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Evaluation of raw soapstone (steatite) as adsorbent of trace elements present in Brazilian spirits

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ABSTRACT

The impact of soapstone (steatite) upon inorganic element contaminant concentrations in alcoholic beverages was investigated. Concentrations of As, Cd, Cu, Ni and Pb levels in 8 Brazilian spirits plus an alcoholic simulant were initially measured, and then measured following each 24 h cycle of exposure to raw soapstone cups, for a total of 4 cycles/sample. The results were compared to the levels established by Brazilian and German regulations. The contact between the spirits and the soapstone reduced the Cu content by up to 50.4% and increased the Ni content by up to 622.2%, especially in the first contact cycle. The exposure of spirits to the soapstone exhibits a linear reduction in the Pb content (18.3–54.5%) while As and Cd levels remained unaltered throughout the experiments. In conclusion, crude soapstone in contact with alcoholic solutions acts as an adsorbent of trace elements (Cu and Pb) while releasing Ni.

1. Introduction

Spirits are one of the most widely produced alcoholic beverages worldwide. In 2009 the global revenue of spirits was 94.31 billion U.S. dollars, and in 2015 the projected revenue of the global spirits industry is estimated to be about 113.78 billion U.S. dollars (Statista, 2015). Despite the fact that almost a quarter (24.8%) of all alcohol consumed worldwide is in the form of unrecorded alcohol, of the recorded alcohol consumption, more than half is consumed in the form of spirits (50.1%), followed by beer (34.8%) and wine (8.0%) (WHO, 2014).

In 2014 Brazil exported cane spirit to 66 countries, with a revenue of US$18.33 million for the sale of 10.18 million liters. In terms of value, the main countries of destiny were: Germany, USA, France, Portugal, Paraguay and Italy, and in terms of volume the main countries of destiny were: Germany, Paraguay, Portugal, USA, France and Bolivia (IBRAC, 2014).

Cane spirit is obtained by distilling the fermented must of sugarcane juice and has some particular sensory characteristics, an alcohol degree of from 38% to 48% by volume at 20 °C, and can have added sugars of up to 6 g L^{-1} (Ministry of Agriculture, Livestock and Supply, 2005). It can be divided into its organic and inorganic fractions, the latter being constituted principally of metal and non-metal ions such as aluminum (Al), arsenic (As), cadmium (Cd), calcium (Ca), lead (Pb), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe) and nickel (Ni), amongst others (Siebalde, Canuto, Lima, & Silva, 2002).

As, Cu and Pb contents above the levels permitted by Brazilian legislation were observed in cane spirits from the State of São Paulo, Brazil (Caldas, Raposo, Gomes Neto, & Barbosa, 2009). In the State of Minas Gerais, Brazil, responsible for 44% of the Brazilian production (CEPA, 2008), it was found that 25% of the cane spirits produced in stills in the south of the state showed Cu contents above the level permitted by the legislation (Fernandes et al., 2007). Cane spirits coming from the Iron Quadrangle in Minas Gerais (QFMG), a region with many steatite deposits were also shown to contain Cu above the legal limits (Fernandes et al., 2013).

Evidence of the contamination of alcoholic beverages by metals has been found throughout the world. Researchers have reported that the quality control of the Greek beverage *Mouro* may be deficient as a function of variation in the Pb content (Soufleros,

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Mygdalia, & Natskoulis, 2004), and wine commercialized in Hungary has shown elevated contents of Cu (20–640 μg L^{-1}), Pb (6–90 μg L^{-1}) and Cd (0.05–16.5 μg L^{-1}), the amplitude of the values being explained by the diversity in origin of the beverage and also by the effect of additives and the equipment used in production (Ajtony et al., 2008). The raw materials, substances intentionally added, type of process and storage are also factors interfering in the metal contents of alcoholic beverages (Ibanez, Carreon-Alvarez, Barcena-Soto, & Casillas, 2008).

Despite the fact that alcoholic beverages have been classified as carcinogenic to humans, levels of inorganic elements such as lead or arsenic could further increase their carcinogenic potential (Lachenmeier, Przybylski, & Rehm, 2012) Hence, the removal of inorganic contaminants from alcoholic beverages in order to conform to legal parameters, and reduce health risks to the consumer, is important.

A recent study provided evidence that the alcohol content of cane spirit and the time of exposure to steatite could influence the transference of inorganic contaminants (Fernandes et al., 2013). Nevertheless the interference of soapstone in the content of contaminants present in alcoholic beverages still needs to be better investigated. Thus the objective of this study was to evaluate the behavior of the inorganic contaminants (As, Cd, Cu, Ni and Pb) present in commercial Brazilian cane spirits when submitted to contact *in natura* with soapstone cups, and evaluate if the amounts found before and after four 24-h cycles of exposure to steatite conformed with the maximum limits established by the Brazilian and German legislations (Ministry of Health, 1965, 2005; BGBl, 2002).

2. Material and methods

Eight distinct brands of cane spirit acquired on the market in Belo Horizonte and Ouro Preto (MG, Brazil) were studied. The selection criteria for the beverages integrating this study considered those produced in the QFMG region and registered in the Ministry of Agriculture (MAPA). In addition to the cane spirits, a simulated alcoholic beverage was also included in the experiment, produced using a 43% (v v^{-1}) ethyl alcohol solution (Merck, Darmstadt, Germany) diluted with deionized water (18.2 MΩ). This additional treatment was carried out with the objective of evaluating the effect of the exposure of ethyl alcohol *in natura* to the steatite cups.

In parallel, twenty seven new soapstone cups, each with a volumetric capacity of approximately 20 mL, derived from the district of Cachoeira do Brumado (Mariana, MG, Brazil), were evaluated. All the cups were washed with potable water using a soft new polymeric sponge and a dilute solution of a commercial detergent, followed by rinsing with potable water and distilled water. They were dried in an incubator at 150 °C for 10 min. The cups were divided into groups of 3 units, giving a total of 9 groups.

The As, Cd, Cu, Ni and Pb contents were determined in the eight brands of cane spirit and in the ethyl alcohol solution before and after contact with the soapstone cups. A part of each of the cane spirits and the ethyl alcohol solution was poured into a group of three new, clean soapstone cups to 2/3 of their capacity (approximately 14 mL). They were then covered with a watch glass and maintained at a constant temperature and under artificial light, in order to prevent any external interference.

Aliquots of each cane spirit and of the ethyl alcohol were removed after 24 h of contact (1 cycle), and four sequential cycles (24 h each) were carried out. Between each cycle the cups were washed and dried as mentioned above. Samples were removed after each cycle for the chemical analyses using a sterile pipette, without any abrasion of the surface of the cup or loss of the contents. The homogenized samples were placed in previously decontaminated glass beakers. The cycle times used were based on Fernandes et al. (2013) and also the fact that many soapstone containers are intended for long term exposure to alcoholic beverages (i.e. pots, barrels, flasks).

The concentrations of the elements As, Cd, Cu, Ni and Pb were determined in each aliquot and also in duplicate blanks prepared in decontaminated glass beakers using the same volumes of liquid adopted for the sandstone cups. For each element the final concentrations were obtained by deducting the contents found in the blanks from the contents found in the aliquots.

2.1. Determination of the inorganic contaminants

For the determinations of As, Cd, Cu, Ni and Pb, 5 mL aliquots of the cane spirit samples and of the simulant were transferred to sterile glass flasks and their volume reduced by half on a digestion block at 80 °C. A volume of 1.25 mL of 65% nitric acid was then added and heated at 95 °C for 2 h. After cooling the solution was quantitatively transferred to a 25 mL volumetric flask and completed to volume with a 5% (v v^{-1}) nitric acid solution, prepared from concentrated 65% nitric acid (Merck, Darmstadt, Germany) and diluted with deionized water (18.2 MΩ) (Fernandes et al., 2013; López-Artíguez, Cameán, & Repetto, 1996).

Analytical curves were constructed as from standard 1000 mg L^{-1} solutions of As, Cd, Cu, Ni and Pb (Merck, Darmstadt, Germany) in the interval from 0.005 to 1.0 mg L^{-1} for As, Cd, Pb and Ni and from 0.025 to 25 mg L^{-1} for Cu.

2.2. Equipment and operational conditions

The contents of the elements under investigation were analyzed by means of emission spectrometry in duplicate, by direct aspiration from the cane spirit samples and simulant, mineralized with nitric acid. The equipment used was an emission spectrometer with a plasma source and inductive coupling (ICP OES) (Vista MPX Varian, Mulgrave, Australia), with axial vision and equipped with a 40 MHz radio frequency source (RF), a charged coupled device (CCD) solid state simultaneous multi-element detector, a peristaltic pump, nebulization chamber and sea spray nebulizer. The system was controlled by the ICP Expert software and used 99.996% pure liquid argon (Air Liquid, SP, Brazil) as the plasma gas.

The optimized experimental conditions for operation of the equipment were: RF power (1000 W); nebulization gas flow rate (0.9 L min^{-1}); principal argon flow rate (15 L min^{-1}); auxiliary argon flow rate (1.5 L min^{-1}); background correction (2 points); integration and reading times (10 s); number of replicates (3); torch configuration (axial) and wavelengths, As (188.980 nm), Cd (214.439 nm), Cu (324.754 nm), Pb (220.353 nm) and Ni (221.648 nm).

2.3. Evaluation of inorganic contaminants

The contents of the inorganic contaminants detected in the cane spirit samples and simulant were evaluated with respect to the maximum levels established by the Brazilian legislation for cane spirit and by the German legislation for wines, since Germany is the main destination for cane spirits produced in Brazil (IBRAC, 2014). The maximum limits in alcoholic beverages for the inorganic contaminants under study, as established by the Brazilian and German legislations are: Cu (5.0 mg L^{-1} and 2.0 mg L^{-1}); As (0.100 mg L^{-1}), Cd (0.020 mg L^{-1} and 0.010 mg L^{-1}); Pb (0.200 mg L^{-1} and 0.250 mg L^{-1}), respectively (BGBl, 2002; Ministry of Agriculture, Livestock and Supply, 2005).

The presence of Ni was considered acceptable if the amount quantified was below 3.0 mg L^{-1} according to the Brazilian