

Simple and efficient elimination of copper(II) in sugar-cane spirits

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Abstract

Cachaça is a distilled alcoholic beverage, produced in large quantities in Brazil, from fermentation of sugar cane juice. It is normally distilled in copper stills, which can sometimes cause contamination with this element, at toxic levels. An efficient method to remove copper ions to lower than 5 ppm in such alcoholic distillates, without perceptible changes in organoleptical properties, was herein developed. This method is based on a treatment with either CaCO_3 or MgCO_3 , which behave as cationic exchangers.

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1. Introduction

Cachaça is a distilled alcoholic beverage largely consumed in Brazil. It is produced by fermentation of sugar cane under various conditions (Aquarone, 1983). The annual production is around 2×10^9 l/year (Vasconcelos, 2003), which makes it one of the world's most popular spirits. However, less than 1% of the volume produced is exported. Efforts have been made to increase the export volume and qualify cachaça as an international Brazilian beverage (Decreto Federal, 2002). Great improvements have been made regarding the knowledge of cachaça's chemical composition in the past decade (Bettin et al., 2002; Boscolo, Bezerra, Cardoso, Lima-Neto, & Franco, 2000; Nascimento et al., 1999; Nascimento, Cardoso, Keukeleire, Lima-Neto, & Franco, 2000; Nascimento, Cardoso, Lima-Neto, & Franco, 1998). Consequently, quality control has been improved, and producers are now more successful at controlling its chemical composition and sensory profile.

Metal elements in distilled beverages come from raw materials, crop treatment or manufacturing processes (Onianwa, Adetola, Iwegbue, Ojo, & Tella, 1999). Cachaça, the

fermented sugar-cane juice, is distilled in copper stills, and the contamination with copper can take place. The producers consider that distillation in copper apparatus is necessary to guarantee good organoleptical properties in the product, due to the catalytic effects of the element on the formation of flavouring. However, it is well known that an adverse effect of copper is the catalytic formation of ethyl carbamate, a carcinogen.

Trace metals, including copper, are known to affect the colour, aroma, and taste of alcoholic beverages. The toxic effects of high concentrations of copper were investigated by Klevay and Forbush (1976), as well as the determination of this element in beverages. Since an excess of copper in alcoholic beverages can cause serious damage to health (Goyer & Cherian, 1995), Brazilian legislation requires that its content in cachaça should be lower than 5.00 mg/l (Brazilian Ministry of Agriculture, 1974). However, in some sugar-cane spirits made by Brazilian producers copper levels may be found above the maximum allowed content and double distillation is often required to minimize this problem.

A few methods have been described for the determination of copper in alcoholic distillates. Due to the low concentration of copper in these beverages, molecular absorption spectrophotometry, flame atomic absorption spectrometry, and X-ray fluorescence have been employed

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for its determination (Capote, Marcó, Alvarado, & Greaves, 1999; Noble, Orr, Cook, & Campbell, 1976; Szobolotzky, 1970). Total reflection X-ray fluorescence (TXRF) and voltammetric methods for the determination of copper in sugar-cane spirits have also been considered (Barbeira, Mazo, & Stradiotto, 1995; Cunha e Silva, Almeida, Valencia, & Nascimento Filho, 2004).

There are only few studies and patents about removing copper ions from beverages, based on the formation of insoluble chelating agents (Wucherpfenning, 1992a, 1992b) or the use of chelating resins (Gravatá, 1992; Kogyo, 2002; Kogyo, 1994; Wucherpfenning, 1992a, 1992b). These methods are relatively cumbersome and depend on chemical variables such as pH, contact time with resin, temperature, and resin particle size.

As an alternative to remove copper ions from alcoholic distillates, a simple and efficient method was developed in order to eliminate this element, by treatment either with calcium or magnesium carbonates.

2. Experimental

2.1. Reagents, samples, and solutions

All solutions were prepared using analytical grade reagents and deionized water (Milli-Q water, 18 M Ω cm, Millipore, Bedford, MA, USA). All glassware and polypropylene flasks were washed with neutron detergent, soaked in 10% v/v nitric acid (Merck, Darmstadt, Germany) and rinsed with deionized water prior to use.

For copper determination by flame atomic absorption spectrometry (FAAS), the standard additions method, SAM, was adopted for correcting transport interference effects, caused by the presence of different amounts of ethanol in the samples. A 1000 mg/l stock solution of Cu(II) nitrate was used to prepare an intermediate standard solution containing 100 mg/l, by appropriate dilution with distilled and deionized water, and then increasing amounts of this solution were added to identical aliquots of each sample. These solutions were diluted to the same final volume, which ensured that any transport effects should be the same (Almeida, Martins, Silva, Moreira, & Araújo, 2003). A SAM plot was built with exact matrix matching between samples and standards.

Sugar cane spirits were purchased in local supermarkets and the procedure for copper removal was applied without any previous treatment.

2.2. AAS spectrometer

A Varian Spectra AA 640 flame atomic absorption spectrometer (Mulgrave, Australia), with background correction using a deuterium lamp, was operated according to the recommendations of the manufacturer for maximum sensitivity with an air–acetylene flame. All measurements were performed at 327.4 nm, using a copper hollow cathode lamp.

2.3. Estimation of exchange constants

A mass of about 0.10 g of CaCO₃ or MgCO₃ solids was added to 25.00 ml of 1.000 $\times 10^{-2}$ mol l⁻¹ copper (II) nitrate in 40% (v/v) ethanol/water medium. The suspension was stirred for 10 min at 25.0 °C in order to reach an exchange equilibrium condition with CuCO₃ formation and release of Ca(II) or Mg(II). The Cu(II) concentration in the liquid phase at equilibrium was determined by FAAS and the molar ratio [M(II)]/[Cu(II)] was calculated, where M is Ca or Mg.

2.4. Procedure for copper removal

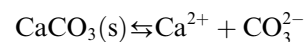
For a volume of 25.00 ml of cachaça (40% v/v ethanol), a mass of about 0.10 g of CaCO₃ (USP grade) or MgCO₃ (AnalaR) was added. This was in large excess in composition to copper elimination.

These samples were stirred for about 10 min and then left to allow full sedimentation of the solid phase. Aliquots of 5.00 ml were taken and made up with distilled water to 10.00 ml and the residual amounts of copper were determined by FAAS.

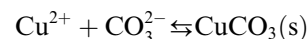
3. Results and discussions

The treatment of cachaça samples with CaCO₃ or MgCO₃ solids has been found to be an efficient process to remove their copper content, and could be adapted by industry, to be used during distillation.

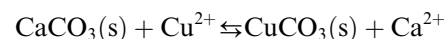
The solid phase acts as a cation exchanger, resulting from the solubility equilibrium of CuCO₃ with CaCO₃ or MgCO₃ (Martell, Smith, & Motekaitis, 1997), based on which an equilibrium constant (K_t) can be estimated:



$$K_{S1} = 3.31 \times 10^{-9} \text{ mol}^2 \text{ l}^{-2}$$



$$K = 1/K_{S2} = 1/3.00 \times 10^{-11} \text{ mol}^2 \text{ l}^{-2}$$



$$K_t = K_{S1}/K_{S2} = [\text{Ca}^{2+}]/[\text{Cu}^{2+}] = 1.10 \times 10^2$$

Similarly, for MgCO₃ the ratio of solubility products led to a higher equilibrium constant, i.e. $K_t = 9.60 \times 10^5$ in aqueous medium. Of course these constants are modified when considering an aqueous ethanol medium, which can affect markedly the exchange equilibrium, particularly for magnesium. In fact, for 40% v/v ethanol (see Section 2), calculated $K_t = 8.6 \times 10^2$ using CaCO₃ and $K_t = 1.16 \times 10^3$ for MgCO₃. For an aqueous ethanol medium, a small increase in K_t was found for Cu(II) exchange with CaCO₃ and a marked decrease for MgCO₃.

It can be seen that the magnitude of these calculated exchange constants are favourable enough to promote an efficient removal of Cu(II) from the alcoholic phase by both CaCO₃ and MgCO₃. The higher solubility magnesium

carbonate, even in ethanol/aqueous medium, is responsible for a more efficient exchange constant. In addition to the exchange phenomena, it is quite possible that adsorption of copper cations on the solid phase can also take place. In aged products, Cu(II) complexes with flavor compounds from wood barrels are certainly formed, which can make the exchange process difficult. Table 1 presents some results obtained for Cu(II) after applying the recommended procedure.

As can be seen in Table 1, the removal was more effective for recently distilled spirits. Aging in wood barrels introduces a complex group of organic flavouring compounds, which can sequester Cu(II), affecting to some extent its removal. If the solid phase is MgCO₃ the efficiency in copper removal is increased as expected, due to a higher *K_t*, but this efficiency is again reduced in for treated aged products.

Calcium(II) or Mg(II) ions were introduced at trace levels (0.3–3 mg l⁻¹) in the treated sample, not only due to the copper ion exchange. In fact, contact with the solid phases of CaCO₃ or MgCO₃ caused some pH change in the samples, as measured after dilution 1:10 v/v (see Table 2). The pH increase after treatment is expected, due to the neutralization of small amounts of weak organic acids, such as acetic acid, and also to an intrinsic solubility of CaCO₃ or MgCO₃, which causes partial hydrolysis:

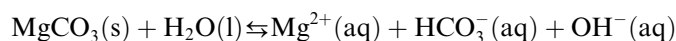
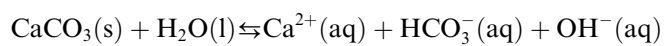


Table 1
Determination of Cu(II) concentrations (mg l⁻¹) in sugar cane spirits by FAAS before and after treatment with solid carbonates

Sample	[Cu (II)] untreated sample	[Cu (II)] after treatment with CaCO ₃	[Cu (II)] after treatment with MgCO ₃
1*	4.05	<0.0074	<0.0085
2*	3.50	<0.0074	<0.0085
3**	12.6	2.20	1.64
4**	10.4	6.84	1.51
5**	5.00	0.76	<0.0085
6*	6.56	<0.0074	<0.0085

* Non-aged cachaça.

** Aged in wood barrel.

Table 2
Changes of pH in sugar cane spirits before and after treatment with solid carbonates, as measured after 1:10 (v/v) dilution with distilled and deionized water

Sample	pH before treatment	pH after treatment with CaCO ₃	pH after treatment with MgCO ₃
1	5.36	7.21	9.93
2	5.27	7.14	7.70
3	5.55	7.98	6.58
4	4.60	7.15	6.67
5	5.30	7.86	6.83
6	5.04	8.35	7.14

Full sedimentation of the solid phase takes place in about 2 h and a completely clear solution is achieved. No perceptible changes in organoleptic properties were found after this treatment. In fact, cachaça is a strongly flavoured beverage and its dominant taste/aroma seems to mask any minor changes in composition caused by pH variation, with possible neutralization of small amounts of organic acids.

The process can be adapted to industrial conditions. As a final recommendation it would be appropriate to treat the alcoholic beverage before aging, or during the industrial process of distillation. In this case the distilled liquid should flow through a filter of a granulated natural carbonates, such as marble or dolomite. Preliminary discussions with cachaça producers have shown concerns about modification of the distillation process, in order to obtain a product virtually free of copper contamination.

4. Conclusions

Solid carbonates of calcium and magnesium act as cation exchangers, removing most of the copper ions from cachaça samples and releasing Ca(II) or Mg(II) to the sample in trace levels, 0.3–3 mg l⁻¹. Better efficiency of removal was obtained using MgCO₃ and this can be explained based on the equilibrium constants involved. The removal was more effective for recently distilled spirits than for those aged in wood barrels, owing to effects caused by organic compounds extracted from wood.

A pH increase for cachaça samples after treatment, which is expected due to both the neutralization of weak organic acids and also to the intrinsic solubility of the added solids. However, the recommended treatment with solid carbonates does not seem to affect the taste of the beverages.

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