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DETERMINATION OF COPPER IN ARTISAN BOOZE SAMPLES PRODUCED IN THE REGION OF ITAPIRA-SP

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Abstract: Booze is a typical and exclusively Brazilian drink that, according to M.A.P.A. (Ministry of Agriculture, Livestock and Supply), is also called sugar cane spirit, and has an alcoholic strength between 38% and 48% by volume at 20°C. W. The artisanal production of booze is commonly carried out in copper stills, which gives better sensory characteristics to the drink. However, during distillation, the formation of verdigris may occur. [$CuCO_3Cu(OH)_2$], that mixes with the final product, causing contamination. The ingestion of large amounts of copper can cause health problems for consumers, affect various organs and even lead to death. In this context, this work aimed to determine the copper content in samples of booze sold in the city of Itapira-SP to verify if they meet the limit of 5 mg/L established by M.A.P.A. For this, the analytical methodology based on volumetry was evaluated. With the method, copper concentrations were found in the samples between 0.3 mg/L and 9.5 mg/L, indicating that some samples are above the limits established by Brazilian legislation.
Keywords: Booze, copper, quantification.

INTRODUCTION

THE BOOZE

According to Decree No. 6,871 of June 4, 2009, which regulates Law No. 8,918 of 1994, booze is defined as a typical and exclusively Brazilian sugarcane spirit, with an alcohol content of between thirty-eight and forty-eight percent by volume., limiting the addition of up to six grams of sugar per liter (M.A.P.A., 2019). Apart from these specifications, the drink is defined only as sugar cane spirit, according to the classification presented in Figure 1 (M.A.P.A., 2019).

In addition to being a national passion, much appreciated and recognized in Brazil, booze has also achieved, in recent years, an increase in its popularity in the international market, where it has been gaining strength and space with large Brazilian exporters, being present in countries such as Paraguay, Germany, United States, France, Portugal, among others. In 2020, due to the pandemic caused by Covid-19, the total revenue generated from the sale of the drink abroad was around US$ 9.5 billion, as shown in figure 2. In 2021, there was an increase of approximately 38 %, with the total revenue generated being US$ 13.17 million, as shown in figure 3 (IBRAC, 2021).

The average consumption of booze per Brazilian is around 6 liters per year, and the production of the drink reaches 1.6 billion liters annually, of which 90% is produced industrially and 10% artisanally (LIMA, 2006).

According to the Brazilian Institute of Booze - IBRAC (2021), booze production comprises 87.0% of the Brazilian production of distilled alcoholic beverages. There are about 40,000 booze producers in Brazil, of which only 955 are registered with the Ministry of Agriculture, Livestock and Supply (M.A.P.A.), as shown in Figure 4. There are almost 5,000 registered booze brands in Brazil, as shown in figure 5, and more than 16 million reais have been invested annually in the production of booze, which corresponds to an annual percentage growth of 4.0% to 5.0% in Brazil and 8.0% abroad (M.A.P.A., 2021).

However, only 1.0% of the total booze produced in Brazil, approximately 9.8 million liters per year, is exported (SOUZA, 2015). This may be directly linked to the contamination of booze by copper, since Brazilian legislation tolerates up to 5 mg/L of copper in sugarcane spirit, going against the grain of foreign regulations that have a lower tolerance, around only 2 mg/L copper (SILVA; PORTELA; ARAÚJO, 2007).

BOOZE PRODUCTION

After centuries of improvement, the booze

PARAMETER	CLASSIFICATION	
DENOMINATION	CANE SPIRIT	SUGARCANE LIQUOR
Alcoholic graduation	38 to 54% by volume	38 to 48% by volume
-Basic ingredient	-Simple alcoholic distillate from sugar cane -Fermented mash of sugarcane juice	-fermented mash from sugarcane juice
Addition of sugars	≤ 6g/L of sugar	≤ 6g/L of sugar

Figure 1 - Parameters for the classification of sugar cane spirit and booze

Source: M.A.P.A. (2019)

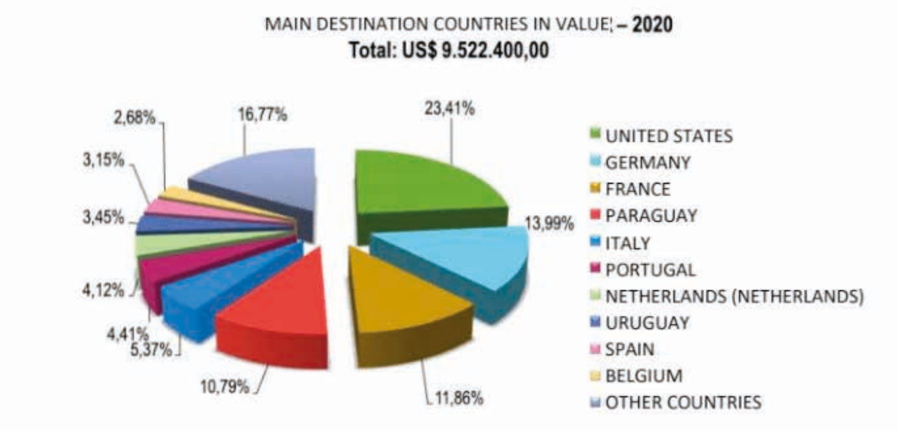

Figure 2 -- Total value obtained from the export of Brazilian booze in the year 2020 and the percentage distribution in value among the main destination countries

Source: IBRAC (2021)

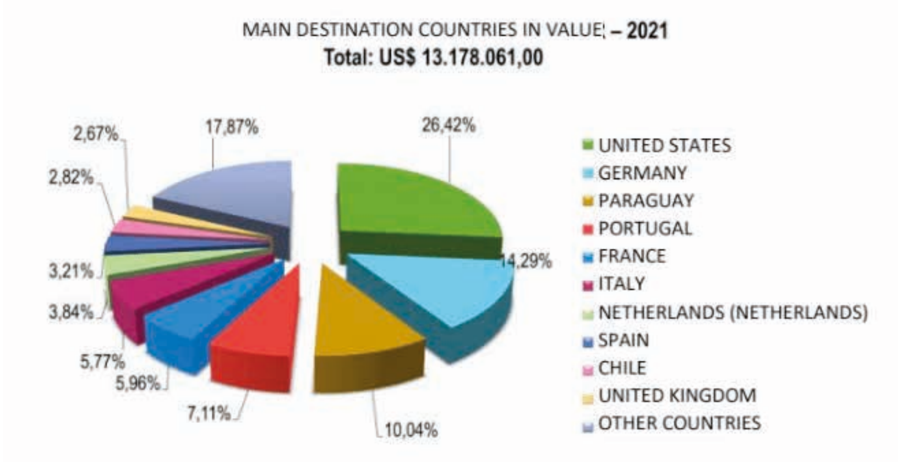

Figure 3 - Total value obtained from the export of Brazilian booze in the year 2021 and the percentage distribution in value among the main destination countries

Source: IBRAC (2021)

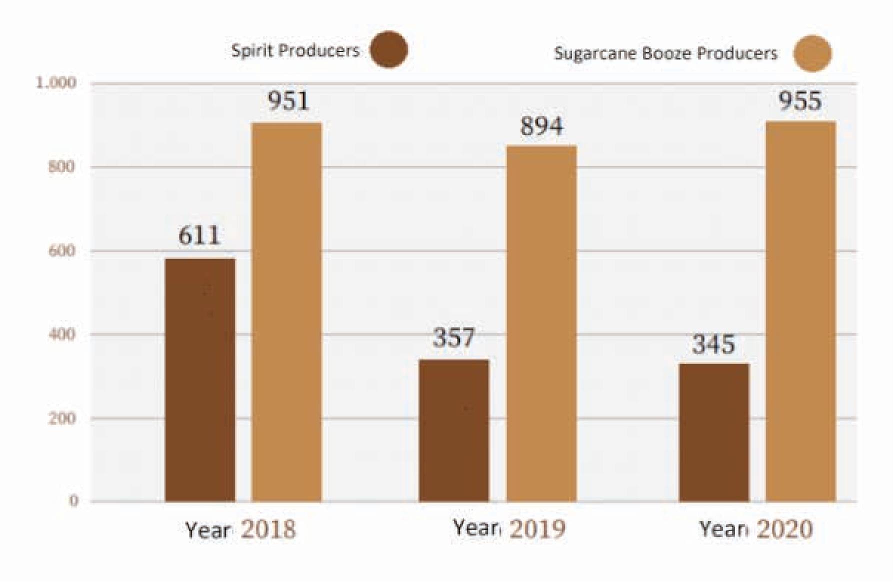

Figure 4 - Brandy and Booze producers registered in the M.A.P.A.
Source: Adapted of M.A.P.A. (2021)

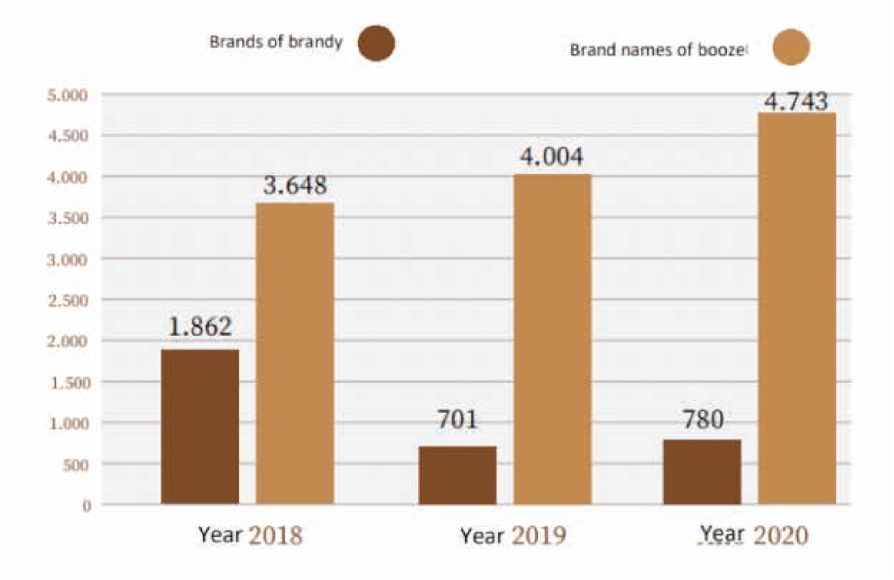

Figure 5 - Brands of Brandy and Booze registered in M.A.P.A.
Source: Adapted of M.A.P.A. (2021)

production process can be divided into five stages: harvesting, milling, fermentation, distillation and aging, which are represented in the flowchart shown in figure 6.

Harvesting the cane is the first step in making booze, and it is done at the right time, with proper handling, so that it arrives fresh, ripe and clean to be crushed. However, sugarcane milling needs to be carried out within 24 hours after harvesting, so that microorganisms do not appear and the sugar content is not reduced (FEITOSA, 2005).

To extract the sugarcane juice, known as the garapa, it is necessary to pass the sugarcane through the mill, which is a machine composed of rotating cylinders that serve to squeeze the sugarcane, extracting its juice. The bagasse is squeezed several times to extract as much cane sugar as possible. Aiming at a better quality of the juice, washing and asepsis of the sugarcane and equipment is recommended in order to reduce the risk of contamination by microorganisms that increase the acidity of the final product (OLIVEIRA, 2010).

The juice that is extracted in the mill carries several impurities that are removed in the filtration, such as large particles of bagasse. Decantation is also performed, which is responsible for removing denser particles. This way, this process helps to improve the quality of the broth for the next step, fermentation (OLIVEIRA, 2010).

The fermentation of the broth takes place in vats, where selected yeasts are added that transform the sugar present in the broth into alcohol. The product resulting from this process is called wine and has up to 12% alcohol (LACERDA, 2003). For an ideal fermentation to occur, the broth must have a concentration of sugars that must be around 15 °Brix. Higher concentrations result in incomplete and slow fermentations, decreasing yeast multiplication. On the other hand, lower concentrations of sugar help in fermentation, making it faster (OLIVEIRA, 2010).

Wine is composed of water, ethanol and various secondary compounds. Such compounds are responsible for the characteristics and quality of the drink. As the alcohol content of booze, according to Decree No. 6,871/2009, must be between 38% and 48%, and fermentation does not allow reaching high levels of alcohol content, a distillation stage is performed (OLIVEIRA, 2010). Distillation consists of boiling the wine until it reaches a temperature of around 78.3 °C, evaporating the alcohol, which is subsequently cooled and condensed, increasing the alcohol content of the drink (LACERDA, 2003).

During the distillation process, the booze is separated into three parts named head, heart and tail, as shown in figure 7. The head and tail, which together represent 20% of the distillate, do not have adequate quality levels for the consumption suffering, then, a new distillation and being transformed into ethanol. The heart, which corresponds to 80% of the distillate, has the best quality level and continues in the process, undergoing aging in selected wooden barrels with the intention of improving the flavor and odor of the drink. After the aging time, the drink is bottled and marketed (FREIRE et al., 2016).

INDUSTRIAL PRODUCTION X CRAFT PRODUCTION

The booze production process can be industrial or artisanal, comprising, in both cases, the same production stages, which differ only in the way in which the distillation of the wine occurs. In the case of industrial production, stainless steel distillation columns, also known as continuous stills, are used. As the industrial production takes place on a large scale, with greater standardization and control, the sensory characteristics of industrialized booze are inferior to those of

Figure 6 - Booze production flowchart

Source: Adapted of AGEITEC (2016)

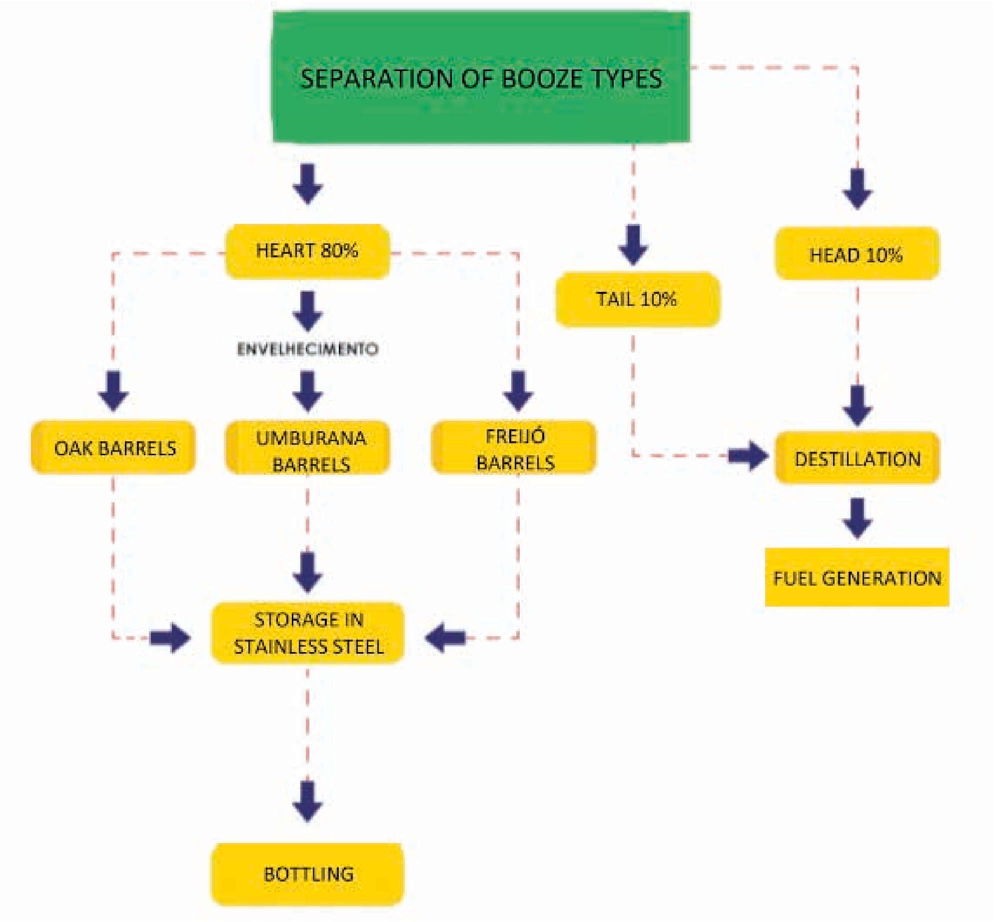

Figure 7 - Types of booze (distilled fractions), aging and bottling.

Source: Adapted of SANTOS *et al. (*2016) artisanal booze (SEBRAE, 2019).

The artisanal production of booze is carried out in copper stills, on a reduced scale, rarely exceeding 100,000 liters per year. And unlike industrial production, which occurs continuously, artisanal production is carried out in batches (SEBRAE, 2019). Copper, the material from which the still used in the artisanal production of booze is made, contributes to the reduction of acidity and the levels of aldehydes and sulfur compounds that give the booze distinctive flavors and odors that harm the final product (SILVA; PORTELA; ARAÚJO, 2007). However, during the beverage distillation process, the formation of copper carbonate [CuCO3Cu(OH)2] may occur on the surface of the metal, known as verdigris. This substance is solubilized by the acid vapors produced during the distillation and, by dragging, ends up contaminating the booze with copper ions (NASCIMENTO, 1998).

HEALTH EFFECTS OF COPPER INTAKE

Like other metals, copper is essential for the proper functioning of the human body, being used by the body in the production of red blood cells and collagen in the skin. It also contributes to bone health, as well as helping to activate the immune system. This metal plays the role of both a cofactor and a component of a series of important enzymes (cuproenzymes) that are essential for cells. It also plays the role of intermediary in redox reactions, where the transfer of electrons between atoms takes place. Copper makes up the enzymes that are part of aerobic metabolism, responsible for using oxygen as fuel to supply energy to cells. In this context, two cuproenzymes (of which copper is part) play a fundamental role: cytochrome-c-oxidase and superoxide dismutase (CATARINENSE PHARMA, 2019).

A diet based on the consumption of 2 to 5 mg of copper per day is recommended (SARGENTELLI; MAURO; MASSABNI, 1995). However, excess of this mineral in the body can cause health problems. Excessive consumption of this metal is rare, and can be done through acidic foods or drinks packed in copper containers, pipes or valves for a long time (JOHNSON, 2021). Due to its affinity with S-H groups of many proteins and enzymes, copper turns out to be toxic, being related to several diseases such as epilepsy, melanomas, rheumatoid arthritis and neurodegenerative diseases, such as Menkes disease, Wilson disease, aceruloplasminemia, sclerosis and Alzheimer's.

The large consumption of this metal causes several problems in the body, such as damaging the kidneys, reducing the production of urine, and can even cause anemia, since it causes the rupture of red blood cells (hemolytic anemia), which can lead to death (JOHNSON, 2021).

VOLUMETRY

Volumetry is a classical quantitative analytical technique widely used to determine the concentration of solutions of acids, bases, metal ions, oxidants, reducers, among others. The volumetric analysis is carried out by determining the volume of a solution, whose concentration is exactly known, which reacts quantitatively with a known volume of the solution that contains the substance to be determined (BACCAN et al., 1979).

A standard solution whose concentration is known exactly is called a standard solution, also called a titrant. The analyte, substance whose concentration will be determined, is called titrated. The objective of volumetry is to reach the stoichiometric point, also known as the equivalence point, since it is at this point that the amounts of standard solution and analyte are stoichiometrically equivalent (VASCONCELOS, 2019).

Volumetric analysis is classified according to the reaction that occurs between the titrant and the titrant, such as neutralization volumetry or acid-base volumetry, oxidation-reduction volumetry, complexation volumetry and precipitation volumetry. The method used in this work to quantify copper in artisanal booze samples was oxidation-reduction volumetry, in which the oxidation process involves a substance losing electrons (reducing agent) to another (oxidizing agent) or a reduction process where a substance gains electrons (oxidizing agent) from another (reducing agent). In either case, the number of electrons lost by the substance undergoing oxidation is always equal to the number of electrons gained by the substance undergoing reduction, in order to maintain the isoelectronic balance of the reaction medium (BACCAN et al., 1979).

OBJECTIVE

The present work aimed to determine the copper content in samples of booze produced by hand in the region of Itapira-SP. For this, a volumetric oxidation-reduction method was used, based on the methodology for determining copper content by volumetry by Silva, Bastos and Costa (2021), to verify whether the copper content in the artisanal booze samples is within the limit of 5 mg/L established by M.A.P.A.

MATERIAL AND METHOD

The method used in the analysis of the booze samples was based on the methodology for determining copper content by volumetry by Silva, Bastos and Costa (2021).

SAMPLING

Samples of booze sold in the city of Itapira-SP and region were collected. According to the Adolfo Lutz Institute (2008), for metal analysis it is not recommended to use glass to store the samples, as this adsorbs the metals on its walls, and it is more appropriate to use polyethylene containers. Therefore, samples of booze produced by hand by 3 different producers were collected and which were packed in polypropylene bottles. A sample of the booze produced by producer 1 was placed in a glass bottle, to allow the evaluation of the interference of this material in the copper content of the sample. For comparative purposes, a sample of industrially produced booze was collected. Table 1 presents the list of booze samples that were collected to be submitted to analyzes to determine the copper content.

Samples	Characteristics
A	Booze from producer 1 stored in polyethylene
B	Booze from producer 2 stored in polyethylene
C	Booze from producer 3 stored in polyethylene
D	Booze from producer 1 stored in a glass bottle
E	industrial booze

Table 1 - Booze samples

Source: Own authorship (2022)

MATERIALS AND REAGENTS

To carry out this work, the following materials, reagents and equipment were used: concentrated hydrochloric acid, ethyl alcohol 40.0% (v/v), starch indicator in suspension at 1.0% (m/v), potassium iodide, 19.6 g/L copper sulfate pentahydrate solution, 0.01 mol/L sodium thiosulphate solution, glassware and volumetric materials.

METHOD

The booze samples were fortified with a standard copper solution before being subjected to volumetric analysis.

To determine the copper content in the standard used for the fortification of the booze samples, 1.0 g of potassium iodide was weighed in a 250 mL Erlenmeyer and 0.5 mL of hydrochloric acid was added sequentially.

concentrate, 1.0 mL of 19.6 g/L copper sulfate pentahydrate solution and 100 mL of 40% ethyl alcohol. This mixture was titrated with a 0.01 mol/L sodium thiosulphate solution, previously standardized, until the mixture acquired a pale yellow color. Then, 3.0 mL of the indicator solution of 1.0% starch in suspension was added and the titration was continued until the color turned to colorless. The copper content in the standard solution was calculated by equation I.

$$Content\ of\ copper\ in\ standard\left(\frac{mg\ Cu^{2+}}{L}\right) = \frac{Vg \cdot M \cdot 63{,}5 \cdot 1000}{Va} \quad \text{(I)}$$

Where:

Vg = volume spent in the titration (L);

63.5 = molar mass of copper ($g.mol^{-1}$);

1000 = mass conversion factor;

M = real concentration of sodium thiosulphate (mol L-1);

Va = standard volume (L).

For the analysis of the spirits samples, 1.0 g of potassium iodide was weighed in a 250 mL Erlenmeyer and sequentially added 0.5 mL of concentrated hydrochloric acid, 1.0 mL of the sulfate solution of copper pentahydrate 19.6 g/L and 100 mL of the booze sample. The mixture was titrated with a previously standardized 0.01 mol/L sodium thiosulphate solution until the mixture acquired a pale yellow color. Then, 3.0 mL of the indicator solution of 1.0% starch in suspension was added and the titration was continued until the color turned to colorless. The copper content in the sample was calculated by equation II.

$$Content\ of\ copper\ in\ sample\left(\frac{mg\ Cu^{2+}}{L}\right) = \frac{((Vg \cdot M \cdot 63{,}5 \cdot 1000) - T \cdot Vf)}{Va} \quad \text{(II)}$$

Where:

Vg = volume spent in the titration (L);

63.5 = molar mass of copper (g.mol-1);

M = real concentration of sodium thiosulphate (mol L-1);

1000 = conversion factor from g to mg;

T = mean concentration determined for the copper standard (mg L-1);

Vf = volume of the copper standard used in the fortification (L);

Va = booze sample volume (in L).

Both the copper standard analysis and the booze samples were performed in duplicate.

RESULTS AND DISCUSSION

The results obtained with the volumetric analysis for the booze samples are presented in Table 2, as well as the limit for the copper content established by M.A.P.A., for comparative purposes.

Sample	Average content of Cu^{2+} (mg/L)	Deviation (mg/L)
A	3,7	0
B	1,1	± 0,4
C	9,5	± 0,7
D	0,7	0
E	0,4	± 0,1
Standard	7931,0	± 220,3
MAP Limit	5,0	---

Table 2 - Copper content determined in booze samples by volumetric analysis

Source: Own authorship (2022)

The results shown in Table 2 allow observing that in samples of artisanal booze A and B, copper contents were found that are below the limit determined by Brazilian legislation. The booze sample C showed a copper concentration 4.5 mg/L above the limit established by M.A.P.A. But when comparing the copper contents determined in samples A and D, which belong to the same producer, but were stored in polyethylene and glass bottles, respectively, it is possible to observe that the adsorption of metals in the glass actually occurs, as pointed out by Instituto Adolfo Lutz (2008). Because, despite being the same booze, sample D, which was stored in the glass bottle, showed a copper concentration 2.94 mg/L below the copper concentration determined for sample A.

The small amount of copper found in the industrially produced booze sample (E) may be related to the copper present in the distilled water used in the preparation of the samples for analysis, and this was not quantified and, therefore, its value was not subtracted from the concentration end found.

The results obtained for the copper content in the samples of artisanal booze point to the lack of application of good manufacturing practices, as with adequate hygiene it is possible to reduce the formation of verdigris. For this, it is recommended that the first distillation be carried out with water and lemon juice in order to remove the basic copper carbonate formed on the still walls and, in order to avoid oxidation of the material, the still and coils must be filled with water during production stops (FRANÇA; SÁ; FIORINI, 2011).

CONCLUSION

Through the volumetric method used, it was possible to determine copper contents in the booze samples in a range of 0.4 mg/L to 9.5 mg/L. Only one of the samples analyzed had almost twice the copper content allowed by M.A.P.A., which demonstrates the lack of cleaning of the stills and the application of good manufacturing practices. The other samples of booze analyzed showed copper levels below the limit established by M.A.P.A. It was noted that the use of glass for booze storage may be appropriate due to the occurrence of copper adsorption by the packaging material, as observed in the results obtained, since the same sample stored in polyethylene presented a copper content of 3, 7 mg/L, while when stored in glass, the determined content was 0.7 mg/L.

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