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ORIGINAL ARTICLE

Identification of volatile compounds, quantification of glycerol and trace elements in distilled spirits produced in Mozambique

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Abstract Distilled spirits, in addition to satisfying the legal requirements with respect to its composition, must possess a sensorial quality capable of satisfying its consumers. The present work describes the analysis of volatile compounds, trace elements and glycerol in thirteen samples of Mozambican spirits collected in different regions of the country. Extraction of volatile components was a accomplished using the headspace SPME technique, the quantification of glycerol was achieved by UV/Vis spectroscopy and the determination of trace elements by atomic absorption spectrometry. Of the 35 volatile compounds identified, 19 were esters, of which ethyl hexanoate, ethyl octanoate, ethyl nonanoate, ethyl decanoate, ethyl laurate, ethyl hexadecanoate, ethyl tetradecanoate, ethyl benzenepropanoate, 3-methylbutyl acetate and isoamyl alcohol were the predominant compounds found in the different samples, contributing to the characteristics and aroma of the beverages. As for glycerol, concentrations below 5 mg L^{-1} were observed in all the samples studied. The samples were found to be contaminated by metals such as copper, lead and zinc. In addition, the results provided information on the quality of Mozambican spirits regarding some aspects related to the determination of metals and glycerol. This information might stimulate producers to be more attentive to the conditions of production and the risks involved in achieving good quality spirits.

Keywords Mozambican spirits · SPME · Inorganic contaminants · Organic compounds

Introduction

Distilled alcoholic beverages are distinguished from one another by the presence of secondary components that form a “bouquet” characteristic of each beverage. These compounds, together with ethyl alcohol, are formed during the fermentation, distillation and aging processes and cause changes in the organoleptic character of the beverages. Contaminating compounds in the beverage can be found in the final product, and they are the principal agents responsible for the toxic, carcinogenic and characteristic properties of the beverages, which depreciate the quality of the drink.

Distilled spirits are a complex beverage composed of different compounds. Alcohols, aldehydes, carboxylic acids, esters, hydrocarbons and carbonyl compounds with three or more carbon atoms are among the secondary compounds. The presence of these compounds in fermented-distilled beverages is common because they are formed during normal metabolism of microorganisms or through reactions involving compounds produced during fermentation, distillation and aging (Cardoso 2013).

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Flavor is an important factor in the selection of foods and beverages, and it determines consumer acceptance of the product. Volatile compounds, along with the other organic compounds, are present in foods in small amounts, and they are responsible for the characteristic flavor. The volatile compounds present in alcoholic beverages, which influence the characteristic flavor, can originate from the raw material used in the manufacture and remain unchanged during the fermentation, distillation and aging process (Santiago et al. 2016).

Glycerol has a positive contribution to sensory characteristics, such as texture, flexibility, viscosity and higher concentrations in wine. It contributes to the sweet taste of wine (Lubbres et al. 2001). Because of the positive sensory effects in wine, several countries add this substance to mask eventual defects in the beverages. Therefore, monitoring has been performed as a form of quality control (Moro et al. 2007). In addition to contamination by organic compounds, heavy metals might also be present in distilled beverages if the materials used are not adequate.

In Mozambique, distilled spirits have been produced under inappropriate conditions and marketed without any regulation by the local government. In consequence, consumers could be exposed not only to low quality beverages, but also to hazardous substances. Therefore, the objectives of this work were the identification of the volatile compounds in different Mozambican spirits using gas chromatography coupled with mass spectrometry (GC–MS) the quantification of the glycerol concentration using a colorimetric method, and the determination of trace elements (copper, lead, cadmium, chromium, iron and zinc) by atomic absorption spectrometry (AAS). Because no official legislation exists in Mozambique to assess the quality of the spirits, the results of the analysis were compared to the limits established by Brazilian legislation.

Materials and methods

Sample

The samples were collected in five provinces of southern and central Mozambique in the Manhiça, Xinavane, Chókwe, Massinga, Mafambisse, Beira and Chimoio districts in August 2016 and May 2017. The Manhiça district is located between the parallels 24°58′49″ and 25°35′46″ South latitude and between the meridians 32°30′51″ and 33°08′14″ East longitude. Xinavane lies at the parallel 25°0′34″ South and at 32°45′04″ East. The Chókwe district is georeferenced between parallels 24°05′ and 24°48′ South and 32°33 and 33°35′ East. The Massinga district is located between the parallels 22°39′ and 23°31′ South and the meridians 34°54′ and 35°36′ East. The district of Mafambisse is located at the parallel 19°32′57″ South and at 34°37′28″ East. The city of Beira is georeferenced at the parallel 19°50′36″ South and at 34°50′20″ East, and the city of Chimoio is located at the parallel 19°06′59″ South and at 33°28′59″ East. All the samples were identified by region of origin and sent to the Laboratory for Quality Analysis of Spirits (LAQA), Department of Chemistry, Federal University of Lavras, Lavras, MG, Brazil. The characteristics of the samples, as well as the region of origin, the alcohol concentration and the raw material used in its production are presented in Table 1.

Identification of volatile organic compounds

The analyses of the volatile compounds in the spirits produced in different regions of Mozambique were achieved on a gas chromatograph coupled to a GC–MS QP2010 Plus mass spectrometer (Shimadzu, Japan) and equipped with an AOC-5000 automatic injector for liquids and gases (Shimadzu, Japan), a split/splitless injection port and an SLBTM column (5% phenyl, 95% dimethylsiloxane), 30 m × 0.25 mm × 0.25 µm. The oven temperature was programmed from 35 to 240 °C at a rate of 4 °C min^{-1}. The carrier gas used was He 5.0 with a flow rate of 1.78 mL min^{-1}. The injector temperature was maintained at 270 °C and operated in 1:4 split mode. The compounds were detected by mass spectrometry at 70 eV in the scan mode (29–600 Da). The temperature of the detector interface and the ion source remained at 240 °C and 200 °C, respectively. The filament was switched on at 1.75 min.

Extractions of volatile components were performed using solid phase microextraction (SPME) of the headspace. Samples were diluted to a concentration of 10%. After dilution, 4-mL aliquots of the samples were added to 20 mL vials, and the extraction was performed at an extraction temperature of 45 °C, extraction time of 50 min and desorption time of 3 min. The extraction was performed using the Divinylbenzene, Carboxen, and Polydimethylsiloxane (DVB/CAR/PDMS) fiber with 30–50 µm Supelco brand film. This fiber was previously conditioned for 1 h at 270 °C according to specifications of the manufacturer.

Compounds were identified by comparing the mass spectra obtained with those in the GC–MS spectral library (Wiley 8 and FFNSC 1.2). The experimental retention indices were calculated and compared with indices reported in the literature (Adams 2007; NIST 2013). Linear alkane standards were used to calculate the retention index of each compound in the sample represented in the GC–MS system. Retention times of the samples were used as the reference standard for calculating the final retention time of the compound. For comparison, similarities above 75%

Table 1 Descrimination of the samples by location of origin and raw material used

Sample	Origin	Raw material	Type	Alcohol conc. (%v/v)
1	Manhiça	Cane	Alembic	40.49 ± 0.01
2	Manhiça	Cane	Alembic	47.38 ± 0.02
3	Xinavane	Cane	Alembic	41.58 ± 0.01
4	Xinavane	Cane	Alembic	40.08 ± 0.01
5	Chokwe	Cashew	Alembic	20.80 ± 0.01
6	Chokwe	Cashew	Alembic	20.96 ± 0.01
7	Massinga	Nuts	Alembic	56.10 ± 0.02
8	Massinga	Nuts	Alembic	55.80 ± 0.02
9	Mafambisse	Cane	Alembic	35.20 ± 0.01
10	Mafambisse	Cane	Alembic	37.06 ± 0.01
11	Beira	Cereal	Alembic	21.30 ± 0.03
12	Chimoio	Cereal	Alembic	58.10 ± 0.01
13	Chimoio	Cereal	Alembic	21.58 ± 0.02

were considered. The equation below represents the calculation of the retention time of the compound identified.

$$\mathrm{LRI} = 100 \times \left(\frac{Tc - Tn}{Tn + 1 - Tn} + n \right)$$

where LRI linear retention index; Tc retention time of the compound of interest; Tn retention time of the hydrocarbon anterior to the compound of interest; Tn + 1 retention time of the subsequent hydrocarbon; n number of carbons of the anterior hydrocarbon.

Quantification of glycerol

Glycerol was determined by the colorimetric method used by Amerine and Ough (1980) and by Bortoletto et al. (2016), in which spectrophotometric measurements were performed at 410 nm. The method is based on the oxidation of glycerol by periodate ions to form formaldehyde, which reacts with acetylacetone in ammoniacal medium to form 3,5-diacetyl-1,4-dihydrolutidine, a yellow substance. The readings were performed on a Shimadzu UV-1601 PC spectrophotometer, and the concentrations were calculated with the aid of an analytical curve previously constructed with standard solutions of glycerol at concentrations of 7.5, 15.0, 22.5, 30.0, 45.0, 60.0, and 90.0 mg L^{-1}. The determination coefficient (R^2) of the linear regression equation for the seven-point analytical curve ($y = 0.025x - 0.1092$) was 0.996, indicating linearity between compound concentration and absorbance. Results were expressed in milligrams of glycerol/liter (mg L^{-1}).

Determination of trace elements

Copper, lead, iron, zinc, cadmium and chromium were determined by Flame Atomic Absorption Spectroscopy using a Varian model Spectr AA 110 Atomic Absorption Spectrophotometer. The analytical curves were constructed using Merck standards of copper, iron, zinc and lead at concentrations that varied from 0.05 to 8.0 mg L^{-1}. The determinations were performed at 324.7 nm for copper; 248.3 nm for iron; 213.9 nm for zinc and 217.0 nm for lead using a hollow cathode lamp. The determinations were performed in triplicate.

For the preparation of samples, method n° 11 of the Manual of Methods of Analysis of Beverages and Vinegars proposed by MAPA (Brasil 2005) was followed. The results were expressed in mg L^{-1} and compared to the parameters described by the Brazilian Legislation (IN n° 13, dated 29/6/2005 of MAPA) (Brasil 2005).

Statistical design

The completely randomized design (CRD) was used. The glycerol data obtained were submitted to analysis of variance, and the means were compared by the Schott-Knott test at the 95% (0.05%) confidence level using the SISVAR (Ferreira 2011) statistical program.

Results and discussion

Cachaças produced in Mozambique can contain components that affect the overall quality of the beverage. Some volatile compounds can be used as markers for the quality of beverages, and heavy metals might not influence the flavor of the beverage, but they can cause harm to consumers' health if they are present in high concentrations.

The volatile compounds identified by GC–MS are listed in Table 2. Of the 35 compounds reported in Table 1, 19 were identified in the different samples of spirits analyzed, including different classes of chemical compounds, an

Table 2 Volatile compounds identified in Mozambican spirits samples HS–SPME–GC–MS

No.	Compounds	Rt (min)	ELRI	TLRI	SAMPLES												
					1	2	3	4	5	6	7	8	9	10	11	12	13
1	3-Methyl-butan-1-ol^{alc}	3.415	x	723	X	X	X	X	X	X	X	X	X	X	X	X	X
2	Hexanal^{ald}	4.531	802	801											X		X
3	Ethylbutanoate^{es}	4.558	803	802	X												
4	4-Mehyl-pentan-1-ol^{alc}	5.597	840	830					X	X							
5	Ethyl 2-methylbutanoate^{es}	5.761	846	850						X							
6	3-Methyl-pentanol-1^{alc}	5.820	848	850					X	X							
7	Ethyl 3-methylbutanoate^{es}	5.891	851	856						X							
8	3-Methylbutyl acetate^{es}	6.589	876	867			X	X		X	X						
9	1-Octen-3-ol^{alc}	10.114	983	978											X		X
10	Ethylhexanoate^{es}	10.682	1000	997	X		X	X		X	X	X	X		X	X	X
11	Ethyl 2-hydroxy-4-methylpentanoate^{es}	13.014	1063	1060					X	X							
12	Octan-1-ol^{alc}	13.469	1075	1063						X	X				X		X
13	1,1-Diethoxy hexane^{ac}	13.994	1089	1092											X	X	
14	Nonanal^{ald}	14.580	1105	1100											X		X
15	1,3-Dioxepane, 2-pentadecyl^{ac}	14.852	1112	–											X		X
16	3-Nonen-1-ol^{alc}	16.441	1156	1157											X		X
17	2-Nonenal^{ald}	16.601	1160	1168											X		X
18	EthylBenzoate^{es}	17.085	1173	1170					X	X					X		X
19	Nonan-1-ol^{alc}	17.150	1175	1172	X	X									X	X	X
20	3-Ethyl-phenol^{h}	17.169	1176	1168	X	X											
21	Menthol^{alc}	17.256	1178	1179		X	X	X					X	X			
22	Ethyloctanoate^{es}	17.857	1194	1197	X	X	X	X	X	X	X	X	X	X	X	X	X
23	Decan-1-ol^{alc}	20.674	1274	1272							X	X					
24	Ethylnonanoate^{es}	21.311	1293	1292							X	X				X	
25	Ethylbenzenepropanoate^{es}	23.105	1347	1350					X	X							
26	Ethylcinamate^{es}	24.014	1374	–	X	X											
27	β-Damascenone^{ce}	24.091	1376	1387	X	X	X	X						X			
28	E-4-Ethyl decenoate^{es}	24.142	1378	–							X	X					
29	Ethyl 9-decanoate^{es}	24.349	1384	1386	X		X	X									
30	Ethyldecanoate^{es}	24.655	1394	1395	X	X							X		X	X	X
31	Ethyllaurate^{es}	30.684	1593	1595	X	X	X	X									
32	Ethyldodecanoate^{es}	30.695	1593	1594	X	X											
33	Isopentyldecanoate^{es}	32.111	1644	1653	X	X	X	X									
34	Ethyltetradecanoate^{es}	36.181	1794	1793	X	X	X	X		X	X	X	X	X		X	
35	Ethylhexadecanoate^{es}	41.144	1989	1992	X	X	X	X	X	X	X	X	X	X	X	X	X

Retention time; *ELRI* estimated linear retention index, *TLRI* theoretical linear retention index, *alc* alcohol, *es* ester, *ald* aldehydes, *ac* acetal, *h* hydrocarbon, *ce* cetone

observation that denotes a great heterogeneity among the samples.

The esters ethyl hexanoate, ethyl octanoate, ethyl nonanoate, ethyl decanoate, ethyl benzenepropanoate, ethyl laurate, ethyl hexadecanoate, ethyl tetradecanoate and the alcohols 3-methylbutan-1-ol, octan-1-ol and nonan-1-ol presented the most intense peaks in almost all the samples, corroborating the work of Santiago et al. (2016), Zacaroni et al. (2017) and Nóbrega (2003).

The compounds ethyl octanoate, ethyl hexadecanoate and 3-methyl-butan-1-ol were present in all the samples. Samples 11 and 13 had a similar volatile composition because they had 14 compounds in common.

β-Damascenone was identified in samples 1, 2, 3, 4 and 10. These samples refer to the beverage that was obtained from sugar cane. Brazilian legislation does not set limits for the presence of ketones in cachaças, but it is known that this group of chemical compounds is important for the sensorial quality of beverages; the isoprenoids class, specifically the ionone group, which can increase the fruity aroma in wines, are significant even in low concentrations (Crupi et al. 2010). Despite their low concentrations, the ionone group has been identified as the most potent floral-fruity odorants in cachaça (De Souza et al. 2006). These substances can also be produced as degradation products after the distillation of tequila or from carotenoids (Prado-Jaramilo et al. 2015).

The high concentrations of the esters in the group of volatile compounds contribute to the aroma of the fruit-flavored distillates (Silva et al. 2000). According to Nóbrega (2003), the most volatile component in the spirits is ethanol, but it is one of the volatile components of least importance for the definition of aroma because its aroma is not very noticeable. Ethanol, as well as other very volatile compounds ethyl acetate, acetaldehyde or propanol were not identified in the samples because of they eluted before 1.75 min (solvent cut of the mass spectrometer to avoid filament damage). However, compounds such as aldehydes, higher alcohols (propyl, butyl and amyl) and esters, although present in lower concentration than ethanol, have more pronounced flavor characteristics and, therefore, a great impact on the aroma of the beverage.

Nonato et al. (2001) extracted volatile compounds by SPME with polyacrylate fiber (PA) and detected a large number of compounds. Of the 38 compounds that were identified, 11 were esters. Santiago et al. (2016) extracted volatile compounds from the headspace of cachaças aged in different wood containers employing SPME with a PDMS/DVB fiber. They identified 51 compounds by GC/MS, of which 20 were esters. Nóbrega (2003) identified volatile compounds relevant to the aroma of cachaça using the adsorbent Tenax-TA, a method of extraction of volatiles never before tested for cachaça, to obtain a dynamic concentration of the volatile compounds present in the headspace of cachaça. They identified and quantified approximately 100 compounds, of which 22 were esters and alcohols, responsible for the flavor of the beverages.

Bento et al. (2015), studying cachaça from the state of Pernambuco, Brazil, identified 30 volatile compounds, mainly esters, using the dynamic vacuum headspace strategy. Zacaroni et al. (2017) extracted volatile compounds from the headspace of cachaças by SPME using a DVB/CAR/PDMS fiber and identified 14 compounds, of which 10 were esters.

Nascimento et al. (2009) reported that the esters present in the distilled beverages come from two different sources: those formed during fermentation by the intercellular secondary metabolism of the yeasts, such as ethyl acetate and ethyl butanoate, and those generated through the interconversion during aging. In the latter case, ethyl syringate and ethyl vanillate are mentioned. The authors evaluated 57 brands of cachaça qualitatively and quantitatively and found that esters of acetic, octanoic, decanoic and dodecanoic acids were present at higher concentrations in cachaça, and 90–95% of the total area of the 14 esters identified were formed from acetic acid.

The data obtained in this study corroborate the research described by Nascimento et al. (2009), Zacaroni et al. (2017), Nóbrega (2003) and Nonato et al. (2001). Of the esters identified, most were related to the principal acids and alcohols that were identified in this work; ethyl octanoate, ethyl nonanoate, ethyl decanoate, ethyl dodecanoate, and 3-methylbutyl acetate. 1,1-Diethoxyhexane was also quantified, corroborating the results of Zacaroni et al. (2017) and Nóbrega (2003), who observed its presence in cachaças. Alcohols are important for the flavor of cachaça because of their characteristic odors. They also act as solvents for other aromatic substances and interfere in the limits of odor of alcoholic beverages (Moreira et al. 2012).

The compounds 3-methyl-butan-1-ol, menthol, octan-1-ol and 1-octen-3-ol were found in larger quantities in samples of Mozambican spirits than in Brazilian cachaça. These results differ from those found by Santiago et al. (2016), Zacaroni et al. (2017) and Nonato et al. (2001), who identified isoamyl, isobutyl and propyl alcohols as the principal constituents of the class of alcohols in Brazilian cachaças.

The mean concentrations of glycerol and the standard deviations obtained for samples of Mozambican spirits are presented in Table 3. The glycerol concentrations ranged from 4.33 to 4.56 mg L^{-1}, which are under the limit established by Brazilian legislation and which were lower than those reported in the literature for Brazilian samples. The different types of raw material and the types of fermentation and distillation employed in the production of the spirits might have contributed to the low concentrations of this compound.

Bortoletto et al. (2016) evaluated the glycerol content in cachaças aged in different types of wood casks and found average glycerol concentrations of 15.73 mg L^{-1} in aged cachaças and 1.39 mg L^{-1} in a newly distilled cachaça that was employed as a control. They observed a lower concentration of this compound in the recently distilled cachaça than in the aged spirits, possibly because of reactions that occurred during aging that led to the increase in the concentration of this compound. Gervasio et al. (2002) determined the levels of glycerol in samples of distilled sugarcane spirits. They found concentrations of 36.3 to 2150 mg L^{-1} for cane spirits, which are much higher than those obtained in the present study.

Table 3 Glycerol and trace elements concentrations in distilled beverages collected in Mozambique

Sample	Glycerol (mg L^{-1})	Copper (mg L^{-1})	Lead (μg L^{-1})	Zinc (μg L^{-1})	Iron (μg L^{-1})
1	4.56 ± 0.05a	ND	1.72 ± 0.11b	ND	ND
2	4.47 ± 0.02b	ND	2.97 ± 0.07a	ND	ND
3	4.47 ± 0.03b	ND	1.76 ± 0.05b	ND	ND
4	4.48 ± 0.03b	7.47 ± 0.15c	1.68 ± 0.05b	5.47 ± 0.06c	ND
5	4.45 ± 0.02c	ND	2.63 ± 0.06a	1.46 ± 0.07d	0.04 ± 0.05a
6	4.45 ± 0.02c	ND	1.68 ± 0.05b	ND	ND
7	4.52 ± 0.05a	ND	2.20 ± 0.05b	ND	ND
8	4.45 ± 0.02c	ND	2.15 ± 0.13b	ND	ND
9	4.33 ± 0.03d	34.83 ± 0.23a	0.94 ± 0.06c	23.01 ± 0.10a	ND
10	4.54 ± 0.04a	28.10 ± 0.17b	0.60 ± 0.04c	19.26 ± 0.12b	ND
11	4.40 ± 0.03c	ND	3.66 ± 0.05a	ND	ND
12	4.43 ± 0.01c	ND	2.28 ± 0.06b	ND	ND
13	4.42 ± 0.01c	ND	1.55 ± 0.05b	ND	ND

The means followed by the same letter in the columns do not differ by the Schott-Knott test at the level of 5% of probability

ND not detected in mg L^{-1} and μg L^{-1}

According to Garcia et al. (2015), problems in the distillation process might also be reasons for the presence of glycerol in distilled beverages. The concentrations of glycerol in these beverages are significantly lower than those encountered in fermented beverages, such as wine, because of the low volatility of glycerol.

The formation of the glycerol can interfere with the fermentation process in an unfavorable way because it is formed via the same route of synthesis as ethanol, and the two pathways compete with each other for the coenzyme NADH. Thus, the synthesis of glycerol is inversely proportional to that of ethanol (Wang et al. 2001). After the fermentation process, some glycerol is carried over during distillation because of its polarity and solubility in water and ethanol. According to Lima and Merçon (2001), glycerol is a molecule synthesized by yeast to maintain cellular redox equilibrium, which is altered during the formation of organic acids and biomass.

The results of the determination of the trace elements of spirits collected in different regions of Mozambique are presented in Table 3. Brazilian Normative Instruction n° 13 of 06/29/2005 determines that the maximum concentration of copper ions should be 5.0 mg L^{-1} for spirits. However, the results obtained ranged from non-detectable to 34.83 mg L^{-1} in the samples analyzed. Samples from the Xinavave and Mafambisse regions corresponded to 21.4% of the spirits that contained copper, and the concentrations in the Mafambisse samples (9 and 10) were statistically greater than the others and different from each other; sample 9 contained the highest copper concentration. There was a significant difference between the two regions, and the concentrations in the samples were beyond the limits required by the Brazilian legislation (Brasil 2005).

Miranda et al. (2008) evaluated the physicochemical profile of spirits aged in oak barrels over a period of 390 days and observed that 15% of the samples contained copper concentrations of 12 mg L^{-1}, this value being greater than the established limit (5 mg L^{-1}). Subsequently, Marinho et al. (2009) analyzed six samples of alembic cachaças and found concentrations of 8.80 mg L^{-1} for two of the samples. This value was higher than that allowed by Brazilian legislation (5 mg L^{-1}). The results obtained by these authors corroborate those found for the samples from the Xinavave and Mafambisse regions in the present study, which are also higher than the legal limit.

Masson et al. (2007) evaluated the quality of 24 spirits produced in Minas Gerais and verified that there were significant differences in the copper concentrations of sugarcane spirits, wherein values ranged from 0.12 to 8.38 mg L^{-1} and from 0.96 to 19.40 mg L^{-1} in the northern and southern regions, respectively. These samples corresponded to 21% of the total samples with values greater than the legal limit.

When studying the kinetics and isotherm of copper adsorption using kaolinites, Duarte et al. (2014) evaluated the physicochemical quality of the cachaça before and after the adsorption. The maximum adsorption capacity of the metal was obtained with K01, K03 and K04 kaolinite (97%, 95% and 90%, respectively). In the results of the physicochemical analysis, all the parameters of the control sample were within the legal limits, except for aldehydes and copper. After the adsorption with the clays, a decrease in the concentrations of these contaminants in the cachaças was observed, although there were no significant differences for some parameters.

According to Cardoso (2013), sanitizing the still is essential to prevent contamination with copper. The authors recommend that a preliminary distillation with lemon juice containing 5 L of the juice for 100 L of water be performed. This solution will remove the basic copper carbonate from the alembic, especially that existing inside the condensing coil. It is known that, unfortunately, many producers do not utilize this preventive measure and end up using adsorbent substances, such as ion exchange resins or activated charcoal, for the removal of the excess copper from the beverage. However, secondary compounds can also be removed in this process. Thus, in the case of the contamination of Mozambican spirits by copper, the lack of hygiene during the production and distillation processes and the material used in the construction of the still are the main factors that could be influencing the concentrations of copper observed in this study.

The concentrations of lead observed in this work ranged from 0.6 to 3.66 mg L^{-1} in the samples analyzed. Brazilian legislation determines the maximum limit of 0.2 mg L^{-1}, which means that all the samples were contaminated with this metal at concentrations well above the legal limit.

Schoeninger and Campos (2011) evaluated lead levels in nineteen Brazilian spirit samples, observed concentrations ranging from 0.154 to 1.90 mg L^{-1}, and found that only four samples (21.05%) contained concentrations below 0.20 mg L^{-1}. Menezes et al. (2008) determined that three samples contained levels of 0.079 mg L^{-1}, 0.184 mg L^{-1} and 0.161 mg L^{-1}, these being below the legal limit.

The lead concentrations measured in samples of spirits collected in different regions of Mozambique were greater than the limits permitted by the Brazilian legislation and diverged from the values found in the studies conducted with Brazilian spirits. Most plants absorb minerals from roots or aerial parts. In this case, the presence of lead in the samples of Mozambican spirits might have been the result of contamination during fertilization or from soil contaminated by this metal because of the proximity of the cane fields to highways (Moreira and Moreira 2004).

Only five of the 13 samples analyzed contained measurable levels of zinc, which represented 38.4%, and these values ranged from 0.08 to 23.01 mg L^{-1}. The IN n°13 (Brasil 2005) does not establish a maximum limit for this metal, but it is known that, according to the WHO recommendation, its concentration should be 5 mg L^{-1} in drinking water because higher concentrations can cause depression of the immune system and gastric symptoms (Pinto et al. 2005). There were significant differences among the samples originating from different regions; the samples collected in Mafambisse contained the highest concentrations of zinc. The presence of zinc in Mozambican spirits might come from the material used in the preparation of the stills and the coils employed in the distillation stages.

Studies carried out by (Souza et al. 2010) on cachaças produced in the state of Rio de Janeiro found zinc concentrations ranging from non-detectable to 2.07 mg L^{-1}. Pinto et al. (2005) analyzed 52 samples of cachaça, and the concentrations of zinc obtained ranged from non-detectable to 3.64 mg L^{-1}, which does not exceed the maximum limit established by the World Health Organization (WHO) for water. Vilela et al. (2006), evaluating the mineral content in the stages of the sugarcane spirit production process, observed that the content varies with the contact with the metallic materials in the process stages. The authors observed a higher concentration of zinc during the distillation stage because of the material used in the construction of the still.

Regarding the analysis of iron in Mozzarella spirits, only sample 5 contained this metal (0.04 mg L^{-1}). There is no limit required by Brazilian legislation for the concentration of this metal in distilled spirits. Studies performed by Nascimento et al. (1999) with 79 samples of cachaça reported that the average levels of iron found were between 0.11 and 0.35 mg L^{-1}. According to these authors, iron, when present in certain concentrations, can alter the sensory characteristics of the beverage. The cadmium and chromium metals were not detected in the spirits collected in the regions of Mozambique.

Conclusion

Volatile compounds belonging to the classes of alcohol, ester, aromatic hydrocarbon, acetal and aldehyde were identified in the 13 samples of spirits produced in different regions of Mozambique from different raw materials, with esters being the predominant compounds. In the samples, low concentrations of glycerol were found, and no significant concentrations were detected for the trace elements zinc, iron, cadmium and chromium, whereas concentrations outside the legal limits were observed for copper and lead.

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