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Short communication

# Ethyl carbamate in cachaça (Brazilian sugarcane spirit): Extended survey confirms simple mitigation approaches in pot still distillation

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ABSTRACT

In 2009, we reported an association between low levels of ethyl carbamate (EC) in pot still cachaças from Paraíba State, Brazil, and distillation in copper pot stills equipped with cooled columns. To strengthen these observations, we extended our study to Pernambuco State and assessed 13 pot still and 20 column still cachaça brands. An EC range from <40 to 532 μg/l was found; 18 brands exceeded the Brazilian limit (150 μg/l), 89% of which were column still types. Mean EC concentration of pot still cachaças was very low (64 μg/l), and was well below the Paraíba study (220 μg/l). An on-site investigation of pot still distilleries associated with <40 μg/l brands showed a connection to differences in the distillation apparatus. Maximising distillation reflux ratios in the ascending parts and minimising exposure to copper in the descending parts (through the use of stainless steel) can reduce EC, and also avoid copper contamination.


## 1. Introduction

Production, market, and definition aspects of cachaça, Brazil's most consumed spirit, were recently described by our group (Nóbrega, Pereira, Paiva, & Lachenmeier, 2009).

Relatively high levels of ethyl carbamate (EC), a multi-site carcinogen in experimental animals and probably carcinogenic to humans (IARC group 2A), have been found in cachaça since the beginning of this century (Andrade-Sobrinho, Boscolo, Lima-Neto, & Franco, 2002; Labanca, Glória, & Afonso, 2008; Lachenmeier et al., 2009), causing concern in Brazil. Recently, these findings have been compounded by a risk assessment study showing that EC poses a significant cancer risk for the Brazilian alcohol-drinking population, with highest exposure arising from cachaça (Lachenmeier et al., 2010).

In 2005, following EC regulations for alcoholic beverages in other countries, the Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA) established an EC limit (150 μg/l) for the beverage, which was to come into effect in June 2010 (DOU, 2005). However, as a result of critical opinions from the cachaça industry, MAPA has recently postponed its effect to June 2012 (DOU, 2010).

In 2009, our group reported an average EC level of 220 μg/l from a survey in pot still cachaças produced in Paraíba State, Brazil, with most brands (~70%) exceeding the 150 μg/l limit. Brand characteristics, particularly distillate and bottle colouration, showed no consistent connection with EC levels. However, when white and yellowish (cask matured) cachaças from the same distilleries were compared, the yellowish type was much more heavily contaminated. Finally, in accordance with the work of Bruno, Vaitsman, Kunigami, and Brasil (2007), our study in Paraíba also showed that brands with low (55–100 μg/l) and high (200–700 μg/l) contamination levels were closely associated with pot stills equipped with cooled and non-cooled columns, respectively (Nóbrega et al., 2009).

To strengthen our observations in Paraíba, a state famous for producing pot still cachaças, we extended our survey to a neighbouring state, Pernambuco, the second in terms of volume of production in Brazil (IBRAC, 2010). A significant part of cachaça production in Pernambuco is carried out in continuous column stills, producing the so-called column still cachaças, therefore we also included this type of beverage in the present survey.

In this paper, we report on quantifying EC in commercial brands of pot still and column still cachaças from Pernambuco State, and

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discuss the results in light of the brands' characteristics, distillation profile, and our previous work in Paraíba State.

## 2. Materials and methods

### 2.1. Sampling of cachaças and selecting distilleries

Duplicate samplings of 33 brands of cachaça, 20 columns still and 13 pots still, produced by 20 companies in Pernambuco State, were conducted from retail outlets in Pernambuco's capital, between April and May 2009. In order to obtain a valid representation of each brand's EC level, samples of different batch codes were purchased. General characteristics of the brands, including the distillation method, were obtained from local inspecting authorities and from label information. All brands of pot still cachaças were single-distilled. Detailed information on distillation was collected during visits to five pot still distilleries, which were selected on the basis of their low or high levels of EC and interest in participating in the project.

### 2.2. Chemicals

Ethyl carbamate (99.0%), for calibration, and propyl carbamate (98.0%), used as an internal standard, were purchased from Chem Service (West Chester, USA) and Aldrich (Milwaukee, USA), respectively. The analytical solutions were dissolved in LC grade ethanol (Merck, Darmstadt, Germany) at 40% (v/v).

An AAS Tritisol® copper standard (Merck, Darmstadt, Germany) was employed to prepare the analytical curves in the determination of copper. Distilled water, subsequently passed through a Milli-Q system, was used to prepare the samples.

### 2.3. Analysis of ethyl carbamate

Preparation of calibration curves and EC analysis by GC–MS were carried out as described by Nóbrega et al. (2009). The limits of detection (LOD) and quantitation (LOQ) were 10 and 40 μg/l of EC, respectively.

### 2.4. Analysis of alcoholic strength

The alcoholic strengths (% volume at 20 °C) of the spirits were determined according to Nóbrega et al. (2009).

### 2.5. Analysis of copper

The copper content was determined by flame atomic absorption spectrometry (Perkin–Elmer model Analyst 200, Germany), as described by OIV (1994). A sample (50 ml) was placed in an open 100 ml beaker and then evaporated under controlled heating (~95 °C) until 10 ml of the sample volume remained. After cooling at room temperature (~20 °C), the sample was transferred to a 50 ml volumetric flask, made to volume with ultrapure water, and then analysed. The calibration curves were constructed by using an external standard method.

## 3. Results and discussion

### 3.1. EC levels, alcoholic strength, and copper concentrations in brands of pot still and column still cachaças

Table 1 shows the EC concentrations (in increasing order), alcoholic strength, and copper concentrations of 13 pot still and 20 column still cachaças brands produced in Pernambuco State.

With respect to copper, an average of 2.2 mg/l was found, with three brands exceeding the limit established by MAPA (5 mg/l; DOU, 2005) for this contaminant (Table 1).

Copper levels were included in this research as result of unexpected data that emerged on profiling pot still distilleries in Pernambuco (see Section 3.2), particularly the use of different construction materials (copper and stainless steel) in distillation apparatus. Taking into account that these differences could have an impact on copper levels, and possibly on EC, we decided to investigate the metal in all the samples (Table 1). It is worth recalling that all profiled distilleries in our previous study (Nóbrega et al., 2009) used pot stills made entirely of copper.

Copper has been shown to play an important catalytic role in cyanide conversion into EC in cachaça (Aresta, Boscolo, & Franco, 2001; Bruno et al., 2007) and, thus, a correlation between EC and copper levels would be worth investigating. However, taking into account that most EC forms ~24–48 h after distillation (Aylott et al., 1990; Riffkin, Wilson, Howie, & Müller, 1989), the correlation is difficult to establish because the commercial cachaças assessed here may have been submitted at some point after distillation, to filtration through cationic exchange resins to reduce copper levels. Moreover, according to Bruno et al. (2007), as little as 0.7 mg of copper per litre of freshly distilled cachaça was enough to promote a complete EC formation, whereas higher concentrations of the metal did not promote any additional catalytic effect. According to local inspecting authorities, this type of filtration is frequently applied by major cachaça blenders. Interestingly, the mean level of copper found for column still cachaças (1.5 mg/l, Table 1) produced by blenders is lower than that for pot still cachaças (3.3 mg/l, Table 1). Another explanation for the lower levels of copper in column still cachaças is the fact that the associated distillation apparatus is frequently constructed of stainless steel.

With regard to cachaças' colour (which reflects wooden cask maturation) and their EC levels, no apparent association was seen between them, as shown by the random distribution of white and yellowish cachaças along the EC concentration range (Table 1). However, when we look at the white and yellowish cachaças produced by distilleries B (brands 03 and 09), C (brands 04 and 10), D (brands 05 and 08), E (brands 06 and 16), H (brands 12 and 23), and J (brands 19 and 30), we see that the EC concentration in yellowish cachaças is much higher than in the corresponding white ones. The smallest effect was seen for brands produced by distillery J, with as much as a 61% increase in the yellowish cachaça. These observations are in line with those obtained by our group previously (Nóbrega et al., 2009).

An EC range from <40 to 532 μg/l was found for the cachaças produced in Pernambuco State, with 18 brands (55%) exceeding the Brazilian limit, 89% of which were column still types. Average EC level for all brands was 181 μg/l, while those specifically for column still and pot still cachaças were 257 and 64 μg/l, respectively (Table 1). Although much higher than pot still cachaças, the mean level of column still cachaças from Pernambuco is well below the average for the same type of product in Brazil (490 μg/l, Lachenmeier et al., 2010).

The average level found in pot still cachaças from Pernambuco State (64 μg/l, Table 1) is considerably lower than the mean value reported for the 25 brands of cachaça in the Paraíba study (221 μg/l, Nóbrega et al., 2009) and the average for pot still cachaças in Brazil (380 μg/l, Lachenmeier et al., 2010).

### 3.2. Distillation profile of selected pot still distilleries and EC levels

Six brands of pot still cachaças from Pernambuco contained EC levels below detection (10 μg/l) or quantitation (40 μg/l) and, therefore, we were particularly interested in profiling the corresponding distilleries (A, B, C, D, and E, Table 1). However, distillery