Critical Evaluation of As, Cd, Cu, Mn, Pb, and Zn Concentrations in Brazilian Artisanal Sugar Cane Spirits by FAAS and GFAAS Using Matrix-matched Calibration

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INTRODUCTION

Sugar cane spirit (cachaça) is a Brazilian distilled alcoholic beverage produced by fermentation of sugar cane with an alcohol content between 38 and 48% (v/v) (1). It is largely consumed in Brazil but is also one of the world's most popular spirits. Thus, quality control is very important in order to obtain a beverage suitable for national consumption, as well as for export (2, 3).

The presence of trace elements in cachaça is due to the natural absorption of nutrients from the soil by the plant (sugar cane) or by contamination either during production or storage. Therefore, the quality of cachaça can be traced to the locality where the sugar cane was cultivated and the type of process used for its production (4).

The cachaça production process involves the preparation of raw material, extraction of sugar cane juice, fermentation, and distillation (5). It is aged in wooden casks and finally bottled, distributed, and marketed (3, 6). In Brazil, especially in the region of Minas Gerais (the state known as the producer of the best and tastiest cachaça in Brazil), it is very common to find cachaça stills (7) which guarantees good taste of this beverage. However, copper may be present in the final product through condensation of the vapors over the compartments of the stills (8). Since copper favors the formation of ethyl carbamate, which is a carcinogenic compound, the beverage must be analyzed periodically (2, 9).

ABSTRACT

Sugar cane spirit (cachaça) is a distilled alcoholic beverage produced by fermentation of sugar cane and widely consumed in Brazil. Thus, for health reasons it is of great importance to evaluate its elemental concentrations. This beverage is usually distilled in copper stills, thus copper may be present in the final product as well as other metallic elements. Using matrix-matched calibration, the concentrations of Cu, Mn, and Zn were determined by flame atomic absorption spectrometry and As, Cd, and Pb by graphite furnace atomic absorption spectrometry in 19 artisanal cachaça samples from the state of Minas Gerais, Brazil. Good results were achieved in terms of sensitivity, precision, and accuracy (RSD <10% and recovery between 86 to 105%). The analytical data show that the As and Pb concentrations were below the limits (100 µg L⁻¹ and 200 µg L⁻¹, respectively) as established by the Brazilian Ministry of Agriculture (MAPA), while three samples had Cu values (10.8, 5.56, and 5.78 mg L⁻¹) above the limit established (5.0 mg L⁻¹). The samples can also be studied by employing Principal Component Analysis to establish their analyte concentrations and geographical origin.

The presence of Cu in cachaça has been investigated by several researchers (2-5, 8, 10-12). However, other trace elements, such as As, Cd, Mn, Pb, and Zn, can also be found which are known to affect the color and the taste of alcoholic beverages (2). The Decree n. 13 of the Brazilian Ministry of Agriculture (MAPA) (1) has established the

maximum allowed levels of Cu, Pb, and As at 5.0, 0.200, and 0.100 mg L⁻¹, respectively, in cachaça. The elements Cu, Mn, and Zn are micronutrients, essential to the human body for many physiological processes related to enzymes, cellular respiration, and bone metabolism, among other functions (13). However, high concentrations of these elements can cause damage to human health, affecting cellular processes and causing various problems – even cancer. On the other hand, As, Cd, and Pb have no known function in the human body and are toxic even in small quantities (13).

The determination of trace elements can be performed by flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS) depending on analyte concentration (2, 6, 10). For the analysis of cachaça samples, the calibration by matrix-matching is an alternative method to ensure an analytical curve with the same conditions as the sample, minimizing matrix effects caused by the viscosity during sample introduction by FAAS and during the pyrolysis step in GFAAS (14). The GFAAS technique is recommended for the determination of As, Cd, and Pb in food and beverage samples since they are usually present at low levels in these samples (10, 15). In the GFAAS measurements, the study of optimal pyrolysis and atomization temperatures and the use of chemical modifiers are critical steps, since the matrix can affect, in different ways, the atomization mechanism of the analytes (16, 17).

In this work, cachaça samples of artisanal origin (homemade sam-

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ples) were investigated. These samples were chosen because in Brazil, especially in Minas Gerais, it is very common to find cachaça stills on small farms, using copper stills for the distillation process. Despite the high control of hygiene during the cachaça production, the quality control of trace elements is minimal. Thus, the main objective of the present work was to investigate the levels of trace elements in Brazilian artisanal cachaça samples from the Minas Gerais state by FAAS and GFAAS, applying the method of calibration by matrix-matching and evaluating the similarities of the samples by employing principal component analysis (PCA).

EXPERIMENTAL

Instrumentation

The analytes were determined using an atomic absorption spectrometer model Solaar M5 Series, Thermo Scientific, USA. All measurements were performed in triplicate. Cu, Mn, and Zn were determined by FAAS, while As, Cd and Pb were determined by GFAAS. The deuterium background corrector (D_2) was used during analyte determination. The experimental conditions by FAAS are listed in Table I.

In the GFAAS mode, the wavelengths used were 193.7 nm (As), 228.8 nm (Cd), and 217.0 nm (Pb), with a band pass of 0.5 nm. The absorbance signals were registered in peak area. The purge gas used was argon and the gas flow was

stopped during the atomization step. For As, Cd, and Pb determination by GFAAS, normal non-pyrolitic tubes were used. Pyrolysis and atomization curves were carried out in order to obtain the optimal temperatures. The total solution volume injected into the furnace was 20 μL , then As 10 $\mu\text{g L}^{-1}$, Cd 2.0 $\mu\text{g L}^{-1}$, and Pb 10 $\mu\text{g L}^{-1}$ were added to a "test sample" named A3. This fortified sample was used for the optimization of the pyrolysis and atomization curves, the temperature ranging in increments of 100 $^{\circ}\text{C}$.

Standard Solutions, Reagents, and Samples

The standards used for the spectrometer calibration were prepared from stock solutions of each analyte with concentrations of 1000 mg L^{-1} As, Cd, Mn, and Pb (Qhemis, Joinville, Brazil), and Cu and Zn (Vetec, São Paulo, Brazil). In the FAAS analysis, the standard concentrations used for the analytical curves varied from 0.10 to 5.0 mg L^{-1} for Cu, from 0.10 to 2.0 mg L^{-1} for Mn and Zn. For GFAAS analysis, the analytical curves of As, Cd, and Pb varied from 5.0 to 30 $\mu\text{g L}^{-1}$ for As, from 0.20 to 4.0 $\mu\text{g L}^{-1}$ for Cd, and from 2.5 to 20 $\mu\text{g L}^{-1}$ for Pb. In each analytical curve, five levels of concentration were prepared. These analytical curves were prepared in 20% (v/v) ethanol (Vetec, São Paulo, Brazil) for matrix-matched calibration. The bottles and glassware used were immersed in an acid bath containing 10% (v/v)

HNO_3 for 24 hours and then rinsed with deionized water. All solutions were prepared using purified water at 18 $\text{M}\Omega\text{-cm}$ from a Milli-Q[®] Direct-Q UV system (Millipore Corporation, USA).

The 19 different artisanal cachaça samples were obtained at local markets in different cities of the Minas Gerais state, such as Juiz de Fora, Tiradentes, Salinas, Montes Claros, Betim, Nova União, and Descoberto.

Sample Analysis and Statistics

The samples were analyzed by simple dilution: 5.00 mL of sample was transferred to a 10.00-mL volumetric flask and brought to volume with deionized water. Thus, the final alcoholic concentration of the sample was around 20% (v/v). The samples were analyzed under optimized instrumental conditions.

The limits of detection (LOD) and quantification (LOQ) were calculated by multiplying the standard deviation (10 blank measurements of signal absorbance) by 3.3 and 10 (LOD and LOQ, respectively) and dividing the result by the slope of the analytical curves. To evaluate the sensitivity, the characteristic concentration (c_0) and the characteristic mass (m_0) were used for FAAS and GFAAS, respectively, calculated by dividing the slope of the byfor 0.0044. For m_0 , this result was also multiplied by the volume introduced into the tube (20 μL) (16, 18).

The precision of the method was verified through the relative standard deviation (% RSD). Since certified reference materials with similar characteristics of the samples were difficult to obtain, the accuracy of the method was evaluated through spike tests as recommended by ANVISA (19). The spike tests were performed in the levels of 1.0 mg L^{-1} for Cu, Mn, and Zn; 10 $\mu\text{g L}^{-1}$ for As; 2.0 $\mu\text{g L}^{-1}$ for Cd; and 10 $\mu\text{g L}^{-1}$ for Pb. The established method was applied to 19 cachaça samples and

TABLE I
Experimental Conditions for Cu, Mn, and Zn Determination by FAAS in Ethanolic Medium

Analytes	Wavelength (nm)	Bandpass (nm)	Gas	Flow Rate (L min^{-1})
Cu	324.8	1.0	Air/ C_2H_2	1.1
Mn	279.5	1.0	Air/ C_2H_2	1.3
Zn	213.9	1.0	Air/ C_2H_2	1.0

the obtained results were used to feed a chemometric software (Statistic® 7.0, StatSoft, USA) in order to perform an exploratory analysis by employing PCA.

RESULTS AND DISCUSSION

In this study, trace element determination in cachaça was performed through matrix-matched calibration. Cachaça contains about 40% (v/v) ethanol, but the samples were diluted with deionized water (1:2) prior to analysis. Thus, the analytical curves were prepared in 20% (v/v) ethanol. The matrix-matched calibration method was simple and fast and was used to match the conditions of the analytical curve with the samples in order to eliminate matrix interferences caused by the presence of ethanol

in the samples (4, 14). Using this method, Cu, Mn, and Zn were determined by FAAS, while As, Cd, and Pb were determined by GFAAS.

Figure 1 presents the pyrolysis and atomization curves for the GFAAS method. The optimal pyrolysis temperature obtained for As was 800 °C since no significant losses were observed up to this temperature. Above 800 °C, As volatilization occurs. For this selected pyrolysis temperature, the optimum atomization temperature was 2100 °C. For Cd, the pyrolysis temperature was 500 °C and the atomization temperature was 700 °C. For Pb, the pyrolysis temperature was 500 °C, while the atomization temperature was 1000 °C. Thus, the main instrumental parameters were evaluated for each

analyte and the chosen heating program for the graphite furnace are listed in Table II. The lifetime of the graphite tube under these conditions was greater than 1000 heating cycles.

Figures of Merit

Regarding the figures of merit, the matrix-matched analytical curves used for analyte determination by FAAS and GFAAS showed good linearity. The linear correlation coefficient of all curves was greater than 0.999, and the % RSD of the standard measurements was <10%. The LOD and LOQ were calculated and the sensitivity was evaluated by c_0 and m_0 . Spike tests were also performed for the cachaça sample, and the results are shown in Table III. It was found that the LOD and LOQ values obtained in this study are lower than the values established by the Brazilian legislation: As (LOQ 2.67 $\mu\text{g L}^{-1}$; value established: 100 $\mu\text{g L}^{-1}$), Cu (LOQ 0.96 mg L^{-1} ; value established: 5.0 mg L^{-1}), and Pb (LOQ 0.405 $\mu\text{g L}^{-1}$; value established: 200 $\mu\text{g L}^{-1}$). These are similar to the values found in the literature (8, 12, 14, 15). Thus, the method proposed in this study can be used to investigate these analytes in artisanal cachaça samples. The Brazilian legislation does not provide the

TABLE II
Heating Programs for As, Cd, and Pb Determination by GFAAS in Ethanol Medium

Step	Temperature (°C)	Ramp Time (°C s ⁻¹)	Hold Time (s)	Argon Flow Rate (L min ⁻¹)
Drying	100	10	30	0.2
Pyrolysis	800 ^a ; 500 ^{b,c}	150	20	0.2
Atomization	2,100 ^a ; 700 ^b ; 1,000 ^c	0	3	0.0
Cleaning	2,500	0	3	0.2

^a As, ^b Cd, ^c Pb.

Fig. 1. Pyrolysis (a) and atomization (b) curves by GFAAS on sample A3 with (a) As 10 $\mu\text{g L}^{-1}$, (b) Cd 2.0 $\mu\text{g L}^{-1}$ and Pb 10 $\mu\text{g L}^{-1}$.

limits for Cd, Mn, and Zn, but the developed method does present adequate sensitivity for these analytes (LOQ: 0.171 $\mu\text{g L}^{-1}$ for Cd, 0.066 mg L^{-1} for Mn, and 0.045 mg L^{-1} for Zn). The values found for m_0 and c_0 are comparable to those found in both the manufacturer's specifications and in the literature (10). It can, therefore, be stated that the sensitivity of the method was in agreement with the expected values. The accuracy was verified by spike tests and the recovery values were between 86 to 105%, indicating that the proposed method is free of matrix interferences under the optimized conditions. For the analyte determination by GFAAS, the use of chemical modifiers was not necessary since under optimized conditions the obtained results were satisfactory in terms of accuracy and precision (RSD <10% for all measurements). In addition, without the use of chemical modifiers, the method is simple and facilitates the application of the method for routine analysis.

The matrix-matched calibration method was applied to analyze 19 different samples and the results are presented in Table IV. Precision was verified through the % RSD of the measurements. For each sample ($n = 3$), the RSD values obtained were <10% for all analytes, with an

average RSD equal to 1.29% for Cu, 1.93% for Mn, 0.92% for Zn, 7.18% for As, 6.46% for Cd, and 5.87% for Pb, indicating good precision of the method.

The concentration of the samples varied from <0.096 to 10.8 mg L^{-1} for Cu, 0.381 to 0.768 mg L^{-1} for Mn, <0.045 to 0.388 mg L^{-1} for Zn, <2.67 $\mu\text{g L}^{-1}$ for As, <0.171 to 0.837 $\mu\text{g L}^{-1}$ for Cd, and <0.405 to 13.0 $\mu\text{g L}^{-1}$ for Pb. According to the Brazilian Ministry of Agriculture, the maximum permitted values for Cu, As, and Pb in cachaça are 5.00 mg L^{-1} , 100 $\mu\text{g L}^{-1}$, and 200 $\mu\text{g L}^{-1}$, respectively (1). For Cu, most of the samples showed values below the maximum allowed value. However, two samples (A8 - 5.56 mg L^{-1} and A19 - 5.78 mg L^{-1}) showed Cu concentrations above the maximum allowed value and one sample (A3 - 10.8 mg L^{-1}) showed a concentration of approximately 2-fold greater than the allowed value. Based on the results, the As and Pb concentrations in the samples were below the established maximum value. The As concentration in the samples ranged from not detected to 2.59 $\mu\text{g L}^{-1}$, but it was not possible to quantify this analyte since all samples showed values lower than the LOQ (2.67 $\mu\text{g L}^{-1}$). In comparison to the other analytes, Mn, Zn, and Cd, MAPA does not provide allowable limits.

However, it was considered important to monitor the other elements in the same samples due to their toxicity and the high consumption of cachaça in Brazil, especially in the state of Minas Gerais, since this drink is an historic and cultural symbol (4, 7, 15). The matrix-matched calibration method showed good accuracy and was simple to use. Even though the standard addition method is used to verify matrix interferences, this method is not appropriate for routine analyses since it requires a large amount of reagents and sample and is also very time-consuming. The matrix-matched calibration method, on the other hand, by matching the ethanol content could be used to minimize physical interferences, such as sample viscosity. Thus, the results demonstrated that the proposed method can be employed for regulatory programs for this kind of product, considering its speed and simplicity. In addition, the analytical results obtained for As, Cd, Cu, Mn, Pb, and Zn are comparable to those found in the literature. Table V lists the concentrations of these elements in cachaça samples obtained in this work and by other authors.

Principal Component Analysis

In order to evaluate the data in relation to its multivariate characteristics, Principal Component Analysis (PCA) was employed as an unsupervised analysis. For this statistical treatment it was necessary to adjust a dataset by autoscaling the data matrix, considering that all variables (concentration of Cu, Mn, Zn, As, Cd, Pb) have at least equal importance in the interpretation of the results (20-22). The table with the autoscaled data matrix was obtained by subtracting the data from the mean value for each sample and for each variable (analyte) and dividing the result by the standard deviation of the data set.

TABLE III
Limits of Detection (LOD), Limits of Quantification (LOQ),
Characteristic Concentration (c_0), Characteristic Mass (m_0),
and Recovery (% Rec.)

Analytes	LOD	LOQ	c_0 (mg L^{-1})	m_0 (pg)	Rec. (%)
Cu	0.032 ^a	0.096 ^a	0.143	-	98.6
Mn	0.022 ^a	0.066 ^a	0.106	-	97.8
Zn	0.015 ^a	0.045 ^a	0.033	-	104
As	0.88 ^b	2.67 ^b	-	29.3	86.5
Cd	0.057 ^b	0.171 ^b	-	0.46	105
Pb	0.135 ^b	0.405 ^b	-	5.22	94.4

^a mg L^{-1} (FAAS), ^b $\mu\text{g L}^{-1}$ (GFAAS).

TABLE IV
Results for Trace Element Determination in Cachaça Samples
Cu, Mn, and Zn Determined by FAAS and As, Cd, and Pb by GFAAS. Concentration $\pm$ Standard Deviation (n = 3)

Sample	Concentration (mg L ⁻¹)			Concentration (µg L ⁻¹)		
	Cu	Mn	Zn	As ^a	Cd	Pb
A1	0.96 $\pm$ 0.01	0.46 $\pm$ 0.02	0.19 $\pm$ 0.01	1.40 $\pm$ 0.17	0.84 $\pm$ 0.06	1.39 $\pm$ 0.14
A2	0.14 $\pm$ 0.01	0.38 $\pm$ 0.02	0.11 $\pm$ 0.01	0.89 $\pm$ 0.06	< 0.171	0.58 $\pm$ 0.01
A3	10.8 $\pm$ 0.01	0.43 $\pm$ 0.01	< 0.045	< 0.88	< 0.171	0.81 $\pm$ 0.08
A4	0.18 $\pm$ 0.01	0.38 $\pm$ 0.01	0.11 $\pm$ 0.01	< 0.88	< 0.171	0.60 $\pm$ 0.03
A5	2.15 $\pm$ 0.01	0.49 $\pm$ 0.01	0.39 $\pm$ 0.01	< 0.88	< 0.171	3.80 $\pm$ 0.11
A6	1.83 $\pm$ 0.01	0.38 $\pm$ 0.01	0.18 $\pm$ 0.01	< 0.88	< 0.171	6.46 $\pm$ 0.22
A7	1.83 $\pm$ 0.01	0.45 $\pm$ 0.01	0.18 $\pm$ 0.01	1.16 $\pm$ 0.10	< 0.171	1.93 $\pm$ 0.16
A8	5.56 $\pm$ 0.05	0.44 $\pm$ 0.02	0.23 $\pm$ 0.01	0.49 $\pm$ 0.06	0.23 $\pm$ 0.02	6.62 $\pm$ 0.23
A9	< 0.096	0.42 $\pm$ 0.01	0.14 $\pm$ 0.01	< 0.88	< 0.171	1.01 $\pm$ 0.08
A10	0.34 $\pm$ 0.01	0.49 $\pm$ 0.01	< 0.045	1.48 $\pm$ 0.14	< 0.171	2.60 $\pm$ 0.19
A11	4.24 $\pm$ 0.02	0.48 $\pm$ 0.01	< 0.045	2.59 $\pm$ 0.14	< 0.171	0.61 $\pm$ 0.05
A12	0.14 $\pm$ 0.01	0.46 $\pm$ 0.01	< 0.045	< 0.88	< 0.171	< 0.405
A13	0.13 $\pm$ 0.01	0.60 $\pm$ 0.01	< 0.045	1.01 $\pm$ 0.12	< 0.171	< 0.405
A14	< 0.096	0.59 $\pm$ 0.01	< 0.045	1.13 $\pm$ 0.07	< 0.171	< 0.405
A15	2.61 $\pm$ 0.01	0.77 $\pm$ 0.01	0.29 $\pm$ 0.01	1.74 $\pm$ 0.08	< 0.171	4.85 $\pm$ 0.46
A16	4.98 $\pm$ 0.01	0.71 $\pm$ 0.01	0.17 $\pm$ 0.01	< 0.88	0.42 $\pm$ 0.03	10.8 $\pm$ 1.0
A17	4.09 $\pm$ 0.05	0.54 $\pm$ 0.01	0.22 $\pm$ 0.01	< 0.88	0.25 $\pm$ 0.01	13.0 $\pm$ 0.3
A18	1.29 $\pm$ 0.02	0.56 $\pm$ 0.01	0.18 $\pm$ 0.01	1.50 $\pm$ 0.10	0.18 $\pm$ 0.01	7.71 $\pm$ 0.18
A19	5.78 $\pm$ 0.02	0.50 $\pm$ 0.01	0.17 $\pm$ 0.01	2.54 $\pm$ 0.01	< 0.171	12.1 $\pm$ 0.2
Mean	2.76	0.50	0.20	1.40	0.38	4.68
Min.	< 0.096	0.38	< 0.045	< 0.88	< 0.171	< 0.405
Max.	10.8	0.77	0.39	2.59	0.84	13.0

^a = As concentration values < LOQ (2.67 µg L⁻¹).

TABLE V
Comparison of Results Obtained for Cu, Mn, Zn, As, Cd and Pb in Brazilian Cachaça Samples

Reference	Concentration (mg L ⁻¹)			Concentration (µg L ⁻¹)		
	Cu	Mn	Zn	As	Cd	Pb
This work	<0.096 - 10.8	0.381 - 0.768	<0.045 - 0.388	<2.67	<0.171 - 0.837	<0.405 - 13
2	3.5 - 12.6	-	-	-	-	-
3	0.55 - 34.0	-	-	-	-	-
4	7.78 - 15.57	-	-	-	-	-
5	0.19 - 22.3	-	-	-	-	-
8	<0.06 - 21.3	-	<0.006 - 3.64	-	-	-
10	0.05 - 8.10	-	-	-	-	-
11	0.67 - 6.70	-	-	-	-	-
12	<0.140 - 5.382	-	-	<1.3	-	1.8 - 216
14	-	<0.014	-	<2.3	-	-
15	-	-	-	-	<0.23 - 0.7	<1.98 - 526

PCA was performed from autoscaled data. Figure 2a shows the sample distribution in which PC1 and PC2 accounts for 54.4% of the explanation. In this figure, six groups were observed with samples 10, 13, 14 (group 1); 2, 4, 9, 12 (group 2); 7, 6 (group 3); 1, 5, 8 (group 4); 15, 19 (group 5); and 16, 17 (group 6). The samples were classified according to the concentration levels of the analytes. For example, samples 6 and 7 had similar values of Cu, Mn, and Zn. However, samples 3, 11, and 18 were not included in any of the groups, since they had a different composition than all of the other samples. For example, sample 3 had the highest value of Cu, while samples 11 and 18 showed similar results for Mn and Pb, but different results for Cu.

On the other hand, the geographical origin of cachaça can also influence the obtained data. Samples 16 and 17 are from the same region and showed similar values for all analytes. The trace elements Mn and Cu seem to be from similar sources, since they are very close in Figure 2b. Thus, classification of the samples includes factors such as type of soil (as well as type of fertilizer and herbicide used

in cultivation), where the sugar cane was grown, characteristics of the production process, and storage of the beverage. However, since the multivariate analysis is capable to show composition patterns, this tool may be useful for the identification of intrinsic characteristics of the samples related to the production site, and also for the investigation of possible sources of contamination.

CONCLUSION

The matrix-matched calibration method allowed for the FAAS determination of Cu, Mn and Zn, and the GFAAS determination of As, Cd, and Pb in artisanal cachaça samples. The method is simple and fast requiring no sample digestion. The spike tests showed recoveries from 86 to 105%, indicating that the method is free of matrix interferences and has good accuracy, even without the use of chemical modifiers and without a pyrolytic graphite tube for GFAAS analysis.

The method was applied to 19 Brazilian artisanal cachaça samples with adequate precision and sensitivity. All results for As and Pb were below the limit established by the Brazilian legislation ($100 \mu\text{g L}^{-1}$ and $200 \mu\text{g L}^{-1}$, respectively). The

results for Cu varied from <0.096 to 10.8 mg L^{-1} . Most of the samples showed values below the maximum allowed value for Cu (5.0 mg L^{-1}), but three samples were above this value (10.8, 5.56, and 5.78 mg L^{-1}). The samples were also classified by PCA according to the concentration levels of the analytes. This means that different contamination profiles can be found, even though their concentrations are low. The results of this study also show that the metals investigated can be used to characterize Brazilian cachaça in relation to its inorganic composition.

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Fig. 2. PC1 versus PC2. (a) Scores plot and (b) loadings plot of cachaça samples.

REFERENCES

1. <http://imanet.ima.mg.gov.br/nova/gec/legislacao/mapa/in13.pdf>. Accessed in 19.12.2014. MAPA Ministério da Agricultura, Pecuária e Abastecimento, Instrução Normativa Nº 13. Regulamento Técnico para Fixação dos Padrões de Identidade e Qualidade para Aguardente de Cana e para Cachaça (2005).
2. E. A. Neves, A. Oliveira, A. P. Fernandes and J. A. Nóbrega, *Food Chem.* 101, 33 (2007).
3. L. F. S. Caldas, B. B. A. Francisco, A. D. P. Netto and R. J. Cassella, *Microchem. J.* 99, 118 (2011).
4. F. G. Pinto, S. S. Rocha, M. H. Canuto, H. G. L. Sielbald and J. B. B. Silva, *Revista Analytica* 17, 48 (2005).
5. R. Garbin, S. B. Junior and M. A. Montano, *Ciência Rural* 35, 1436 (2005).
6. J. G. Ibanez, A. Carreon-Alvarez, M. Barcena-Soto and N. Casillas, *J. Food Comp. Anal.* 21, 672 (2008).
7. http://www.agencia.cnptia.embrapa.br/Repositorio/Cachaca_de_Minas_000fjd717w802wyiv809gkz51uz0mxbc.pdf Accessed in: 06 July 2015. Silva, L. H. A., Rocha, L. E. V., Lima, I. B. And Santos, G. C. 2006. Cachaça de Minas e desenvolvimento rural: uma análise do cooperativismo como impulso para o agronegócio.
8. K. Miranda, A. G. G. Dionísio and E. R. Pereira-Filho, *Microchem. J.* 96, 99 (2010).
9. A. M. R. Machado, M. G. Cardoso, A. A. Saczk, J. P. Anjos, L. M. Zacaroni, H. S. Dórea and D. L. Nelson, *Food Chem.* 138, 1233 (2013).
10. N. M. Caldas, J. L. Raposo Jr., J. A. G. Neto and F. Barbosa Jr., *Food Chem.* 113, 1266 (2009).
11. R. A. Labanca, M. B. A. Glória, V. J. P. Gouveia and R. J. C. F. Afonso, *Quim. Nova* 29, 1110 (2006).
12. S. A. N. Rocha, A. F. Dantas, H. V. Jaeger, A. C. S. Costa, E. S. Leão and M. R. Gonçalves, *Spectrochim. Acta A* 71, 1414 (2008).
13. F. A. Azevedo and A. A. M. Chasin, *Metais: gerenciamento da toxicidade*. São Paulo: Atheneu (2003).
14. M. H. Canuto, H. G. L. Sielbald, M. B. Franco and J. B. B. Silva, *At. Spectrosc.* 25, 140 (2004).
15. D. Oshita, A. P. Oliveira, J. A. Gomes Neto and M. Moraes, *Ecl. Quim.* 28, 91 (2003).
16. A. M. S. Mimura, M. A. L. Oliveira, V. S. T. Ciminelli and J. C. J. Silva, *Journal of AOAC International* 99(1), 1 (2016).
17. J. B. B. Silva, *Quim. Nova* 27, 528 (2004).
18. B. Welz, *Atomic Absorption Spectrometry*. 2nd ed. VCH (1985).
19. <http://www.anvisa.gov.br/divulga/public/series/laboratorios.pdf>. Accessed in 30.08.2015. ANVISA, Guia para Qualidade em Química Analítica. Uma Assistência à Habilitação.
20. P. R. M. Correia and M. M. C. Ferreira, *Quim. Nova* 30, 481 (2007).
21. A. P. Fernandes, M. C. Santos, S. G. Lemos, M. M. C. Ferreira, A. R. A. Nogueira and J. A. Nóbrega, *Spectrochim. Acta B* 60, 717 (2005).
22. R. A. Sousa, W. B. Neto, R. J. Poppi, N. Baccan and S. Cadore, *Quim. Nova*, 29, 654 (2006).