Effects of progressive freeze concentration on craft beer: Volatile compounds, sensory profile, and physicochemical characteristics

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Abstract

Craft beers are becoming increasingly popular due to their developed and complex flavours, and there is a potential market for developing concentrated products; thus, freeze concentration can exploit this opportunity. In this work, the changes in physicochemical properties, volatile organic compounds, and sensory profiles of three craft beers (Witbier, Bitter, and Porter) after applying progressive stirred freeze concentration (PSFC) were evaluated, both on the concentrated liquid fraction and the ice fraction. After freeze concentration, increasing the concentration of all physicochemical characteristics in the three beers was possible. It was also possible to preserve the distribution of the volatile components in the liquid fractions and change it in the ice fractions. Significant differences were found in the sensory analysis of the concentrated liquid and the recovered ice fractions, and they were associated with the changes in the volatiles and the physicochemical properties. PSFC presents an opportunity to develop new beer products since both fractions show the potential to be commercialized.

Keywords: craft beer, freeze concentration, volatile compounds, sensory profile.

1 Introduction

Beer is a complex product with five major components and over 800 organic compounds from the raw materials, the brewing process or storage, as shown in Figure 1 (Buiatti, 2008; Verhagen, 2010). Some of these compounds are nonvolatile compounds, such as polyphenols or hops alfa-acids (Bertuzzi et al., 2020; D. O. Carvalho & Guido, 2022; Cortese et al., 2020; Gonzalez Viejo et al., 2019; Sohrabvandi et al., 2012; Verhagen, 2010), and others are volatile compounds, such as alcohols, aldehydes, and furans (Alves et al., 2020; Coelho et
Overall, the interaction of all these compounds affects the flavour, giving each brew distinctive profile (Alves et al., 2020).

Figure 1. The approximate composition of an average beer by volume percentage (Buiatti, 2008; Verhagen, 2010). The other composition is related to organic volatile and nonvolatile compounds.

Beer can be divided into two categories: industrial beer, usually brewed by bottom fermentation (Lager type), and craft beer, traditionally produced by top fermentation (Ale type) (Fang et al., 2022; Palmioli et al., 2020). The growing demand for diversity, quality, and sensory complexity, named the “flavour revolution”, has opened an opportunity for craft ale beers worldwide (Aquilani et al., 2015; Callejo et al., 2020; Gómez-Corona et al., 2016) because they have more developed and complex flavours than the Lager type (Tang & Li, 2017). The industry of craft beer continues to expand because its consumers look for novel and complex flavour profiles, which creates an opportunity for diversification of beer styles, flavour qualities, and intensities and the development of new products based on new technologies and ideas (Jaeger et al., 2020; Tang & Li, 2017; Villacreces et al., 2022). It is possible to modify the concentration of the compounds responsible for flavour, thus generating concentrated beer products, highlighting the attributes consumers value most (Miyawaki et al., 2016; Osorio et al., 2023; Wu et al., 2017).

Therefore, it is necessary to use a technique that allows the removal of water, avoiding the impact of compounds sensitive to temperature or the loss of volatiles, such as freeze concentration (FC), which is a method based on removing water from a solution by cooling and freezing until high purity ice crystals are formed and separated (Miyawaki & Inakuma, 2021). FC has shown promising results regarding the concentrations achieved and the preservation or enhancement of organoleptic properties and bioactivity (Almeida et al., 2023; Barros et al., 2021; Haas et al., 2022; Moreno et al., 2015; Orellana-Palma et al., 2017; Orellana-Palma, Tobar-Bolaños, et al., 2020; Samsuri et al., 2020). Several FC techniques are grouped into three categories: suspension, layer, and block (Miyawaki & Inakuma, 2021). Suspension FC is a high-performance process but involves high investments and operation costs (Sánchez et al., 2009). Therefore, improving other more affordable techniques, such as progressive FC, is essential. For example, the progressive stirred freeze concentration (PSFC) quickly achieves a high concentration index, although it may have ice layer occlusion (Masuda et al., 2022; Moussaoui et al., 2021; Muñoz et al., 2019; Osorio et al., 2018).
First, PSFC has been applied to ethanol–water solutions (Osorio et al., 2018). In addition, FC has been applied to alcoholic beverages such as wine, increasing the concentration of alcohol and other molecules such as polyphenols (Petzold et al., 2016) and improving the sensory profile (Wu et al., 2017). More recently, Osorio et al. (2023) applied falling-film FC to a commercial Lager beer to modify its sensory profile. Other products obtained by FC have been applied to the analysis of volatile organic molecules (VOMs), such as apple juice (Orellana-Palma, Lazo-Mercado, et al., 2020) and coffee extracts (Moreno et al., 2015).

To the best of our knowledge, no studies have been performed regarding the impact of FC on beer volatile compounds. Therefore, there is a research opportunity to study the behaviour of different volatile organic compounds present in beer and their effect on the sensory profile in the PSFC process. This paper aims to study the changes in the sensory profile of three craft ale beers after applying PSFC. Physicochemical parameters such as total solids content, ethanol concentration, total polyphenols, bitterness, colour, and the VOM profile, by its relative area percent, were evaluated before and after the FC process to determine the viability of PSFC as a novel process to develop concentrated beer products from three types of craft ale beer.

2 Methodology.

2.1 Sample preparation

Since the “flavour revolution” presents an opportunity for craft ale beers (Callejo et al., 2020) and colour guides consumers’ categorization of beer types (Casales-garcia et al., 2023), three craft ale beers within the range from pale to dark from Bogotá Beer Company brewery (BBC, Colombia) were selected: Witbier (pale), Bitter (amber), and Porter (dark). Before each FC test, the beers were degassed in a stirred tank at room temperature at 300 rpm for one hour, as suggested by the American Society of Brewing Chemists (ASBC) (ASBC Methods of Analysis, 2010).

2.2 Progressive stirred freeze concentration Protocol

All progressive stirred freeze concentration (PSFC) tests were carried out with a stirring speed of 300 rpm (Osorio et al., 2018). The freezing temperature (Tc) for Witbier and Porter was -15 °C, while that for Bitter was -20 °C. PSFC tests were carried out with the same
arrangement used in prior works (Osorio et al., 2018), as shown in Figure 2. For each test, 900 g of the degassed sample was used. The Tc was defined according to the type of beer. The FC process was performed until an ice fraction of 0.6 was achieved, from 45 to 75 minutes. After that, the concentrated liquid was removed and weighed. Subsequently, the equipment temperature was increased to 0 °C to separate the ice layer and defrost at room temperature. The concentrated liquid and ice fractions were separated at the end, and everything described in numerals 2.4 to 2.8 was analysed.

Figure 2. Experimental setup for progressive stirred freeze concentration (PSFC) (Osorio et al., 2018)

2.3 Data analysis

The summary of the response variables applied to the PSFC is shown in Table 1.

Table 1. Response variables used for progressive stirred freeze concentration.

All the response variables reported in Table 1 were calculated at the end of the operation at the desired ice fraction. The average ice growth rate (Eq. 4) was calculated considering mainly the ice conditions (mass, concentration, and density), heat transfer area and operation time (Chen et al., 1998; Moreno et al., 2014; Osorio et al., 2018).

2.4 Physicochemical characterization

The physicochemical parameters were measured in triplicate with a CDR BeerLab® (CDR, Firenze, Italy). This equipment has been used for several beer studies (Albanese et al., 2017, 2018; Ciriminna et al., 2018; Gernat, Brouwer, et al., 2020; Gernat, Penning, et al., 2020; Scarano et al., 2018). Five kits were used: fermentable sugars (resolution 0.01 g/L), alcohol content (resolution 0.1%), total polyphenols (resolution 1 mg/L), bitterness on the International Bitterness Unit (IBU) scale (resolution 0.1), and colour on the Standard Reference Method (SRM) scale (resolution 0.1). In addition, the total solids content was determined by taking an aliquot of 5 g and drying it at 60 °C until it reached a constant weight (ISO, 2018; Osorio et al., 2023).

2.5 Volatile compound analysis

Volatile compound analysis was performed considering the ASBC Beer-48 (ASBC Methods of Analysis, 2012), with changes suggested by Alves and Tian (2020;2010). All samples
(original, liquid, and ice) were extracted by headspace-solid phase microextraction (HS-SPME). For this purpose, 10 mL of each sample was placed in a 20 mL glass vial, and to improve the extraction efficiency by salting-out, 0.2 g of NaCl was added and equilibrated for 60 minutes in the sealed vial at 18 °C with magnetic stirring. The headspace was collected on a DVB/CAR/PDMS fibre (50/30 μm thickness; Supelco Inc., Bellefonte, PA, USA) over 30 minutes and directly injected (5 min desorption time) into an Agilent 7890B gas chromatograph coupled to a selective mass detector Agilent 5977A in splitless mode. Mass spectra were recorded with electronic ionization at 70 eV in the mass range 40-300 m/z. An HP-FFAP fused silica column (J&W Scientific, 50 m x 0.25 mm i.d., 0.32 μm film thickness) was used. The column oven temperature was programmed to increase from 40 (after 1 min) to 180 °C at 1.7 °C/min and then to 220 °C at 30 °C/min. The inlet temperature was maintained at 250 °C, and the carrier gas was 1.5 mL of He/min. The linear retention indices were calculated according to the Kovats method using a mixture of normal paraffin C_{10}-C_{24} as an external reference. Compound identification was achieved by matching the query mass spectrum to the reference NIST/EPA/NIH Mass Spectral Library 2014 (2.2) database (acceptance criteria higher than 90%) and by comparing the retention index with those reported in the literature (AM, 2023; NIST Mass Spectrometry Data Center, 2006; The Good Scents Company, 2018). All measurements were made in triplicate. The results are shown as the relative area percent for each compound.

2.6 Sensory Analysis

Sensory profiles were developed by multidimensional approximation for the original sample, concentrated liquid, and ice fractions of PSFC in triplicate. Before the sensory analysis, all samples were carbonated using DrinkMate® (iDrink, Ann Harbour, USA), bringing the CO₂ concentration to saturation and storing the samples at 4 °C. The analysis was developed in two sessions at the certified Laboratory for Food Sensory Analysis, Universidad de Antioquia (Medellín, Colombia). The analysis was conducted according to ISO 11035, 3972, 5496, and 8586. The panellists were selected and trained according to ISO 8586 (ISO, 2023) and were a group of 4-8 trained judges, both men and women, aged between 25 and 60, in healthy conditions. The set of relevant descriptors that gave the maximum information on sensory attributes was identified and selected according
to the ISO 11035:1994 standard (ISO, 2015). The reference standard solution for each sensory attribute was selected according to ISO 3972 and 5496 (ISO, 2006, 2011). The descriptors were valued on a rating scale of 0 to 5, except for global impact, where a scale of 1 to 3 is used where 3 is high and 1 is low. Likewise, statistically significant differences were determined (p< 0.05).

2.7 Statistical Analysis
The freeze concentration tests were performed in triplicate. One-way analysis of variance (ANOVA) was applied to the results with a significance level of 95% with a Tukey test to determine significant differences between the physicochemical characteristics of each sample and the FC results. The volatile compound analysis was carried out in triplicate for each sample, and ANOVA was applied to the relative area percent for each compound with a significance level of 95%. A Dunnet test was used to establish the significance of the difference between the concentrated liquid and the ice fraction regarding the original sample. For the sensory analysis, ANOVA was applied to the results with a significance level of 95%, with a Tukey test to establish the significance of the difference between the intensity of the descriptors. The statistical analysis was performed using the Minitab 18 software package (Minitab Inc, Pennsylvania, USA).

3 Results
3.1 PSFC results and physicochemical characterization.
PSFC was performed on Witbier, Bitter, and Porter up to a 0.6 ice fraction. The physicochemical characterization of the concentrated liquid, ice fraction, and original sample are shown in Table 2. The results of the FC response variables are shown in Figure 3.

<table>
<thead>
<tr>
<th>Table 2. Physicochemical characterization of the original sample, concentrated liquid, and ice fraction for Witbier, Bitter, and Porter. Uppercase letters within the same column denote significant differences (P&lt;0.05) for each physicochemical parameter.</th>
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<tr>
<td>Figure 3. Concentration index (CI) and average distribution coefficient (Kapp) for Witbier (yellow-dotted bar), Bitter (orange-diagonal bar), and Porter (black-striped bar). Uppercase letters denote significant differences (P&lt;0.05) for each physicochemical parameter.</td>
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</table>

Applying the FC process to the three beers under the conditions studied was possible. First, the total solid concentration is shown in Table 2, where Witbier had the highest CI for total solids, with a value of 1.4 (Figure 2). This beer had the lowest initial concentration. The
lowest CI was for Porter, with a significantly higher initial total solid concentration than Witbier and Bitter. Accordingly, the highest \( K_{\text{app}} \) was also for Porter. This could be because an increase in the initial concentration leads to higher molecular interactions and, thus, lower separation efficiency (Petzold & Aguilera, 2009). Some of the molecules found in the total solids, such as carbohydrates and peptides, may impact the beer’s flavour, mainly its sweetness, fullness, mouthfeel, and foam stability (Depraetere et al., 2004; Verhagen, 2010). Other molecules that could be part of these solids are fermentable sugars, which are highly relevant to the sweetness of beer (Bertuzzi et al., 2020). The values of fermentable sugars found for Bitter and Porter are consistent with those reported in other craft beer studies, although those found for Witbier are slightly lower (Bertuzzi et al., 2020; Preedy, 2008). Porter also shows the lowest CI for fermentable sugars and the highest \( K_{\text{app}} \), possibly because of the interaction of higher molecular weight compounds from the Maillard reaction (Mosher, 2017; Uald-Lamkaddam et al., 2021).

Regarding ethanol, CI values between 1.27 and 1.32 were obtained, with the highest value for the lowest initial concentration being Witbier, although there were no significant differences between the beers. Additionally, ethanol showed higher values of \( K_{\text{app}} \) than total solids and fermentable sugars, which may occur due to the reinforcement of the hydrogen bonds by the presence of ethanol (Li et al., 2018), where water acts as a proton donor and ethanol as a proton receptor (Jiang et al., 2022). These values are lower than those reported in PSFC systems in ethanol–water solutions (Osorio et al., 2018) under similar conditions. The presence of other beer components increases the initial concentration and molecular interactions; a small number of organic compounds strengthen the hydrogen bond structure of water-ethanol (Qin et al., 2022).

Significant differences were found between the CI and \( K_{\text{app}} \) of ethanol and total solids for Witbier and Bitter, which is evidence of selective migration, a phenomenon previously described in other matrices’ FC processes (Dantas et al., 2021; Meneses et al., 2021; Nakagawa et al., 2009). These phenomena could appear due to the difference in the size of the molecules, their diffusivity, and the occlusion of the system (Vuist et al., 2022; Xu et al., 2022). Different kinds of chemical compounds are present in beer; however, the main carbohydrates are maltose and sucrose (Buiatti, 2008). The diffusivity of maltose in water
(between 1.7 and 5% w/w) has been reported to be between 4.8 and 5.1 x10^{-5} \text{ cm}^2/\text{s} (Uedadaira 
& Ueddaira, 1969), while that of sucrose is 4.9 x10^{-5} \text{ cm}^2/\text{s} (Hills et al., 2011). Ethanol 
between 3\% and 6\% w/w presents higher values, between 5.5 and 6.3 x10^{-5} \text{ cm}^2/\text{s}, in 
carbonated water-ethanol solutions (Khaireh et al., 2021). Although the diffusivity of ethanol 
is more remarkable, it presents a higher $\bar{R}_{\text{app}}$ value, probably because the diffusion coefficient 
of ethanol falls to a minimum as its concentration increases (Zhang et al., 2006). The size 
relationship between ethanol and maltose and the diffusivity values found show that ethanol 
should have a lower $\bar{R}_{\text{app}}$ value concerning total solids, which did not occur. This 
phenomenon can be attributed to solute premelting, wherein solutes form a solute-rich 
premelted film around the ice layer (Uhlmann et al., 1964). This film is thermodynamically 
stable at temperatures below the bulk melting point and exhibits remarkable sensitivity to the 
presence of solutes (Tyagi et al., 2020). The concave curvature of the solidification front 
plays a crucial role in this process, as it promotes lateral solute diffusion, causing the front to 
accelerate and encase the object with the solute-rich premelted film (Lin et al., 2020). 
Consequently, solutes find themselves entrapped within the advancing ice front despite their 
higher diffusion rate, owing to the formation of the premelted film (Saint-Michel et al., 2017; 
Tyagi et al., 2020), and therefore leading to a higher occlusion.

However, the values of CI obtained in PSFC were higher than those reported in beer in falling 
film FC, although the beers evaluated in this work have a more complex composition than 
lagers (Osorio et al., 2023). It is possible that the agitation system allows for better mass 
transfer than the falling film system. The volumetric concentration ratio in the falling film 
system is generally not as high. The flowing speed is insufficient to achieve a high ice purity 
with sufficient stirring at the ice–liquid interface (Miyawaki & Inakuma, 2021).

In addition, the $\bar{v}_{\text{ice}}$ for Witbier and Porter was 4.8 and 4.5 µm/s, respectively, similar to 
those reported in ethanol–water solutions in the same FC process (Osorio et al., 2018), while 
that of Bitter was 6.4 µm/s, probably because of the difference in the freezing temperature 
that causes a higher heat transfer. Some authors have reported a $\bar{v}_{\text{ice}}$ value of 8 µm/s as the 
critical freezing rate (Nakagawa et al., 2010; Petzold et al., 2016), so it is possible to confirm 
that the FC of the beers was possible under the conditions studied. Ethanol-based products
may require relatively higher freezing rates due to the depression of the freezing point and the need for a higher heat transfer rate (Vuist et al., 2020).

For the colour of the beers, the colour changes concerning the original sample were greater in the pale beer (Witbier), which makes sense as it also presented the highest CI value for total solids, where melanoidins could be found. This compound comes from nonenzymatic reactions and is initially yellow, orange, and red before it turns brown as the Maillard reaction is allowed to proceed (Bamforth, 2009; Pieczonka et al., 2021; Van Doorn et al., 2019). Although Porter showed the lowest CI for total solids, the colour change was the second highest, which could be related to the concentration of polyphenols. In addition to melanoidins, polyphenols can modify the colour of beer (Bamforth, 2009).

Overall, the total polyphenol concentration was similar to that reported in the literature for similar types of beer (Bertuzzi et al., 2020; D. O. Carvalho & Guido, 2022; Verhagen, 2010), with Witbier having the lowest initial concentration of total polyphenols, followed by Bitter and Porter. Wheat beers usually presented low total polyphenols (Bertuzzi et al., 2020; Cheiran et al., 2019), allowing a higher concentration at the liquid fraction (by 1.26 times), the highest increase among the 3 samples. Bitter has higher initial total polyphenols than Witbier, as expected due to the higher amount of hops used in this style of beer (Bertuzzi et al., 2020; Breda et al., 2022; D. O. Carvalho & Guido, 2022). Additionally, Porter had the highest initial concentration of polyphenols, which was expected since some polyphenols have a higher concentration in dark beers and stout types (Verhagen, 2010). However, the CI of the total polyphenols of Porter was the lowest due to interactions between melanoidins and the polyphenols.

In this study, only the Witbier had a significant difference in the original IBU compared to the Bitter and the Porter. It allows a higher increase in bitterness related to the other styles. Porter had the lowest IBU increase (1.17 times), possibly due to the occlusion of these molecules caused by the chemical interaction with proteins (Bamforth, 2009) that could also be trapped in the ice, with Porter being the style with the highest concentration of total solids. The litter liquid fraction has the highest IBU value statically, probably because of the lower occlusion of proteins compared to Porter.
In general, the freezing temperatures used in this study allowed similar ethanol CIs to be obtained for the three types of beer, while the solids were only different for Porter beer (which had the highest initial solid content). The CI and Kapp reached for the other physicochemical parameters were significantly different since these are more distinctive in each type of beer. Furthermore, the occlusion of Porter beer solids led to a higher occlusion in fermentable sugars and total polyphenols, possibly due to the interactions between these molecules.

3.2 Volatile analysis

The volatile organic metabolites (VOMs) of the initial extract, the liquid, and the ice fractions of PSFC of three beer styles were identified and quantified through GC–MS. Figure 4 shows the representative chromatogram of the original sample of Witbier, Bitter and Porter. Table 3 shows the experimental retention index (RI), literature value of RI, odour note, and the relative amount in each sample (% area percentage). ANOVA was applied with Dunnet’s test to find significant differences in the relative composition by the area percentage of each compound in the concentrated liquid and the ice fraction to the original sample (p<0.05). The type of VOMs were alcohols (30%), followed by esters (26%), terpenes (17%), and furan and ketones (9% each); the remaining composition corresponded to an aldehyde and a carboxylic acid. This distribution is similar to that reported by Alves et al. (2020), showing a higher predominance of higher alcohols, those containing more carbon atoms than ethanol (Colicchio et al., 2011), and a lower presence of aldehydes.

In addition to ethanol, beer contains several alcohols derived mainly from yeast metabolism and hops and malts, commonly known as higher alcohols. These compounds are formed as byproducts of amino acid synthesis and catabolism (Olaniran et al., 2017), usually exhibit intense aromas, and can warmly affect taste. Higher alcohols are the direct precursors of esters and contribute to favourable beer flavour (Verhagen, 2010). They also may contribute to beer texture in the mouth (mouthfeel), and floral aromas from some of these contribute to the pleasing aroma (Buiatti, 2008). Some of the most relevant alcohols were 3-methyl-1-butanol and phenylethyl alcohol. All alcohols and acids present in beer are theoretically...
capable of esterification reactions, creating many esters (Buiatti, 2008). Overall, esters give the beer a fruity character (Verhagen, 2010). Some of the most common esters in beer are 3-methyl-butyl acetate, ethyl hexanoate, ethyl octanoate, and phenylethyl acetate (Alves et al., 2020; Buiatti, 2008; Verhagen, 2010). Conversely, terpenes are natural compounds primarily from the hop and in minor proportion from malt (Buiatti, 2008). Additionally, terpene and lipid degradation pathways may interact to form new terpenes (Bettenhausen et al., 2018). Furthermore, in most beer, terpenes are associated with floral and fruity notes, and some of the most common are β-myrcene and linalool (Bettenhausen et al., 2018; Eyres & Dufour, 2008; Martins et al., 2018). Other VMOs in beer are carbonyl compounds, such as aldehydes and ketones, and are essential for the quality of the beer because some of them are characterized as possible off-flavours (Bamforth, 2009), while compounds such as Furans constitute a significant class of compounds formed during the Maillard reactions (Alves et al., 2020).

Figure 5 shows the VOMs in Witbier fractions. In the original sample, approximately 52% of the area corresponds to esters, the most predominant compounds for Witbier, possibly due to the presence of wheat in its fabrication, which gives the beer more unique aromatic compounds (Villacreces et al., 2022). Among these compounds, ethyl octanoate has the highest relative composition, the same as that reported in Lager beer by Alves et al. (2020). Ethyl octanoate has been highly associated with fruity and floral notes in beer, while ethyl hexanoate and heptanoate have also been associated with wine–brandy notes. In addition, terpenes occupy 20% of the area, mainly by linalool, which is a suitable marker compound for hoppy floral flavour, and in minor proportion by citronellol (floral, citrus aroma) and limonene, with citrus notes, which are very characteristic of Witbier beers (Strong, 2021). Witbier had the highest terpene relative concentration among the three beers. Higher alcohols represent approximately 15% of the total area, with the major participation of 3-methyl-1-butanol (whiskey, malty, burnt) and 2-phenylethanol (floral, alcohol, honey). 1-Nonanol and 1-octanol are associated with orange peel notes, a key ingredient in Witbier production (Strong, 2021). The furans found in the Witbier were 2-acetylfuran and 2-furanmethanol, related to coffee, burnt, nutty, caramel, sugarcane, and burnt sugar, respectively (AM, 2023; ASBC Methods of Analysis, 2017; Burdock, 2005).
After the PSFC process, the relative distribution of VOMs in Witbier was preserved for the concentrated liquid. However, two compounds were no longer detected: 6-methyl-5-hepten-2-one and 1,2-dimethyl-cyclopent-2-ene-carboxylic acid. On the other hand, at the ice fraction, 26% of the total VOMs in the original sample had a significant change. The proportion of esters decreased by approximately 14% compared to the original sample, mainly because of a significant increase in ethyl octanoate. In addition, the relative composition of 3-methyl-1-butanol, ethyl hexanoate, 2-methyl-3-pentanone, and linalool significantly changed. Finally, 6-methyl-5-hepten-2-one was no longer detected in the ice fraction.

On the other hand, the original Bitter sample presents a predominance of higher alcohol VOMs, nearly 40% by relative concentration, mainly from 3-methyl-1-butanol (19%) and 2-phenylethanol (14%), which have been reported to independently contribute to the overall beer aroma (Kishimoto et al., 2018). It also has a higher relative amount of 1-hexanol, 1-heptanol, and 1-nonanol than Witbier beer, which is related to an alcoholic, fatty, green flavour. Additionally, it has 1-pentanol, an aliphatic alcohol produced by yeast with a pleasant odour and burning taste (Burdock, 2005; Tang & Li, 2017). The esters represent 34.3% of the total area, mainly from ethyl hexanoate and 3-methyl-butyl acetate. However, Bitter beer had the lowest relative concentration of esters compared to Witbier and Porter. Terpenes also had a significantly lower proportion than Witbier, although β-myrcene was detected in the original sample. This compound has been associated with the ripeness of the hops and is a potent odourant in beer (Briggs et al., 2004), with a resinous, spicy aroma, which is distinctive for a Bitter style (ASBC Methods of Analysis, 2017; Piggott, 2012; Strong, 2021). At the concentrated liquid fraction, there was a significant change in the relative concentration of two compounds: ethyl octanoate increased its participation, while 2-methyl-3-pentanone decreased it to the original sample. On the other hand, ethyl octanoate and 1-octanol increase their relative concentrations at the ice fraction. Overall, 91% of the VOMs’ relative abundance was preserved in both fractions.

Finally, Porter showed a higher proportion of esters (47.3%), followed by higher alcohols (31.3%). The major relative concentration in esters was related to ethyl hexanoate and 3-methyl-butyl acetate (22.5 and 15.5%, respectively), while in alcohols were 3-methyl-1-
butanol and 2-phenylethanol, with 18.2% and 10%, respectively. These four compounds were also reported as the most abundant VOMs in a Belgian Dark Strong Ale, another dark beer from the Ale family (Coelho et al., 2019). It also presented a higher relative concentration of 1,2-dimethyl-cyclopent-2-ene-carboxylic acid, an acid compound with no reported flavour, that had been found in sorghum beer and wine made from goji berries (Budner et al., 2021; Yuan et al., 2016). The lower proportion of terpenes related to Witbier could be explained by using dark malts in the production of Porter because terpenes are significantly higher in pale beers than in dark beers (Paszkot et al., 2023). Ninety-six percent of the VOMs preserve their relative abundance in the concentrated liquid, with only a significant decrease in the limonene relative concentration. In addition, at the ice fraction, five compounds had a significant decrease in their relative concentration: ethyl heptanoate, ethyl hexanoate, 1,2-dimethyl-cyclopent-2-ene-carboxylic acid, 2-phenylethyl acetate, and 6-methyl-5-hepten-2-one, leading to a significant change of 22% in the VOM relative concentration.

Several authors have shown the ability of various FC techniques to maintain the volatile profile in coffee and fruit beverages (Moreno et al., 2015; Orellana-Palma, Lazo-Mercado, et al., 2020; Orellana-Palma, Tobar-Bolaños, et al., 2020; Ramos et al., 2005). This work shows the PSFC potential to preserve (the concentrated liquid of three beers) and modify (the ice fraction of Witbier and Porter) the relative concentration of VOMs of three Ale beers. It was achieved by not rehydrating the original sample, evaluating the concentrated product, and the fraction of ice recovered. A similar result was found by Wu et al. (2017) in Cabernet Sauvignon Wine, where FC led to higher amounts of esters and higher alcohols as well as a lower volatile acid content. The effect of changes in WOMs on the sensory profiles of the samples had to be evaluated. These results are shown in Section 3.3.

3.3 Sensory Analysis

The sensory analysis of the original sample of the three types of beer was carried out, and it was compared with the profiles of the concentrated liquids and the ice fractions obtained.
from each one after the PSFC process. In addition, the sensory profiles were associated with
the volatile compounds detected in Section 3.2 and the information in Table 2.

First, in Figure 6, the sensory profile of the original sample of Witbier beer can be observed.
This beer shows a balanced aromatic profile, with similar values for alcohol, malty, sweet,
floral, and hoppy notes, with slightly lower fruit and acid notes. Regarding flavour, this
sample showed sweet, floral, fruity, hoppy, and alcoholic flavours, with less intense notes of
acid and malt. This profile could be associated with a higher proportion of esters and terpenes
(Bettenhausen et al., 2018; Paszkot et al., 2023; Sharp et al., 2017). Additionally, it was
possible to identify green and tobacco-related flavours related to hexyl acetate and 2-
phenylethyl acetate, respectively. Alcohol flavours and aromas are not only due to the ethanol
in the beer but also to 3-methyl-1-butanol and 2-phenylethanol. In addition, floral notes can
be associated with 2-phenylethyl acetate and citronellol, while fruity notes are mainly
associated with the esters ethyl hexanoate and ethyl heptanoate. Ethyl octanoate and linalool
give floral and fruity flavours, which had the major participation in the GC area (Table 3).
The sweetness could be related mainly to the fermentable sugars discussed in Section 3.1.
Additionally, Witbier presented the lowest intensity in this descriptor among the three beers,
being the one with the lowest °IBU. In this same sense, although polyphenols have no aroma,
they impact several beer characteristics, such as astringency, haze, colour, and body
(Colicchio et al., 2011). Witbier presented the least astringency, with the lowest total
polyphenol content associated with this characteristic (Aron & Shellhammer, 2010).

Nine of the twenty-three descriptors significantly increased in the concentrated liquid
compared to the original sample. Although the relative composition of the VOMs did not
significantly change, it is possible that an increase in the concentration of the molecules
occurred but maintained the same distribution, thus increasing the flavour intensity. In
addition, the rise in the hop aroma could be associated with increased alfa acids related to the
IBUs. The increase in total solids raises the beer’s body, highlighting the malty flavours, just
as the increase in fermentable sugars presented an increase in the sweet flavour. Finally, the
increase in total polyphenols was reflected in a significant increase in astringency. Although
several descriptors significantly changed, the global impact still presented the highest value
(3), possibly by maintaining the distribution of VOMs. In the ice fraction, the decrease in the
intensity of fruity aroma and floral taste could be associated with the significant decrease in
the participation of ethyl octanoate (de Lima et al., 2023; Yang et al., 2022). The malty and
sweet taste increase could be related to the increase in the relative area of 3-methyl-1-butanol
(Coelho et al., 2019). Additionally, the occlusion of total solids may allow for maintaining
the beer’s body. Even though the ice fraction has a lower concentration of all
physicochemical parameters and a decrease in three sensory descriptors compared to the
original sample, it maintains its global impact at the highest value. Its new VOM profile may
have made this an attractive light beer.

Figure 6. Sensory profile of the original sample of Witbier (Bars) vs. concentrated liquid (Continuous green line) and ice
fraction (Blue dotted line). Significant differences p<0.05 for concentrated liquid are Diamonds and Squares for ice
fraction, relative to the original sample. The abbreviations correspond to Odour (O), Taste (T), and somatosensory (SS).

Figure 7 shows that Bitter is a more complex beer than Witbier. It has more malty, alcoholic,
and sweet aromas, possibly because of the higher proportion of higher alcohols, mainly 3-
methyl-1-butanol, 2-phenylethanol, and 1-pentanol, associated with alcoholic, malty, honey,
and sweet notes (ASBC Methods of Analysis, 2017; Coelho et al., 2019; Kishimoto et al.,
2018). It also had a major proportion of ethyl hexanoate (rather than the ethyl octanoate in
Witbier), which has more wine and brandy aromas (de Lima et al., 2023; Yang et al., 2022).
Its taste is characterized by a strong bitterness, being the beer with the highest initial °IBU;
its higher ethanol content compared to the Witbier and predominant green notes in the
flavour, possibly associated with the 6-methyl-5-hepten-2-one (de Lima et al., 2023). This
description corresponds to that expected for this type of beer, given that the balance may vary
fairly, even between malt and hops, and may be somewhat bitter (Strong, 2021). The
concentrated liquid showed a significant increase in three descriptors (yeast flavour, tobacco
flavour, and astringent sensation) and decreased malty aroma. As in Witbier, the increase in
astringency can be explained by the increase in total polyphenols in the sample. The increase
in tobacco flavour could be related to changes in 2-phenylethyl acetate. An increase in green
flavour was obtained in the ice fraction, possibly related to 1-heptanol. The fruity flavour is
related to the increase in the 1-octanol and ethyl octanoate proportion (Coelho et al., 2019).
The most marked change in the VOM profile between the original and the liquid and ice
fractions was the increase in the relative abundance of ethyl octanoate, which may be the
cause of the reduction in the global impact of both fractions because it has been reported that
when this compound exceeds its threshold, it gives the beer an undesirable flavour (Olaniran et al., 2017).

Finally, Figure 8 shows that the higher descriptors of Porter are bitterness and body, which makes sense since this beer had a higher value of total solids concentration and an IBU similar to the Bitter beer. 2-Ethyl hexenal may contribute to the bitter flavour (Burdock, 2005). The green taste could be associated with 1-hexanol, 1-heptanol, hexyl acetate, 6-methyl-5-hepten-2-one, and limonene, while the roasted taste is related to furans, 2-acetyl-furan, and 2-furanmethanol (ASBC Methods of Analysis, 2017; Burdock, 2005). The alcohol taste came from ethanol and higher alcohols (ASBC Methods of Analysis, 2017; Burdock, 2005).

Nineteen descriptors were maintained in the concentrated liquid, while the remaining 3 significantly decreased, although Table 3 shows that all physicochemical characteristics increased. Dark beer perception could be affected by its colour because it is expected to be more bitter, have a higher alcohol content, and have more body than pale beer (F. R. Carvalho et al., 2017; Reinoso-Carvalho et al., 2019). The colour rise in concentrated liquid may generate a higher expectation of bitterness, alcohol content, and body, generating a lower score for not meeting these expectations (Reinoso-Carvalho et al., 2019). At the ice fraction, 14 of the 22 descriptors were preserved, while the aroma acid rose and the other 8 descriptors were significantly reduced: sweet and roasted aroma, bitter, alcohol, green, roasted taste, and the body.

The global impact of the samples was evaluated from 0 to 3 and is shown in Figures 4-6. The Witbier beer obtained a value of 3, its concentrated liquid, and the ice fraction. It opened an opportunity to develop new products for this type of beer: creating two fractions with different sensory profiles and changes in the physicochemical properties and volatile composition was achieved, and the global impact was still preserved. A similar case occurred for the Porter, where the global impact was preserved for the concentrated liquid and the ice fraction. The Bitter beer global impact decreased from 3 to 2 in the concentrated liquid and
ice fractions. This is likely due to their characteristics: the balance can range from fairly even between malt and hops to somewhat bitter, and its drinkability is critical to the style (Strong, 2021). Previous works presented the viability of applying FC to modify the sensory profile of Lager beer (Osorio et al., 2023). However, this is the first study to apply a VOM profile and to the ice fraction to relate it to sensory changes and changes in physicochemical characteristics. The changes in sensory profiles show the possibility of applying FC to develop beer products.

4 Conclusions

Progressive stirred freeze concentration was successfully applied to three types of craft beers: Witbier, Bitter, and Porter. The concentrated liquids obtained after PSFC from the three beers increased the ethanol content, total solids, total polyphenols, and fermentable sugars and changed the colour and bitterness compared to the original sample. Additionally, the freeze-concentrated beer products presented changes in the relative composition of the volatile components by area percentage in GC analysis, with Witbier changing the most, mainly in alcohols and esters. Likewise, the products obtained sensory profiles different from the original ones, linked to the physicochemical and volatile changes.

However, the physicochemical characteristics found in the recovered ice fractions are still within the quality parameters defined for each type of beer due to the occlusion phenomena, where changes in the relative concentration of VOMs were found and related to changes in the sensory profile. Hence, both fractions obtained after applying PSFC show the potential to be commercialized.

This presents an opportunity to develop new beer products by applying freeze concentration technology since both a concentrated and a lighter product were possible with different sensory profiles and with changes in the physicochemical properties and volatile distribution.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Consent to participate in the publication
The authors approve the publication and their respective participation in this research without restriction.

Author contributions
M. Osorio: investigation, methodology, formal analysis, visualization, writing—original draft. F.L. Moreno: formal analysis, writing—review & editing, supervision. E. Hernández: formal analysis, writing—review & editing, supervision. Annamaria Filomena-Ambrosio: sensory analysis & writing—review. Coralia Osorio: Volatile analysis & writing—review. Ruth Yolanda Ruiz-Pardo Ruiz: conceptualization, resources, formal analysis, writing—review & editing, supervision, project administration, funding acquisition.

5 Bibliography


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Table 1. Response variables used for progressive stirred freeze concentration.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice fraction (f)</td>
<td>( f = \frac{\text{Ice mass}}{\text{Initial mass}} ) (1)</td>
<td>(Miyawaki et al., 2012; Nakagawa, Maebashi, et al., 2010)</td>
</tr>
<tr>
<td>Concentration index (CI)</td>
<td>( CI = \frac{\text{Liquid Solute concentration}}{\text{Initial solute concentration}} ) (2)</td>
<td>(Moreno et al., 2014b; Nakagawa et al., 2009)</td>
</tr>
<tr>
<td>Average distribution coefficient (( \overline{K}_{\text{app}} ))</td>
<td>( \overline{K}_{\text{app}} = \frac{\text{Ice Solute concentration}}{\text{Liquid solute concentration}} ) (3)</td>
<td>(Miyawaki et al., 2012; Moreno et al., 2014a)</td>
</tr>
<tr>
<td>Average ice growth rate (( \overline{v}_{\text{ice}} ))</td>
<td>( \overline{v}<em>{\text{ice}} = \frac{\text{mass}</em>{\text{ice}} (1 - \text{Solute concentration}<em>{\text{ice}})}{\text{time Area density}</em>{\text{ice}}} ) (4)</td>
<td>(Chen et al., 1998; Moreno et al., 2014a; Osorio et al., 2018)</td>
</tr>
</tbody>
</table>
Table 2. Physicochemical characterization of the original sample, concentrated liquid, and ice fraction for Witbier, Bitter, and Porter. Uppercase letters within the same column denote significant differences (P<0.05) for each physicochemical parameter.

<table>
<thead>
<tr>
<th>Beer</th>
<th>Fraction</th>
<th>Ethanol % (w/w)</th>
<th>Total solids % (w/w)</th>
<th>Fermentable sugars % (w/w)</th>
<th>Colour (SRM)</th>
<th>Total Polyphenols (mg/l)</th>
<th>Bitterness (°IBU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Witbier</td>
<td>Original</td>
<td>4.12% ± 0.14B</td>
<td>3.65% ± 0.24C</td>
<td>0.42% ± 0.03B</td>
<td>2.5 ± 0.4A</td>
<td>169.3 ± 4B</td>
<td>8.3 ± 0.5A</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>5.45% ± 0.21CD</td>
<td>5.12% ± 0.31DE</td>
<td>0.59% ± 0.05CD</td>
<td>3.5 ± 0.7A</td>
<td>213.5 ± 4C</td>
<td>14.3 ± 0.4B</td>
</tr>
<tr>
<td></td>
<td>Ice</td>
<td>2.20% ± 0.57A</td>
<td>1.45% ± 0.07A</td>
<td>0.18% ± 0.06A</td>
<td>1.5 ± 0.8A</td>
<td>100.0 ± 3A</td>
<td>5.6 ± 0.8A</td>
</tr>
<tr>
<td>Bitter</td>
<td>Original</td>
<td>4.61% ± 0.26BC</td>
<td>3.89% ± 0.07C</td>
<td>0.68% ± 0.02D</td>
<td>11.9 ± 0.8C</td>
<td>305.3 ± 8D</td>
<td>18.8 ± 0.5C</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>5.85% ± 0.36D</td>
<td>5.30% ± 0.28DE</td>
<td>0.98% ± 0.01B</td>
<td>13.5 ± 0.7C</td>
<td>370.0 ± 20E</td>
<td>30.8 ± 1.1E</td>
</tr>
<tr>
<td></td>
<td>Ice</td>
<td>2.75% ± 0.21A</td>
<td>1.80% ± 0.28A</td>
<td>0.24% ± 0.06A</td>
<td>8.8 ± 0.4B</td>
<td>208.5 ± 5C</td>
<td>23.4 ± 3.4D</td>
</tr>
<tr>
<td>Porter</td>
<td>Original</td>
<td>4.14% ± 0.44B</td>
<td>4.73% ± 0.31D</td>
<td>0.63% ± 0.04CD</td>
<td>30.5 ± 1.3E</td>
<td>408.0 ± 7F</td>
<td>18.0 ± 0.8C</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>5.33% ± 0.19CD</td>
<td>6.00% ± 0.42E</td>
<td>0.69% ± 0.01D</td>
<td>36.5 ± 0.7F</td>
<td>438.5 ± 2G</td>
<td>21.0 ± 1.4CD</td>
</tr>
<tr>
<td></td>
<td>Ice</td>
<td>2.34% ± 0.2A</td>
<td>2.83% ± 0.24B</td>
<td>0.53% ± 0.01C</td>
<td>26.3 ± 0.4D</td>
<td>375.0 ± 7E</td>
<td>17.4 ± 0.8BC</td>
</tr>
</tbody>
</table>
Table 3. VOMs distribution by relative area percentage in GC analysis for each type of beer and fraction evaluated.

<p>| Peak | Compound                  | CAS Number | RI&lt;sub&gt;Ca&lt;/sub&gt; | RI&lt;sub&gt;&lt;sub&gt;Ca&lt;sup&gt;A&lt;/sup&gt;&lt;/sub&gt;&lt;/sub&gt; | Flavor Category | Relative percentage area |                  |                  |                  |                  |
|------|---------------------------|------------|-----------------|---------------------------------------|-------------------|--------------------------|                  |                  |                  |                  |
|      |                           |            |                 |                                       |                   |                           | Witbier          | Bitter           | Porter           |                  |
|      |                           |            |                 |                                       |                   |                           | Original | Liquid | Ice     | Original | Liquid | Ice    | Original | Liquid | Ice     |                  |                  |
| 1    | 2-Methyl-3-pentanone      | 565-69-5   | 1025            | 1003                                  | Herbal, mint      | 0.67 ± 0.14               | 0.64 ± 0.10     | 1.00 ± 0.14*   | 1.47 ± 0.16   | 1.14 ± 0.09*   | 1.40 ± 0.09   | 1.35 ± 0.06 | 0.84 ± 0.07 | 1.14 ± 0.65 |
| 2    | 3-Methyl-butyl acetate    | 123-92-2   | 1111            | 1128                                  | Fruity, apple,    | 6.30 ± 2.95               | 6.62 ± 1.40     | 11.30 ± 3.64  | 10.68 ± 2.61  | 9.86 ± 1.31    | 10.15 ± 3.21  | 15.50 ± 2.91 | 11.23 ± 0.94 | 12.36 ± 11.22 |
| 3    | ß-Mycene                  | 123-35-3   | 1143            | 1158                                  | Herbal, metallic, | 0.02 ± 0.03               | 0.06 ± 0.02     | 0.06 ± 0.06   | 0.14 ± 0.07   | 0.11 ± 0.09    | 0.10 ± 0.04   | 0.44 ± 0.06  | 0.23 ± 0.05   | 0.48 ± 0.57  |
| 4    | Limonene                  | 138-86-3   | 1180            | 1206                                  | Citrus, green,    | 0.35 ± 0.25               | 0.25 ± 0.06     | 0.22 ± 0.19   | 0.21 ± 0.03   | 0.20 ± 0.06    | 0.22 ± 0.06   | 0.31 ± 0.04  | 0.14 ± 0.08*  | 0.29 ± 0.06  |
| 5    | 3-Methyl-1-butanol        | 123-51-3   | 1206            | 1209                                  | Alcohol, malty,   | 8.60 ± 1.80               | 8.75 ± 0.94     | 14.58 ± 0.16* | 19.44 ± 3.69  | 17.88 ± 1.60   | 20.02 ± 1.87  | 18.24 ± 0.13 | 14.57 ± 1.67 | 24.30 ± 9.09 |
| 6    | Ethyl hexanoate           | 123-66-0   | 1223            | 1226                                  | Fruity, strawberr | 8.97 ± 2.74               | 9.67 ± 1.55     | 13.51 ± 1.14* | 19.32 ± 3.43  | 17.65 ± 2.21   | 19.82 ± 3.66  | 22.54 ± 0.70 | 15.27 ± 5.61 | 9.09 ± 7.22* |
| 7    | 1-Pentanol                | 71-41-0    | 1248            | 1253                                  | Balsamic, fusel   | 0 ± 0                     | 0.03 ± 0.05     | 0.35 ± 0.60   | 2.67 ± 3.14   | 1.51 ± 1.03    | 1.30 ± 1.02   | 1.04 ± 1.60  | 0.41 ± 0.44   | 1.07 ± 1.41  |
| 8    | Hexyl acetate             | 142-92-7   | 1262            | 1268                                  | Fruity, green     | 0.19 ± 0.02               | 0.16 ± 0.05     | 0.22 ± 0.02   | 0.19 ± 0.06   | 0.19 ± 0.03    | 0.17 ± 0.03   | 0.41 ± 0.11  | 0.37 ± 0.26   | 0.07 ± 0.06  |
| 9    | Ethyl heptanoate          | 106-30-9   | 1321            | 1327                                  | Fruity, berry     | 0.11 ± 0.01               | 0.11 ± 0.01     | 0.11 ± 0.05   | 1.29 ± 1.01   | 1.45 ± 0.58    | 1.61 ± 0.68   | 1.21 ± 0.52  | 1.26 ± 0.46   | 0.08 ± 0.07* |
| 10   | 6-Methyl-5-hepten-2-one   | 110-93-0   | 1328            | 1319                                  | Mushroom, earthy  | 0.02 ± 0.03               | 0 ± 0           | 0 ± 0         | 0.26 ± 0.23   | 0.18 ± 0.19    | 0.08 ± 0.02   | 0.11 ± 0.04  | 0.08 ± 0.03   | 0.02 ± 0.03* |
| 11   | 1-Hexanol                 | 111-27-3   | 1345            | 1355                                  | Fruity, fatty,    | 0.08 ± 0.02               | 0.08 ± 0.01     | 0.05 ± 0.09   | 0.21 ± 0.10   | 0.13 ± 0.02    | 0.29 ± 0.07   | 0.17 ± 0.03  | 0.09 ± 0.08   | 1.13 ± 1.85  |
| 12   | 1,2-Dimethyl-cyclopent-2-ene-carboxylic acid | Not reported | 1351       | 1367                                  | Not reported      | 0.01 ± 0.01               | 0 ± 0           | 0.03 ± 0.05   | 0.15 ± 0.05   | 0.19 ± 0.07    | 0.16 ± 0.04   | 4.16 ± 0.57  | 4.86 ± 0.54   | 1.11 ± 0.75* |</p>
<table>
<thead>
<tr>
<th></th>
<th>Substance</th>
<th>RI (AM, 2023; NIST Mass Spectrometry Data Center, 2006; The Good Scents Company, 2018)</th>
<th>Flavor category</th>
<th>Description</th>
<th>Journal Pre-proof</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Ethyl octanoate</td>
<td>106-32-1 1437 1435</td>
<td>Fruity, pineapple-like</td>
<td>36.06 ± 6.57 31.17 ± 4.58 11.91 ± 4.27* 1.68 ± 0.51 16.59 ± 8.15* 12.86 ± 2.01* 6.54 ± 5.35 16.23 ± 4.70 8.24 ± 12.86</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1-Heptanol</td>
<td>111-70-6 1456 1454</td>
<td>Leafy, green</td>
<td>0.23 ± 0.33 0.52 ± 0.64 0.18 ± 0.12 0.73 ± 0.48 0.63 ± 1.05 1.12 ± 0.75 0.45 ± 0.50 0.19 ± 0.15 0.28 ± 0.37</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2-Ethyl hexenal</td>
<td>645-62-5 1484 1491</td>
<td>Bitter, rancid</td>
<td>0.24 ± 0.06 0.23 ± 0.07 0.65 ± 0.58 0.40 ± 0.16 0.35 ± 0.05 0.46 ± 0.08 0.11 ± 0.14 0.30 ± 0.07 0.30 ± 0.18</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2-Acetyl-furan</td>
<td>1192-62-7 1496 1497</td>
<td>Sweet, balsamic, burnt, nutty</td>
<td>1.38 ± 0.29 1.34 ± 0.29 1.04 ± 0.69 0.07 ± 0.07 0.07 ± 0.06 0.05 ± 0.04 0.42 ± 0.21 0.53 ± 0.27 0.63 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Linalool</td>
<td>78-70-6 1543 1540</td>
<td>Fruity, floral, muscat lemon</td>
<td>19.44 ± 3.95 14.73 ± 2.89 29.27 ± 2.01* 3.23 ± 0.27 3.77 ± 0.47 3.55 ± 0.85 1.84 ± 0.59 1.51 ± 0.22 1.88 ± 0.50</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1-Octanol</td>
<td>111-87-5 1552 1554</td>
<td>Fatty, sweet, fruity</td>
<td>0.76 ± 0.78 1.04 ± 0.87 0.06 ± 0.11 0.32 ± 0.20 0.81 ± 0.31 0.99 ± 0.02* 0.95 ± 0.46 0.41 ± 0.21 0.39 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>2-Furanmethanol</td>
<td>98-00-0 1643 1650</td>
<td>Caramel, burnt sugar, creamy</td>
<td>2.12 ± 3.10 2.23 ± 1.40 0.02 ± 0.03 0.19 ± 0.04 0.11 ± 0.03 0.18 ± 0.07 0.86 ± 0.15 0.88 ± 0.06 1.16 ± 0.24</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1-Nonanol</td>
<td>143-08-8 1672 1666</td>
<td>Fatty, citrus, orange</td>
<td>0.45 ± 0.08 0.94 ± 1.04 0.18 ± 0.19 3.39 ± 3.40 1.19 ± 1.69 0.91 ± 0.76 0.47 ± 0.52 1.02 ± 1.52 1.19 ± 1.69</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Citronellol</td>
<td>106-22-9 1769 1762</td>
<td>Floral, rose, citrus</td>
<td>0.36 ± 0.05 0.54 ± 0.24 0.42 ± 0.06 0.53 ± 0.08 0.44 ± 0.08 0.43 ± 0.07 0.40 ± 0.06 0.47 ± 0.04 0.35 ± 0.17</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>2-Phenyethyl acetate</td>
<td>103-45-7 1808 1810</td>
<td>Floral, rose, fruity</td>
<td>0.77 ± 0.12 0.89 ± 0.10 0.84 ± 0.10 1.12 ± 0.16 1.12 ± 0.10 0.97 ± 0.06 1.23 ± 0.04 1.31 ± 0.16 0.89 ± 0.20*</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>2-Phenylethanol</td>
<td>60-12-8 1899 1903</td>
<td>Floral, sweet, honey</td>
<td>5.29 ± 0.99 6.11 ± 0.49 6.45 ± 0.80 14.01 ± 3.28 13.70 ± 2.05 12.79 ± 1.54 10.01 ± 1.27 12.87 ± 0.86 13.43 ± 2.31</td>
<td></td>
</tr>
</tbody>
</table>

*Represents significant differences between the original sample and the evaluated fraction (p<0.05)
Figure 1. The approximate composition of an average beer by volume percentage (Buiatti, 2008; Verhagen, 2010). The other composition is related to organic volatile and non-volatile compounds.
Figure 2. Experimental setup for progressive stirred freeze concentration (PSFC)
Figure 3. Concentration Index (CI) and Average distribution coefficient (Kapp) for Witbier (Yellow-dotted bar), Bitter (Orange-diagonal bar), and Porter (Black-stripped bar). Uppercase letters denote significant differences (P<0.05) for each physicochemical parameter.
Figure 4. GC analyses on DB-FFAP column of volatile compounds from Witbier (A), Bitter (B), and Porter (C) original beers (without concentration) obtained by HS-SPME. Peak numbers correspond to the compound numbers in Table 3.
Figure 5. VOMs profile by the chemical group in the original sample, concentrated liquid, and ice fraction of Witbier, Bitter, and Porter by area percentage of the GC-MS spectra.
Figure 6. Sensory profile of the original sample of Witbier (Bars) vs. concentrated liquid (Continuous green line) and ice fraction (Blue dotted line). Significant differences $p<0.05$ for concentrated liquid are Diamonds and Squares for ice fraction, relative to the original sample. The abbreviation corresponds to Odor (O), Taste (T), and somatosensory (SS).
Figure 7. Sensory profile of an original sample of Bitter (Bars) vs. concentrated liquid (Continuous green line) and ice fraction (Blue dotted line). Significant differences p<0.05 for concentrated liquid are Diamonds and Squares for ice fraction, relative to the original sample. The abbreviation corresponds to Odor (O), Taste (T), and somatosensory (SS).
Figure 8. Sensory profile of an original sample of Porter (Bars) vs. concentrated liquid (Continuous green line) and ice fraction (Blue dotted line). Significant differences p<0.05 for concentrated liquid are Diamonds and Squares for ice fraction, relative to the original sample. The abbreviation corresponds to Odor (O), Taste (T), and somatosensory (SS).
1 Progressive stirred freeze concentration is applied to three craft ale beers.
2 The technique increases the concentration of beer's physicochemical properties.
3 The volatile compounds distribution was preserved for the concentrated liquid.
4 Changes sensory profile of concentrated liquid and ice fractions were found.
5 Progressive stirred FC presents an opportunity to develop new beer products.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: