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Determination of volatile compounds in Brazilian distilled cachaça by using comprehensive two-dimensional gas chromatography and effects of production pathways

Patterson P. de Souza [a], Zenilda de L. Cardeal [a,*], Rodinei Augusti [a], Paul Morrison [b], Philip J. Marriott [b,**]

[a] Chemistry Department, ICEx, Federal University of Minas Gerais, Av. Antônio Carlos 6627, Belo Horizonte 31270-901, MG, Brazil
[b] Australian Centre of Research Separation Science, RMIT University, School of Applied Sciences, GPO Box 2476 V, Melbourne 3001, Australia

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ABSTRACT

Comprehensive two-dimensional gas chromatography (GC × GC) was applied to the study of cachaça production. Effects of bidistillation, and the use of charcoal filtration in the production of artisan cachaça, as well as the effects of multi-distillation on volatile products in commercial cachaça were investigated. Volatile compounds were collected and concentrated onto a polyacrylate solid-phase microextraction fibre, and analyzed using GC × GC on a non-polar (BPX5)–polar (BP20) column set. More than 100 compounds, comprising various homologous series were tentatively identified using MS library matching and comparison with retention indices. Phthalate organic contamination following the use of ion exchange resin for removal of copper ion was evident. Charcoal successfully removes this contamination product. Prediction of compounds within particular homologous series aids component identification.

1. Introduction

Cachaça, which is obtained from sugarcane, is the third most consumed distilled alcoholic beverage (after vodka and soju) in the world. Whilst approximately 1.3 billion litres of cachaça is produced per year in Brazil [1,2], only 0.5% is exported. In the past, due to the poor quality of the cachaça product, it was sold at a low price. However in recent times, it may command close to US$120/L for the more elaborate cachaça brands, due to improved production technology. To increase the quality as well as the aggregate value of the beverage, modifications in the steps of production or post-production procedures have been incorporated following the experience of production of other beverages, such as whisky or vodka.

Usually, manufacturers of artisan cachaça use physical filters to remove solid impurities from the casks. In addition, use of an ion exchange resin after the alembic distillation to reduce copper content and a charcoal filter to reduce the acid content is reported in the industry.

In a typical production, each 100 L of heart portion (the main distillation objective), accompanies 30 L of other less valuable fractions (the head + tail portions). In the final production, the total amount of (head + tail) is too large a volume to be simply discarded. One possible solution is to re-distill the (head + tail) fractions and combine this with product from the heart fraction and thereby increase the overall production yield.

Distilled beverages – whisky, tequila, cachaça and others – consist of exceedingly complex mixtures of many different compounds. For whisky samples, more than 1000 compounds were reportedly identified [3] and other authors suggest 800 volatile compounds, several tens of which can have odour-impact [4]. This large number of compounds becomes problematic in analysis when using one-dimensional gas chromatography (1D-GC), since unresolved peaks certainly will arise. In this scenario, comprehensive two-dimensional gas chromatography (GC × GC)[5] is a valuable alternative for qualitative [6,7] and quantitative [8] applications. GC × GC involves the use of two columns with different separation characteristics serially coupled through a suitable interface that allows peaks from the primary column to be transferred onto the second column for an additional separation step. The focusing obtained through the modulation process reduces the peak width, and thus is accompanied by peak height and sensitivity increase [9,10]. Hyphenating GC × GC to time-of-flight mass spectrometry (TOF-MS) brings other advantages such as full mass spectral acquisition and improved library matching quality at trace levels, and

* Corresponding author.
** Corresponding author. Tel.: +61 3 99252632.
E-mail addresses: zenilda@ufmg.br (Z.d.L. Cardeal), philip.marriott@rmit.edu.au (P.J. Marriott).

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mass spectral continuity, which allows for deconvolution of spectra for any peaks that remain co-eluted after the GC × GC step [11] although often the increased resolution of peaks allows generation of pure peaks in the initial instance.

Rodrigues et al. [4] used headspace solid-phase microextraction (HS-SPME) to determine the volatile content in wine, beer and whisky. The efficiency of several fibres was tested, and compounds were identified by MS library searching, and Kovatś retention index (RI) matching, for the semi-quantitative procedure established. For whisky, five different fibres were employed to contrast their extraction efficiency and 55 compounds were tentatively identified, such as esters, aldehydes, alcohols, ketones and others. HS-SPME was used also by Cardeal et al. [2] to identify more than 70 compounds in cachaça samples. A comparison of fingerprints obtained by GC × GC of head, heart and tail fractions was performed; differences in the fingerprints of cachaça aged in different woods were studied.

In this work, HS-SPME with GC × GC was employed to study cachaça production pathways. Firstly, the 2D chromatogram of the heart fraction was compared with that of the (head + tail) bidistillate. The effects of using ion exchange resin and charcoal filters on the volatile composition of cachaça samples were also studied. Finally, the volatile composition of industrial cachaça produced by a multi-distillation process was compared with another commercial cachaça sample produced by fractional column distillation. Similar homologous series were tentatively identified in samples for the purpose of discussion of comparative headspace qualitative composition.

2. Experimental

2.1. Samples

2.1.1. Study of effect of bidistillation process

The difference between the heart and (head + tail) bidistilled product was studied in samples collected directly from a small cachaça production facility located in Brumadinho City, in Minas Gerais state, Brazil. This production uses a copper alembic to distill samples and the cachaça heart portion ethanol content is measured at 40 °GL (Gay-Lussac; 40 mL of alcohol in 100 mL of solution) and mixed portion of (head + tail) bidistilled product measures 55 °GL. The alcohol concentration of all samples was corrected to 40 °GL to improve and normalize the use of SPME.

2.1.2. Study of the effect of charcoal filtration

To study the effect of charcoal filtration, cachaça samples were collected in a production in Vianópolis City. The samples of 50 mL volume each were collected in three different stages: before the resin (sample "b/res"), after passage through the resin, but before the charcoal filter (sample "a/res-b/char") and after the charcoal filter (sample "a/char"). All samples were collected in duplicate, with alcohol concentration corrected to 40 °GL.

2.1.3. Study of effect of multi-distillation process in commercial cachaças

The commercial cachaça samples were selected from a multi-distillation process, and also were taken as unique (discrete) cuts during the distillation process. Both processes used column distillation. These samples were sourced from different factories.

2.2. Sampling and SPME of headspace compounds

Aliquots of 1.00 mL of the cachaça samples were diluted with 9.00 mL of deionized water containing 0.5 g of NaCl. This solution was hermetically closed with a Teflon septum and aluminum cap in a 20 mL vial. To sample and concentrate the headspace compounds an 85 μm polyacrylate (PA) SPME fibre with manual holder (Supelco, Bellefonte, PA, USA) was used. The SPME parameters used were 60 °C and 25 min for extraction, similar to the conditions utilized previously by the same research group [2,12]. The fibre was introduced in the GC injector for thermal desorption at 240 °C for 60 s.

2.3. Instrument and method

The system used was a GC × GC/TOF-MS instrument incorporating a HP 6890 (Agilent Technologies, Burwood, Australia) gas chromatograph equipped with a Pegasus III time-of-flight mass spectrometer (LECO, St. Joseph, MI, USA). In the modulation step for the GC × GC technique a longitudinally modulated cryogenic system (LCMS; Chromatography Concepts, Doncaster, Australia) was used. The period of modulation was 6 s, and the temperature of the cryotrap was controlled by an oven temperature tracking modulation system, maintaining the difference between oven and cryotrap at −140 °C. The TOF-MS spectral storage rate was 100 Hz, using a mass range of 40–500 u and multi-channel plate voltage of 1700 V. Data were processed using LECO Corp. ChromaTOF™ software with both NIST v2.0 (2005) and Adams essential oils mass spectral libraries used for spectral matching. A series of alkanes (C8–C22) were analyzed using the same method to establish first dimension retention indices, in order to tentatively identify the compounds by comparison with literature (either from the NIST 2005 library, or from literature sources [13]).

The non-polar/polar column set (all columns were from SGE International, Ringwood, Australia) consisted of a BPX5 (5% phenyldimethyl polysilphenylene-siloxane phase) first dimension (^{1}D) column of 30 m length, 0.25 mm I.D. and 0.25 μm film thickness (d_f), with a BP20 (poly(ethylene glycol) phase) second dimension (^{2}D) column of 1.5 m length, 0.1 mm I.D. and 0.1 μm d_f.

The oven temperature program commenced at 35 °C (held for 5 min), raised to 210 °C at 3 °C/min, then raised to 240 °C at 40 °C/min and held for 10 min at 240 °C. The carrier gas used was helium at flow rate of 1.3 mL/min. The transfer line for the GC × GC/TOF-MS system was a 0.50 m deactivated fused silica column with 0.1 mm I.D. (0.21 m inside the transfer line and 0.29 m inside the oven) from SGE International. The transfer line temperature was 250 °C.

3. Results and discussion

Table 1 shows the compounds tentatively identified in cachaça samples by using MS library matching and retention index criteria. Compounds in this table were assembled into homologous groups comprising the same functionality or substituent, in which the difference is one or more carbons in the alkyl chain. The high mass spectral quality is a result of the resolution improvement afforded by GC × GC, increasing the library matching metric such that most compounds identified exhibited in excess of 900 in mass spectral similarity between the experiment and library data.

The chromatographic structure of homologous series in the 2D space represented by GC × GC operation makes it relatively easy to identify these related compounds [14,15], and with this method it was possible to identify a large number of different functional groups, for both polar and non-polar compounds. The variation in retention indices obtained is considered reasonable (<3%), if one takes into account that the literature values were determined in a one-dimensional system, with a non-polar column phase (5% phenyl methylpolysiloxane). In this work, the system is bi-dimensional, and although the first dimension column has a