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# Physicochemical, microbiological and microscopic evaluation of artisanal rapaduras produced in Cuiabá, Mato Grosso, Brazil

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**ABSTRACT.** The aim of this work was the physicochemical, microbiological and microscopic evaluation of artisanal rapaduras produced in Cuiabá, Mato Grosso State, Brazil. The determination of the proximal composition, pH and the microscopic analyses were made according to the Association of Official Analytical Chemists (AOAC). The concentrations of minerals and toxic metals were quantified by flame atomic absorption spectrometry. The Coliforms at 45°C and *Salmonella sp*. were determined according to the American Public Health Association (APHA). The results obtained were: moisture (6.09 to 16.34%), ash (0.07 to 1.88%), insoluble solids (0.11 to 11.3%), pH (4.73 to 5.61), proteins (0.21 to 0.47%), sucrose (13.15 to 43.89%), and reducing sugars (10.96 to 26.28%). Significant differences were found between the samples ($p \leq 0.05$) as well as nonconformities in relation to national regulations. The mineral contents showed significant differences between lots of samples ($p \leq 0.05$) and some lots presented Cd and Pb concentrations above the maximum values allowed by Brazilian legislation. High quantities of unwanted materials were detected and none of the samples presented microbiological contamination. The results suggest the creation of technical standards for quality control for the production of rapaduras to ensure food safety.

**Keywords:** quality, food safety, non-centrifugal sugar, chemical composition.

## Avaliação físico-química, microbiológica e microscópica de rapaduras artesanais produzidas na cidade de Cuiabá, Mato Grosso, Brasil

**RESUMO.** O objetivo deste trabalho foi a avaliação físico-química, microbiológica e microscópica de rapaduras artesanais produzidas em Cuiabá, Mato Grosso, Brasil. A determinação da composição proximal, pH e as análises microscópicas foram feitas de acordo com a *Association of Official Analytical Chemists* (AOAC). As concentrações dos minerais e metais tóxicos foram quantificadas por espectrometria de absorção atômica em chama. Os Coliformes a 45°C e *Salmonella SP* foram determinados de acordo com a *American Public Health Association* (APHA). Os resultados obtidos foram: umidade (6,09 a 16,34%), cinzas (0,07 a 1,88%), sólidos insolúveis (0,11 a 11,3%), pH (4,73 a 5,61), proteínas (0,21 a 0,47%), sacarose (13,15 a 43,89%) e açúcares redutores (10,96 a 26,28%). Diferenças significativas foram encontradas ($p \leq 0,05$) entre as amostras, bem como, inconformidades em relação a regulações nacionais. O conteúdo mineral apresentou diferenças significativas entre os lotes das amostras ($p \leq 0,05$) e alguns destes apresentaram concentrações de Cd e Pb acima dos valores máximos permitidos pela Legislação Brasileira. Foram detectadas elevadas quantidades de matérias estranhas e nenhuma das amostras apresentou contaminação microbiológica. Os resultados sugerem a criação de normas técnicas de controle de qualidade para a produção de rapaduras a fim de garantir a segurança alimentar.

**Palavras-chave:** qualidade, segurança alimentar, açúcar não centrifugado, composição química.

## Introduction

Rapadura - also known as non-centrifugal raw cane sugar, raw cane sugar, molasses, brown sugar, panela, papelon, jaggery, chancaca, piloncillo, gur, kokuto in other countries - is a solid product that comes from concentrating the hot broth of previously clarified sugar cane (*Saccharum officinarum*

*L.*); other ingredients may be added as long as they do not mischaracterize the final product (Brasil, 2005; Sarwar et al., 2009).

This food has a high nutritional value due to the presence of carbohydrates, proteins, vitamins and minerals such as potassium, calcium and iron, besides having characteristics of a natural and

organic product (Jaffe, 2015). Moreover, it can be considered an integral sweetener that preserves most of the nutrients present in sugar cane, making it possible to preserve a greater nutritional value when compared to refined sugar and other synthetic sweeteners (Mujica, Guerra, & Soto, 2008; Generoso et al., 2009; Guerra & Mujica, 2010; Maria, Correal, & Jaffe, 2013; Jaffe, 2015).

Some authors also report medicinal properties associated with the consumption of rapadura, such as decreased pulmonary lesions associated with smoking, reduced clastogenic effects caused by arsenic, high antioxidant action and an anti-sclerotic function (Jaffe, 2012).

Rapadura is produced and consumed in several countries in the world—India being the world's largest producer with approximately 6.8 million tons per year, and responsible for 67% of the world's production. In Latin America, Colombia is the largest producer and consumer, with a production of 1.5 million tons per year and an average consumption estimated at 19 kg per inhabitant per year (Mujica et al., 2008; Generoso et al., 2009; Guerra & Mujica, 2010).

Brazil is the fifth largest producer worldwide and the second in Latin America, with an annual production of 420,000 tons and with an average consumption of approximately 1.5 kg per inhabitant per year. In Brazil, rapadura is traditionally consumed by the population of the north, northeast and midwest, being marketed in most cities in these regions at farmers' markets and, to a lesser extent, in supermarkets. Currently, the Brazilian School Feeding Program (PNAE) considers rapadura a staple food and estimates that approximately 45 million meals served in public schools contain this product (Centec, 2004; Silva, Cristale, Ribeiro, & Marchi, 2011).

Rapadura production in Brazil is basically a traditional agro-industrial and artisanal process, being characterized by poorly organized production using rudimentary methods, creating a lack of control over the physical, chemical and microbiological aspects of this food and exposing it to the presence of materials, micro-organisms and chemicals harmful to human health. Furthermore, due to the lack of product surveillance, tampering is common in the manufacturing process of rapadura, decreasing its nutritive value (Delgado & Delgado, 1999).

However, despite the fact that rapadura is a widely consumed product in Brazil and part of school lunches in many municipalities, there are few scientific studies related to quality control, and in addition, no current legislation is related to physical-chemical quality of this product.

With this in mind, the aim of this study was the physicochemical, microbiological and microscopic evaluation of artisanal rapadura produced in Cuiabá city, Mato Grosso State, Brazil.

## Material and methods

Two artisanal solid rapadura lots of nine samples produced in Cuiabá were collected and identified by number. The samples were then divided into four parts, reduced to laboratory samples, powdered and stored in previously decontaminated containers and kept in a cool, dry place.

The ash content was determined using the incineration residue obtained by heating in a muffle furnace (Fornitec®, Model MDS) at 550°C, the moisture gravimetrically by drying in a kiln (FANEM® 520, Model A-HT) at 100°C at atmospheric pressure. The quantification of the reducing sugars into glucose and non-reducing sugars into sucrose were made by volumetry using the Fehling method. Protein content was determined using a modified Kjeldahl method (TECNAL®, model TE-0363). The percentage of insoluble solids was determined by gravimetry (Analytical balance Marte®, model AW220 with accuracy of ± 0.0001 g). The potential of hydrogen (pH) was determined by direct potentiometry in an aqueous solution of 10% (w v$^{-1}$) (pH meter Tecpon®). All determinations were made in triplicate, according to the recommendations of the Association of Official Analytical Chemists (AOAC, 2012) and the Instituto Adolfo Lutz (IAL, 2008).

Analysis of variance (ANOVA) with the post-hoc Tukey test ($p < 0.05$) was used to identify any significant differences among the samples. These statistical procedures were performed using Assistat® software version beta 7.7.

The results obtained for the proximal composition were compared with the national technical standards of physicochemical quality for solid rapaduras from Ecuador NTE INEN 2331 (Instituto Ecuatoriano de Normalización [Inen], 2002), Colombia NTC 2546 (Republic of Colombia, 2004) and India (Food Safety and Standards Authority of India, 2011) - since Brazil does not have specific technical standards applicable to the control of physical-chemical quality of rapaduras - and with the analytical values reported by the Brazilian Table of Food Composition (TACO, 2011).

The concentrations of the minerals [sodium (Na), potassium (K), magnesium (Mg), iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn)) and potentially toxic metals (cadmium (Cd), chromium (Cr) and lead (Pb)] were determined by direct dilution of the rapadura samples into deionized

water at a ratio 1.0% (w v$^{-1}$) and subsequent quantification by flame atomic absorption spectrometry (FAAS) (Flores et al., 2007).

For the quantification of analyses, FAAS analyses were performed using a SpectrAA 220 instrument (Varian®) fitted with hollow cathode lamps. The aspiration rate of the working standard solutions or samples was adjusted to 2.00 ± 0.2 mL min$^{-1}$. The measurements were carried out according to the manufacturer's recommendations.

An analytical balance with an accuracy of ± 0.0001 g (Model AW 220, Marte, São Paulo State, Brazil) was used for weighing the samples. Micropipettes (Boeco, Germany) with adjustable volumes of 5-50, 50-200, and 100-1000 $\mu$L were used for the preparation of the standard solutions.

High purity deionized water (resistivity 18.2 MΩ cm, Milli-Q system, Millipore®, Bedford, MA, USA) was used for the preparation of the standard solutions and samples. The standard solutions were prepared by sequential dilution of 1000 mg L$^{-1}$ aqueous stock solutions (Carlo Erba®, Italy). All flasks and glassware were washed with tap water, immersed in 6.0% (v v$^{-1}$) HNO$_3$ solution for at least 24 hours, and rinsed thoroughly with deionized water.

The determination of the limits of detection (LD) and linear correlation coefficients employed analytical curves constructed using the external standardization method. The following concentration ranges (in mg L$^{-1}$) were used: 0.0-100.0 (Na); 0.0-6.0 (K); 0.0-100 (Ca); 0.0-25.0 (Mg); 0.0-10.0 (Fe); 0.0-8.0 (Pb); 0.0-5.0 (Cu); 0.0-3.0 (Zn); 0.0-0.5 (Mn); 0.0-3.0 (Cd); 0.0-1.0 (Cr). The LD values were determined according to the method described by Currie (1999). All measurements were made in triplicate ($n = 3$).

The ANOVA with the post-hoc Tukey test ($p < 0.05$) was used to identify any significant differences among the samples and lots. These procedures were performed using Assistat® software version beta 7.7.

The concentrations of minerals and toxic metals determined in the samples were compared with the values suggested by TACO (2011), and the maximum values allowed by Decree No. 55871 of 26 March 1965 by the Brazilian Sanitary Surveillance Agency that provides limits for heavy metals in foods, such as incidental additives (Brasil, 1965), and Resolution No. 42, of 29 August 2013 by the Brazilian Sanitary Surveillance Agency that provides technical regulations for the Southern Commom Market (Mercosul) on maximum levels of inorganic contaminants in food (Brasil, 2013) .

Microbiological analyses were done according to RDC Resolution No. 12 of 2 January 2001 by the Brazilian Sanitary Surveillance Agency, which approves the technical regulations on microbiological standards for food and determines that for rapaduras should be analyzed for coliforms at 45°C g$^{-1}$ (mL) and *Salmonella* sp 25 g$^{-1}$ (mL) (Brasil, 2001).

To determine the most probable number (MPN) of coliform bacteria at 45°C and *Salmonella* sp., published methodologies referenced by APHA (American Public Health Association) (Swanson, Mislivec, Hitchins, & Lancette, 1992) were used.

The microscopic evaluation was made according to guidelines from the method 945.79 by AOAC (2012). For evaluation of macroscopic and microscopic materials standards defined by the Brazilian Sanitary Surveillance Agency in RDC Resolution No. 14 of 28 March 2014 were used, which define the tolerance limits and other measures for macroscopic and microscopic foreign matter in food and beverages (Brasil, 2014).

## Results and discussion

The results obtained for the determination of the proximal composition are shown in Table 1.

Significant differences were also observed ($p \leq 0.05$) in relation to the percentage of insoluble solids and, six samples exhibited insoluble solids content in accordance with the maximum values allowed by Indian and Ecuadorian laws; samples 1, 6 and 7 had values above the stipulated amount.

**Table 1.** Proximal composition and pH (mean ± relative standard deviation %, $n = 3$) of artisanal rapaduras.

| Sample | Insoluble solids | Moisture | Ash | Protein | Reduction Sugars | Sucrose | pH |
|---|---|---|---|---|---|---|---|
| | g 100 g$^{-1}$ | | | | | | |
| 1 | 2.43±0.01[bc] | 6.34±0.03[b] | 0.63±0.03[b] | 0.21±0.27[a] | 17.19±0.14[ab] | 31.36±0.14[a] | 5.43±0.00[a] |
| 2 | 0.92±1.31[c] | 7.13±0.01[b] | 0.56±0.25[b] | 0.28±0.28[a] | 18.68±0.07[ab] | 27.73±0.01[a] | 4.94±0.04[bc] |
| 3 | 0.41±1.23[c] | 6.17±0.04[b] | 0.41±0.47[b] | 0.33±0.35[a] | 20.22±0.09[ab] | 26.21±0.80[a] | 4.90±0.01[c] |
| 4 | 0.31±0.83[c] | 8.27±0.03[b] | 1.88±0.25[a] | 0.31±0.56[a] | 17.47±0.37[ab] | 27.13±0.93[a] | 5.45±0.03[a] |
| 5 | 0.32±1.04[c] | 8.45±0.14[b] | 0.36±0.52[b] | 0.25±0.47[a] | 16.28±0.01[ab] | 32.77±0.14[a] | 4.88±0.00[c] |
| 6 | 9.56±0.25[a] | 16.34±0.02[a] | 0.07±0.45[b] | 0.35±0.22[a] | 10.96±0.05[b] | 43.89±0.26[a] | 5.35±0.03[ab] |
| 7 | 11.30±0.43[a] | 7.65±0.04[b] | 0.49±0.05[b] | 0.47±0.12[a] | 14.37±0.16[b] | 33.63±0.19[a] | 5.61±0.01[a] |
| 8 | 0.11±0.49[c] | 6.09±0.21[b] | 0.30±0.67[b] | 0.22±0.50[a] | 26.28±0.04[a] | 21.45±1.10[b] | 4.73±0.01[c] |
| 9 | 0.79±0.26[c] | 8.03±0.00[b] | 0.37±0.04[b] | 0.26±0.64[a] | 20.07±0.03[ab] | 13.15±1.04[c] | 5.47±0.00[a] |
| TACO | - | 7.1 | 1.1 | 1 | - | - | - |
| India | 2 (Max) | 10 (Max.) | 6 (Max) | - | - | 60 (Min.) | - |
| Colombia | - | 9.0 (Max.) | 0.8 (Min.) | 0.2 (Min.) | 5.5 (Min) | 83 (Max.) | - |
| Ecuador | 1 (Max.) | 7.0 (Max.) | - | - | 5.5 -10 | 75-83 | 5.9 (Min.) |

Values followed by the same letter (a, b, or c) in the same column indicate no significant difference between the samples at the 5% confidence level.

The high percentage of insoluble solids in rapaduras can be attributed to the use of hydrated lime to correct the acidity of the juice that generates the formation of insoluble calcium phosphates and contamination of sediments in the clarification stage (Mosquera, Carrera, & Villada, 2007).

Moisture is considered an important parameter for the quality of rapadura, since high values can promote inversion of sugars and the formation of mold, thus resulting in the formation of decomposition products unfavorable to sensory characteristics and the quality of the food (Tiwari, Sanjeev, & Prakash, 2004; Mosquera et al., 2007). With the exception of sample 6, all samples had moisture content according to the maximum allowed by India and Colombia. Regarding values in accordance with maximum values allowed by Ecuadorian law, only samples 1, 3 and 8 are in accordance for the moisture content. Only sample 6 showed significant differences ($p \leq 0.05$) compared to the moisture content, and this difference can be attributed to the packaging and storage of the product. Mosquera, Carrera, and Villada (2007) suggests adding a drying step during the production process of the rapaduras (banging step) in order to reduce moisture and ensure the same quality. Sarwar et al. (2009) states that the type of cane sugar and the form of storage of rapadura can also influence the variation of moisture content.

All samples revealed levels of ash according to the maximum value allowed by Indian law and the Colombian rule; only sample 4 meets the minimum stipulated value. Sample 4 also showed a value above what is reported by Taco, and significant differences ($p \leq 0.05$) in comparison with other samples. The ash content is an important parameter of rapadura quality as it indicates the amount of essential minerals present in the food. However, higher values may be associated with excessive use of hydrated lime in the clarification stage, or the use of hydrated lime with a high level of impurities (Mosquera et al., 2007; Mujica et al., 2008; Guerra & Mujica, 2010).

All pH values in the samples are below the minimum stipulated by the Ecuadorian norm, which is 5.9 and showed significant differences ($p \leq 0.05$) between them. Low pH values may be associated with the inefficient use of hydrated lime in the juice clarification step, which makes removal of impurities difficult and promotes the inversion of sucrose (Guerra & Mujica, 2010).

There were no significant differences in the samples ($p > 0.05$) in relation to the percentage of protein, and they are in accordance with the minimum value allowed by Colombian legislation.

The levels of reducing sugars present in the samples are higher than allowed by Ecuadorian law and, as for the Colombian standards, meet all the minimum values allowed. Significant differences ($p \leq 0.05$) were found between the samples, which can be attributed to the use of non-standardized processes among producers. High levels of reducing sugars can be linked to the broth processing at high temperatures, which is undesirable to the quality of rapadura, as it increases the hygroscopicity, and consequently affects the texture and stability of the final product (Verma & Maharaj, 1990; Tiwari et al., 2004).

The percentage of sucrose in the samples ranged from 13.15 to 43.89%, and significant differences ($p \leq 0.05$) were found. These results are well below those stipulated by the technical standards of Ecuador and India. Uppal, Sharma, and Sidhu (2002) found sucrose levels between 88.4 and 90.2% in rapadura produced in India. Low sucrose values can be assigned to the sucrose inversion caused by factors such as the variety of raw material, degree of maturity and type of cut of sugar cane, humidity, broth acidification, conditions and storage time (Mosquera et al., 2007).

The Table 2 shows the results obtained in the determination of the concentration of essential minerals and heavy metals in the artisanal rapadura samples.

The mineral with the highest concentration in most of the batches was K, followed by Ca and Mg. These results are in accordance with the work described by Jaffe (2015), indicating that these minerals are the ones with the highest concentration in the rapadura.

The K values found in all samples are below the recommended by TACO, and significant differences were found ($p \leq 0.05$) between batches of the same sample, except for samples 1 and 9. For calcium, 25% of samples had Ca values above the recommended values, and no significant differences were observed between batches of the same sample, except for sample 9. As for Mg, only sample 1 presented levels above the indicated values, while other samples were below the values reported by TACO and, except for samples 1 and 9, significant differences were observed between batches ($p \leq 0.05$).

The values of K, Ca and Mg found in this study are below those reported in the literature. Guerra and Mujica (2010) determined the mineral composition of Venezuelan commercial and handmade granulated rapadura where concentrations ranged from 246.5 to 936.0 mg K 100 $g^{-1}$, 132.35 to 256.07 mg Ca 100 $g^{-1}$ and 28.26 to 102.58 mg $Mg^{-1}$ 100 g.

**Table 2.** Mineral composition and potentially toxic metals concentration (mean ± relative standard deviation %, n = 3) of artisanal Brazilian rapaduras.

| Sample | Lot | Ca | K | Mg | Fe | Na | Mn | Zn | Cu | Cr | Pb | Cd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | mg kg^{-1} | | | | | | |
| 1 | A | 646.1±6.6[a] | 36.2±4.4[a] | 772.8±7.1[a] | 21.5±4.6[a] | ≤ LD | 6.6±2.8[a] | 0.23±0.0[a] | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| | B | 631.3±2.7[a] | 37.4±2.9[a] | 774.2±4.3[a] | 18.4±4.7[b] | ≤ LD | 5.2±2.4[b] | 0.17±4.0[b] | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 2 | A | 555.9±3.1[a] | 1355.9±1.1[a] | 92.9±0.5[b] | 4.7±2.1[b] | 56.3±6.7 | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD | 1.2±0.0 |
| | B | 555.9±3.1[a] | 32.8±4.5[b] | 142.3±2.9[a] | 12.1±4.0[a] | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD | 3.3±0.0 | ≤ LD |
| 3 | A | 98.7±1.2[a] | 1394.3±0.6 | 41.1±1.0[b] | 1.2±7.9[b] | 59.9±4.1 | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD | 1.2±0.1 |
| | B | 98.7±1.2[a] | AV* | 71.1±2.4[a] | 16.4±3.5[a] | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 4 | A | 448.5±0.7[a] | 1398.7±1.1[a] | 94.4±0.5[b] | 3.6±4.0[b] | 60.7±6.3[a] | 0.5±8.3[b] | ≤ LD | ≤ LD | ≤ LD | ≤ LD | 1.2±0.1 |
| | B | 448.5±0.7[a] | 94.7±7.4[b] | 476.7±2.9[a] | 35.2±2.7[a] | 60.7±6.3[a] | 11.7±3.6[a] | 0.18±0.0 | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 5 | A | 35.6±6.7[a] | 1530.0±0.5[a] | 332.0±0.5[a] | 41.1±1.0[a] | 85.0±1.7[b] | 14.5±1.2 | ≤ LD | 2.2±6.8 | ≤ LD | 5.9±0.0 | 1.3±0.0 |
| | B | 35.6±6.7[a] | 26.8±7.4[b] | 39.0±8.2[b] | 15.0±8.2[b] | 355.6±4.1[a] | ≤ LD | 0.07±9.4 | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 6 | A | 68.5±1.1[a] | 4370.9±0.4[a] | 43.5±1.9[a] | 10.4±2.4 | 563.9±0.7 | 0.34±0.0 | ≤ LD** | ≤ LD | ≤ LD | 2.6±0.0 | ≤ LD |
| | B | 68.5±1.1[a] | 24.8±3.2[b] | 25.7±3.8[b] | ≤ LD | ≤ LD | ≤ LD | 0.06±10.9 | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 7 | A | 40.6±5.8[a] | 3971.4±0.2[a] | 95.7±1.3[a] | 1.29±0.0[b] | 497.8±0.5[a] | ≤ LD | ≤ LD | 1.2±0.0 | ≤ LD | ≤ LD | ≤ LD |
| | B | 40.6±5.8[a] | 28.5±5.4[b] | 39.3±3.4[b] | 18.3±0.5[a] | 84.7±18.9[b] | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 8 | A | 45.2±4.1[a] | 3747.7±0.6[a] | 53.1±3.8[a] | 9.5±3.5[b] | 459.6±0.9 | 0.61±0.0 | ≤ LD | 1.0±0.0 | ≤ LD | ≤ LD | 1.0±0.0 |
| | B | 45.2±4.1[a] | 25.5±8.2[b] | 33.6±7.8[b] | 24.6±0.1[a] | ≤ LD | ≤ LD | 0.08±8.3 | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| 9 | A | 180.1±4.0[b] | 27.4±6.0[a] | 281.4±3.4[a] | 31,4±0,1[a] | 545.4±0.3 | 8.9±2.9[b] | 0.21±3.3[a] | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| | B | 208.6±2.7[a] | 27.7±4.1[a] | 269.1±7.2[a] | 32,5±4.1[a] | ≤ LD | 9.5±0.9[a] | 0.18±3.3[b] | ≤ LD | ≤ LD | ≤ LD | ≤ LD |
| Taco | | 300 | 4590 | 470 | 44 | 220 | 16.6 | 6.0 | 1.7 | - | - | - |
| Brasil (1965) | | - | - | - | - | - | - | 50 | 30 | 0.10 | 0.80 | 1.0 |
| Brasil (2013) | | - | - | - | - | - | - | - | - | - | 0.10 | - |

*Anomalous Value; LD: instrumental detection limit; Values followed by the same letter (a, b, c, or d) in the same column indicate no significant difference between the samples at the 5% confidence level.

The Fe concentrations are below the analytical results reported by Taco in all samples, and significant differences were found (p ≤ 0.05) between batches, except for sample 9. The Fe content in the samples was found close to the values obtained in other papers. Guerra and Mujica (2010) found results in the concentration range from 1,60 to 3.87 mg 100 g^{-1} of Fe. The use of rapadura for improved child nutrition, especially to meet the needs of Fe, was the result of a study by Arcanjo, Pinto, Arcanjo, Amici, and Amâncio (2009) who reported on the importance of using rapadura in children's school meals to prompt a reduction in anemia due to increased hemoglobin levels.

Five samples of rapadura presented batches with levels of Na above those reported by TACO, and significant differences were found (p ≤ 0.05) among the batches regarding this element. All samples showed levels of Zn, Mn and Cu below the values reported by TACO and significant differences were also found among the batches. Guerra and Mujica (2010) found levels from 24.8 to 45.4 mg Na 100 g^{-1}, 0.4 to 0.5 mg Zn 100 g^{-1}, 0.4 to 1.6 mg Mn 100 g^{-1}, 0.3 to 0.7 mg Cu 100 g^{-1}, and also highlighted the variability of the concentrations of these elements between batches and samples. All samples showed chromium concentrations below the instrumental detection limit.

The significant differences found between the concentrations of minerals in batches of a sample and the variability of the mineral concentrations between samples may be related to agroecological factors such as the type and degree of the sugar cane's maturation, soil type, climate, use of fertilisers and pesticides, the type of cultivation and handling and also the factors of the manufacturing process, such as quality and quantity of hydrated lime used during the clarification and broth's extraction efficiency (Guerra & Mujica, 2010; Mosquera et al., 2007; Jaffe, 2015).

Three batches of rapadura presented Pb levels above the maximum values allowed by Brazilian legislation and Mercosul. In the case of Cd, four batches had levels above the maximum allowed value for this contaminant. The presence of these two contaminants in the batches analyzed may be associated with environmental contamination of the production area of the raw material plant, use of phosphate fertilizers, liming of soil and agrochemicals.

Jaffe (2015) also observed that the percentage of the components of non-centrifugal raw sugar showed differences within same product in one country or region and otherwise named products of different countries. It is essential that the causes of these variances are better evaluated so to permit international standardization and optimization of the industrial process.

The results of microbiological analysis indicated the absence of coliforms bacteria at 45°C and *Salmonella sp.*, and are within the standards established by the Brazilian legislation for rapaduras.

These results can be attributed to rapadura having a high concentration of sugars, which can hinder the proliferation of microorganisms. Furthermore, the high temperature used for a long

period of time in the broth can eliminate microorganisms from the raw material and the craft processing. According to Bassett and Mcclure (2008), heat is commonly used to inactivate pathogens in food. However, in many cases, heat can alter the sensory properties of the product, unless there is a housing to be removed before consumption.

Another point to take into account is if the modeling, cooling, cutting and packing steps of rapadura were done under appropriate, hygienic conditions. For Metaxopoulos, Kritikos, and Drosinos (2003), manipulation errors often contribute to high microbial counts. These include factors such as use of improper temperatures, utensils and contaminated instruments, unfit transport vehicles and lack of food handler hygiene.

The macroscopic and microscopic analysis indicated the presence of impurities and unwanted materials (Figure 1), and the absence of mites and insects. These results indicate that the evaluated samples of artisanal rapadura are in disagreement with the RDC Resolution No. 14 of 28 March 2014 (Brasil, 2014). This verifies the need for a review of the current legislation in order to establish limits for foreign matter, based on data that reflect the reality of the rapadura production in Brazil.
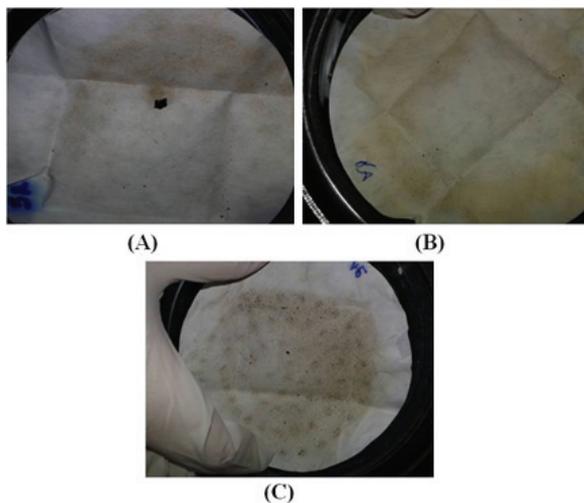


**Figure 1.** Illustrations of the results obtained in the microscopic evaluation (A: sample 5; B: sample 6 and C: sample 9).

The high amount of impurities and undesirable materials found may be associated with several factors, such as the use of sugar cane harvested with burning action, the excessive browning during the concentration step, inefficient cleaning of sugar cane during harvesting, inefficient cleaning of the broth after grinding, and concentration and the use of old raw material with a long wait time for production after harvesting. The presence of these impurities in

rapadura samples can also indicate possible contamination of these products by chemicals such as polycyclic aromatic hydrocarbons (PAHs) (Silva et al., 2011).

## Conclusion

The proximate composition and mineral content showed significant differences between the samples and also discontinuities regarding National Regulations. Cd and Pb concentrations were found to be above the maximum levels allowed in some batches. In addition, a large amount of unwanted materials was detected in all samples. Regarding the microbiological analysis, the samples were not contaminated by *Coliforms* at 45°C or *Salmonella sp*.

These results can be attributed to agroecological and manufacturing factors. In this context, greater oversight is necessary as well as the creation of technical standards related to standardization of manufacturing, management of raw materials and quality control.

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## References

Arcanjo, F. P., Pinto, V. P., Arcanjo, M. R., Amici, M. R., & Amâncio, O. M. (2009). Effect of a beverage fortified with evaporated sugarcane juice on hemoglobin levels in preschool children. *Revista Panamericana de Salud Publica, 26*(4), 350-354.

Association of Official Analytical Chemists. (2012). *Official methods of analysis*. Arlington, VA: AOAC.

Bassett, J., & Mcclure, P. (2008). A risk assessment approach for fresh fruits. *Journal of Applied Microbiology, 104*(4), 925-943.

Brasil. (1965). *Agência Nacional de Vigilância Sanitária Decreto nº 55871, de 26 de março de 1965. Modifica o Decreto nº 50.040, de 24 de janeiro de 1961, referente a normas reguladoras do emprego de aditivos para alimentos, alterado pelo Decreto nº 691, de 13 de março de 1962*. Brasília, DF: DOU.

Brasil. (2001). *Agência Nacional de Vigilância Sanitária. Resolução RDC n.º 12, de 2 de janeiro de 2001. Aprova o Regulamento Técnico sobre padrões microbiológicos para alimentos*. Brasília, DF: DOU.

Brasil. (2005). *Agência Nacional de Vigilância Sanitária. Resolução RDC n.° 271, de 22 de setembro de 2005. Aprova o Regulamento Técnico para açúcares e produtos para adoçar*. Brasília, DF: DOU.

Brasil. (2013). *Agência Nacional de Vigilância Sanitária. Resolução RDC n.º 42, de 29 de agosto de 2013. Dispõe sobre o regulamento Técnico MERCOSUL sobre limites máximos de contaminantes inorgânicos em Alimentos*. Brasília, DF: DOU.

Brasil. (2014). *Agência Nacional de Vigilância Sanitária. Resolução RDC n.° 14, de 28 de março de 2014. Dispõe sobre matérias estranhas macroscópicas e microscópicas em alimentos e bebidas, seus limites de tolerância e dá outras providências*. Brasília, DF: DOU.

Centec. (2004). *Produtor de cana-de-açúcar: Cadernos tecnológicos*. Fortaleza, CE: Edições Demócrito Rocha.

Currie, L. A. (1999). Detection and quantification limits: origins and historical overview. *Analytica Chimica Acta, 391*(2), 127-134.

Delgado, A. A., & Delgado, A. P. (1999). *Produção do açúcar mascavo, rapadura e melaço*. Piracicaba, SP: Alves.

Flores, P. F., Santos Junior, D., Roldan, P. S., Oliveira, A. P., Gomes Neto, J. A., & Krug, F. J. (2007). Evaluation of W-Rh permanent modifier for lead determination in sugar by graphite furnace atomic spectrometry. *Sensing and Instrumentation for Food Quality and Safety, 1*(4), 176-182.

Food Safety and Standards Authority of India. (2011). Ministry of health and family welfare. *food safety and standards (food products standards and food additives) regulations.* New Delhi, IN: Food Safety and Standards Authority of India.

Generoso, W. C., Borges, M. T. M. R., Ceccato-Antonini, S. R., Marino, A. L. F., Silva, M. V. M., Nassu, R. T., & Verruma-Bernardi, M. R. (2009). Avaliação microbiológica e físico-química de açúcares mascavo comerciais. *Revista do Instituto Adolfo Lutz, 68*(2), 259-268.

Guerra, M. J., & Mujica, M. V. (2010). Propriedades físicas e químicas de rapaduras granuladas. *Ciência e Tecnologia de Alimentos, 30*(1), 250-257.

Instituto Adolfo Lutz. (2008). *Métodos físico-químicos para análise de alimentos*. São Paulo, SP: IAL.

Instituto Ecuatoriano de Normalización. (2002). *Panela sólida: requisitos. INEN standard 2331/2002*. Quito, EC: Inen.

Jaffe, W. (2012). Health effects of Non-Centrifugal Sugar (NCS): a review. *Sugar Tech, 14*(2), 87-94.

Jaffe, W. (2015). Nutritional and functional components of non centrifugal cane sugar: A compilation of the data from the analytical literature. *Food Analysis and Composition, 43*(1), 194-202.

Maria, G., Correal, C. M., & Jaffe, W. (2013). Panela: the natural nutritional sweetener. *Agro FOOD Industry Hi Tech, 24*(6), 44-48.

Metaxopoulos, J., Kritikos, D., & Drosinos, E. H. (2003). Examination of microbiological parameters relevant to the implementation of GHP and HACCP system in Greek meat industry in the production of cooked saugages and cooked cured meat products. *Food Control, 14*(5), 323-332.

Mosquera, S. A., Carrera, J. E., & Villada, H. S. (2007). Variables que afectan la calidad de la panela procesada en el Departamento del Cauca. *Facultad de Ciencias Agropecuarias, 20*(5), 17-27.

Mujica, M. V., Guerra, M., & Soto, N. (2008). Efecto de la variedad, lavado de la caña y temperatura de punteo sobre la calidad de la panela granulada. *Interciência, 33*(8), 598-603.

Republic of Colombia. (2004). *Ministério de la Protección Social. Resolución Número 2546 de 6 de agosto de 2004, reglamento técnico de emergencia a través del cual se señalan los requisitos sanitarios que se deben cumplir en la producción y comercialización de la panela para el consumo humano y se dictan otras disposiciones*. Bogota, CO: Ministério de la Protección Social.

Sarwar, M. A., Hussain, F., Nadeem, M. A., Ghaffar, A., Bilal, M., Umer, M., & Chattha, A. A. (2009). Performance of different sugarcane strains for physico-chemical characteristics of jaggery. *Journal of Agriculture & Social Sciences, 5*(1-2), 40-42.

Silva, F. S., Cristale, J., Ribeiro, M. L., & Marchi, M. R. R. (2011). Polycyclic aromatic hydrocarbons (PAHs) in raw cane sugar (rapadura) in Brazil. *Journal of Food Composition and Analysis, 24*(3), 346-350.

Swanson, R. C., Mislivec, P. B., Hitchins, A. D., & Lancette, G. A. (1992). *Compendium of methods for the microbiological examination of foods*. Washington, DC: Apha.

Taco. (2011). *Tabela de composição de alimentos*. Campinas, SP: Nepa-Unicamp.

Tiwari, G., Sanjeev, K., & Prakash, O. (2004). Evaluation of convective mass transfer coefficient during drying of jaggery. *Journal of Food Engineering, 63*(2), 219-227.

Uppal, S., Sharma, S., & Sidhu, G. (2002). Effect of storage temperature on jaggery (gur) quality of different sugarcane varieties. *Journal of Food Science Technology, 39*(5), 549-551.

Verma, V., & Maharaj, N. (1990). Moisture absorption isotherms of jaggery. *Journal of Stored Product Research, 26*(2), 61-66.