± 0.08	nd	555.43 ± 4.89	nd	nd
12	0.41 ± 0.06	1.44 ± 0.07	nd	570.89 ± 0.52	1.05 ± 0.01	nd
13	1.52 ± 0.02	0.29 ± 0.03	0.98 ± 0.04	160.5 ± 11.25	0.95 ± 0.01	nd
14	1.40 ± 0.02	0.27 ± 0.02	0.98 ± 0.06	162.73 ± 12.94	0.93 ± 0.01	nd
15	1.33 ± 0.03	0.31 ± 0.04	0.84 ± 0.08	153.96 ± 4.98	0.90 ± 0.01	nd
16	6.70 ± 0.10	3.78 ± 0.10	0.98 ± 0.06	296.65 ± 17.11	0.96 ± 0.01	nd
17	6.40 ± 0.05	4.03 ± 0.07	0.82 ± 0.05	320.66 ± 15.35	0.96 ± 0.02	nd
18	5.50± 0.04	3.95 ± 0.04	1.03 ± 0.01	314.91 ± 14.51	0.94 ± 0.02	nd
19	1.27 ± 0.00	0.36 ± 0.03	0.89 ± 0.03	299.85 ± 27.44	0.84 ± 0.02	nd
20	1.31 ± 0.09	0.32 ± 0.03	0.92 ± 0.06	298.13 ± 5.87	0.80 ± 0.02	nd
21	1.31 ± 0.03	0.32 ± 0.02	0.90 ± 0.01	284.77 ± 11.38	0.85 ± 0.02	nd
22	1.12 ± 0.03	0.66 ± 0.01	0.75 ± 0.03	420.72 ± 20.90	0.81 ± 0.02	nd
23	1.40 ± 0.05	0.86 ± 0.02	0.74 ± 0.08	406.15 ± 9.85	0.80 ± 0.04	nd
24	1.11 ± 0.03	1.07 ± 0.04	nd	423.12 ± 7.62	0.89 ± 0.01	nd
25	0.10 ± 0.06	0.73 ± 0.04	nd	477.81 ± 32.25	0.76 ± 0.00	1.07 ± 0.01
26	0.17 ± 0.03	0.46 ± 0.00	nd	538.38 ± 4.93	0.71 ± 0.01	0.90 ± 0.01
27	1.40 ± 0.05	0.69 ± 0.01	nd	517.16 ± 16.56	0.77 ± 0.00	1.08 ± 0.01

[1]($mg.L^{-1}$); [2]($mg.100\ mL^{-1}$ of anhydrous alcohol); 3 ($\mu g.L^{-1}$); nd: non-detected. The results highlighted do not comply with the standards of identity and quality of cachaça regulated by the Normative Instruction No. 13 of June 29, 2005.

Twenty (74.1%) of the twenty-seven samples analyzed had ethyl carbamate (EC) concentrations above the maximum allowed limit of 210 $\mu g.L^{-1}$, among them only three samples (11.1%) met the international requirement for this compound. The concentrations of ethyl carbamate above the allowed limit ranged from 217.79 ± 17.87 to 570.89 ± 0.52 $\mu g.L^{-1}$.

High contents of this contaminant has been reported in Brazilian cachaças over the past ten years, with average levels of 770 $\mu g.L^{-1}$: in 71 samples, Labanca et al. (2008) found

35% with contents between 500 and 1000 μg.L^{-1} and 12% with contents 10 times higher than the maximum allowed limit by Brazilian law; Bortoletto and Alcarde (2005) found average of 221 μg.L^{-1}; Chreem et al. (2015) found values between <5 and 683 μg.L^{-1}. All these reports corroborate with the results found in this study.

Some authors believe that the cachaça distillation in copper stills promotes the formation of the metal-catalyzed EC (Andrade-Sobrinho et al., 2002; Aresta et al., 2001; Bruno et al., 2007; Masson et al., 2014), others have demonstrated the non-correlation between copper and EC concentration in cachaças (Anjos et al., 2011; Mendonça et al., 2016; Zacaroni et al., 2011).

Anjos et al. (2011) concluded that the storage of cachaça in both wood barrels and glass containers influences ethyl carbamate formation, significantly increasing this contaminant concentration. The authors identified that light also affects ethyl carbamate formation, as they detected 13.63 μg.L^{-1} of carbamate in the cachaça stored in glass as early as the second month of storage, whereas the same concentration was only recorded in the cachaça stored in oak barrel on the ninth month. Santiago et al. (2016) periodically followed the chromatographic profile of ethyl carbamate in the production and aging of cachaça in amburana barrels. The authors observed that the concentration of ethyl carbamate throughout the production process and during aging was below the maximum allowed limit by law for this compound.

The results of our study and the others mentioned in this paper show that Brazilian cachaça consumers have been intensively exposed to ethyl carbamate. It is still not clear how ethyl carbamate forms in the spirit (Cardoso, 2013), which compromises the adoption of measures to avoid this contaminant in the production process of the Brazilian cachaça, but it does not exempt the producer from the search for a solution. The contents of ethyl carbamate found in cachaças produced in Bahia are a concern because of the potential risk it poses to consumers

4. Final Considerations

Regarding the quality standards, 74.1% of the samples were not in conformity with the limit established by the law concerning the contents of toxic compounds such as copper, furfural, or ethyl carbamate. Therefore, it is important to monitor contaminant levels in the Bahian sugarcane spirit and adopt measures to reduce the contamination rate in order to improve its quality. In addition, improvements must be made in the process to improve the quality of aged Brazilian sugarcane spirit.

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Conflict of Interest

The authors declare no conflicts of interest.

Authors' Contributions

All authors approved the final article

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