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EVALUATION OF THE PROFILE OF VOLATILE ORGANIC COMPOUNDS IN INDUSTRIAL AND CRAFT BEERS

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ABSTRACT

The objective of this work was to determine the influence of some analytical parameters in craft and industrial beers characterization and to search for possible correlations between these parameters by use of chemometrics. For this purpose, the levels of color and bitterness were quantified by spectrophotometry and the concentrations of acetaldehyde, ethyl acetate, methanol, ethanol, propanol, iso-butanol and iso-amyl alcohol by gas chromatography with detection by flame ionization with a headspace sampler (HS - GC-FID). The results were evaluated by the student analysis for the means, at a confidence level of 95% ($\alpha = 0.05$). Principal Component Analysis (PCA) was applied as a tool to assess the influence of analytical parameters to characterize industrial or craft beers. The results showed that, the levels of bitterness, color, ethanol, isoamyl alcohol, methanol and propanol are statistically different in craft and industrial beers. On the other hand, considering the PCA results, it is possible to attribute the parameters bitterness, color, acetaldehyde, methanol, ethanol, propanol, iso-butanol and iso-amyl alcohol as the better ones to characterize as craft beers, while the industrial beers were better characterized by the presence of ethyl acetate. Regarding the correlation matrix, it revealed that the parameters color, propanol and iso-amyl alcohol are correlated with the alcoholic content of beer, regardless of whether it is craft or industrial.

Keywords: Craft beer, Gas chromatography, Headspace, Industrial beer, Principal component analysis

INTRODUCTION

Beers are beverages derived from alcoholic fermentation, a process in which brewing yeasts use a substrate of malted barley wort or malt extract to produce ethanol, carbon dioxide and other minor compounds. The wort go through the cooking process before the start of fermentation, together with the addition of hops or hop extract to make up the drink. Furthermore, malted barley or malt extract may be replaced by a brewing adjunct in the constitution of the wort (**Brazil, 2019b; Bortoleto & Gomes, 2020; Gomes, Yoshinaga & Bortoleto, 2020**).
Considering the classification between industrial and craft beer, every country generally has its own legal definition, regulating what is craft beer, and therefore commercial beer. (**Buiatti, Guglielmotti & Passaghe, 2021**). In general, craft beer comes from small breweries that use traditional methods to produce beer, omitting pasteurization at the end of the process, prioritizing quality rather than quantity (**Rosales *et al.*, 2021**). In Brazil there is no legal definition of craft beers, but beers do not use a pasteurization process, is called draft beer (**Brazil, 2019a**).
Another difference commonly distinguishing craft beers from commercial beers is raw materials. Indeed, industrial beers are often made with cheaper ingredients, in order to minimize the costs of production. (**Buiatti, Guglielmotti & Passaghe, 2021**). But the question is: do craft beers differ from industrial beers regarding the main volatile organic compounds present in them? Beer volatiles, which are responsible for the aromas and flavors, belong mainly to the groups of esters, alcohols, usually higher or fusel alcohols, aldehydes and acids. Off-aromas development is a special concern for craft breweries, which do not tend to use pasteurization and / or filtration processes (**Viejo *et al.*, 2019**).
In order to know in detail how different is craft and commercial beer, this work aimed to quantify and correlate volatile organic compounds, color and bitterness parameters in twenty-six samples of beer. The influence of the beer process was also analyzed and for that it was applied multivariate analysis using Principal Component Analysis.

MATERIAL AND METHODS

All analyzes were conducted at the FATEC Piracicaba "Dep. Roque Trevisan" - Paula Souza Center.

Samples

The samples were purchased from the local commerce in the city of Piracicaba, in the state of São Paulo, Brazil and are presented in Table 1. For all analyses, regardless of whether they were industrial or craft beers, the samples were decarbonated for 5 minutes in a magnetic stirrer (**Bortoleto & Gomes, 2020; Gomes, Yoshinaga & Bortoleto, 2020**) aiming at the release of carbon dioxide (**IAL, 2008**) and subsequent analysis of bitterness, color and quantification of the volatile organic compounds.

Table 1 Parameter values reported on the labeling of craft (CB1-CB18) and industrial (IB1-IB8) beers.

Sample	Ethanol[a]	Colour[b]	Bitterness[c]	Sample	Ethanol[a]	Colour[b]	Bitterness[c]
CB1	6.5	ND[d]	45	CB14	6.8	18	50
CB2	6.5	ND[d]	45	CB15	10.0	40[e]	30
CB3	6.1	9[e]	34	CB16	7.0	ND[d]	23
CB4	4.9	7	22	CB17	ND[d]	ND[d]	ND[d]
CB5	4.3	6	9	CB18	ND[d]	ND[d]	ND[d]
CB6	5.5	4	10	IB1	5.0	ND[d]	9
CB7	7.5	30	22	IB2	4.7	ND[d]	12
CB8	8.5	23	25	IB3	4.7	ND[d]	ND[d]
CB9	4.5	14[e]	30	IB4	5.0	ND[d]	ND[d]
CB10	5.3	5	12	IB5	4.8	ND[d]	ND[d]
CB11	5.5	14	24	IB6	4.5	ND[d]	ND[d]
CB12	7.5	20	25	IB7	4.8	ND[d]	ND[d]
CB13	7.5	30	22	IB8	4.5	ND[d]	ND[d]

Source: Authors. [a]Concentration in % (v/v). [b]SRM. [c]IBU. [d]ND: Not declared. [e]EBC.

Bitter and color analysis

For bitterness and color analysis, the reference methods by Normative Instruction No. 65/2019 (**Brazil, 2019a**) were used. Considering bitterness analysis, the extraction of alpha acids in iso-octane was performed with samples acidified with hydrochloric acid. The phases were separated by centrifugation and the spectrophotometric measurement were realized at a wavelength of 275 nm, using the EBC 9.8 protocol (**Analytica-EBC, 2005**). The color was determined by the

EBC 9.6 protocol, in which samples are measured at 430 and 700 nm in a spectrophotometer (**Analytica-EBC, 2005**).

Chromatographic analysis of volatile compounds

For the chromatographic analysis of volatile compounds, a gas chromatograph (PerkinElmer®, model Clarus 600) with a flame ionization detector (FID) and an automatic sampler with headspace (CTC Analytics, Pal System) was used. The column was a WAX (30 mx 0.25 mm – 0.25 µm) from Nova Analytics and the conditions were adjusted, according to **Bortoleto & Gomes** (**2020**).
The identification of the compounds was performed by comparing the profile obtained with the chromatographic profile of the following standards: acetaldehyde, dimethylsulfide (DMS), ethyl acetate, methanol, ethanol, diacetyl, propanol, iso-butanol, isoamyl and iso-amyl acetate, using the n-hexanol as an internal standard. Deionized water was used (18.2 MΩ conductivity at 25°C) and the reagents were from Sigma-Aldrich. Quantifications of volatile compounds were performed based on external analytical curves of five standard concentration points, all prepared in ethanol at 5% (v/v), with the exception of the analytical curve for ethanol, which was prepared in deionized water. The retention times (TR), concentration ranges and correlation coefficients obtained are shown in Table 2.

Table 2 Retention time, concentration range, line equation, correlation coefficient.

Compounds	TR (min)	Concentration range (mg L^{-1})	Line equation	R²
Acetaldehyde	2.15	1.12 – 44.80	Area = 0.014 + 0.005C(mg L^{-1})	0.993
Dimethylsulfide (DMS)	2.39	1.02 – 40.80	Area = -0.027 + 0.061C(mg L^{-1})	0.991
Ethyl acetate	3.77	1.11 – 44.20	Area = 0.007 + 0.027C(mg L^{-1})	0.995
Methanol	4.01	1.03 – 41.20	Area = 0.001 + 0.001C(mg L^{-1})	0.993
Ethanol[a]	4.67	0.50 – 10.00[a]	Area = 9.174 + 5.843C(v/v)	0.998
Diacetyl	5.29	1.13 – 45.00	Area = 0.016 + 0.008C(mg L^{-1})	0.991
Propanol	6.43	11.60 – 58.00	Area = 0.008 + 0.006C(mg L^{-1})	0.985
Iso-Butanol	7.23	11.00 – 55.00	Area = 0.038 + 0.014C(mg L^{-1})	0.984
Isoamyl acetate	7.62	10.20 – 51.00	Area = -0.198 + 0.061C(mg L^{-1})	0.977
3-methyl-1-butanol (Iso-amyl alcohol)	8.76	58.75 – 293.75	Area = -0.206 + 0.015C(mg L^{-1})	0.990

Source: Authors. [a]Concentration in % (v/v)

Data analysis

The results were submitted to Student's t test at a significance level of α = 0.05, using the RStudio software (Version 1.3.1093). To investigate the parameters that influenced the characterization of the samples, Principal Component Analysis (PCA) was used using the OriginPro 2021 software (Student Version 9.8.0.200) **(ORIGINPRO, 2021).** Furthermore, Pearson's correlation coefficients were calculated between the chemical compounds determined for craft and industrial beers. The magnitude of the coefficient can be interpreted as: 0.00 to 0.10 - “insignificant”; 0.10 to 0.39 - "weak"; 0.40 to 0.69 - "moderate"; 0.70 to 0.89 - “strong”; and 0.90 to 1.00 - “very strong” **(Schober, Boer & Schwarte, 2018).**

RESULTS AND DISCUSSION

Physicochemical and chromatographic analysis

Eighteen samples of craft beer (CB1- CB18) and eight industrial beers (IB1- IB8) are presented in Table 3 with results of the color, bitterness and volatile organic compound concentrations.

Table 3 Results obtained from the analysis of volatile compounds, colour and bitterness of the craft beer (CB1-CB18) and industrial beer (IB1-IB8).

Sample	Styles	Fermentation	Ethanol[a]	Colour[b]	Bitterness[c]	Acetaldehyde[d]	Ethyl acetate[d]	Methanol[d]	Propanol[d]	Iso-Butanol[d]	Iso-amyl alcohol[d]
CB1	IPA	Ale	6.5 ± 0.2	18 ± 1	47 ± 1	2.02 ± 0.17	24.35 ± 0.24	5.05 ± 0.23	35.84 ± 0.44	31.02 ± 0.91	91.99 ± 3.25
CB2	IPA	Ale	6.4 ± 0.2	20 ± 1	45 ± 1	2.42 ± 0.21	11.89 ± 0.99	4.54 ± 1.40	33.99 ± 0.32	23.69 ± 0.08	89.95 ± 0.09
CB3	Belgian Saison	Ale	6.7 ± 0.3	18 ± 1	31 ± 1	ND[e]	41.69 ± 2.55	ND[e]	26.89 ± 0.52	27.86 ± 0.36	130.47 ± 4.10
CB4	American Blonde Ale	Ale	5.3 ± 0.2	13 ± 1	29 ± 1	8.81 ± 0.09	36.27 ± 0.24	5.09 ± 2.13	40.94 ± 0.75	35.67 ± 2.02	92.46 ± 2.36
CB5	Pilsen	Lager	4.4 ± 0.5	10 ± 1	10 ± 1	6.45 ± 0.13	24.64 ± 0.59	ND[e]	27.66 ± 0.51	18.03 ± 0.28	85.27 ± 0.86
CB6	Witbier	Ale	5.4 ± 0.4	7 ± 1	8 ± 1	9.02 ± 1.04	30.35 ± 3.49	7.86 ± 0.56	47.49 ± 5.57	21.12 ± 2.21	98.07 ± 7.37
CB7	Belgian Dubbel	Ale	8.0 ± 0.9	86 ± 1	19 ± 1	7.83 ± 0.37	ND[e]	5.22 ± 2.36	38.26 ± 1.39	18.33 ± 0.52	128.52 ± 0.41
CB8	Wee Heavy	Ale	8.4 ± 0.2	80 ± 1	13 ± 1	16.56 ± 0.20	26.39 ± 0.17	ND[e]	56.67 ± 0.75	ND[e]	156.40 ± 0.13
CB9	Session Rye IPA	Ale	5.2 ± 0.2	20 ± 1	13 ± 1	2.62 ± 0.04	13.30 ± 0.38	5.55 ± 0.77	27.08 ± 0.95	27.57 ± 1.82	74.82 ± 6.39
CB10	Weizen	Ale	5.6 ± 0.5	13 ± 1	6 ± 1	7.28 ± 0.32	38.87 ± 2.16	6.07 ± 0.35	ND[e]	26.84 ± 0.98	162.37 ± 4.21
CB11	Red Ale	Ale	4.7 ± 0.2	80 ± 1	22 ± 1	3.05 ± 0.60	13.40 ± 3.06	ND[e]	31.33 ± 4.64	34.94 ± 5.06	96.68 ± 9.36
CB12	Rauchbock	Lager	6.1 ± 0.7	80 ± 1	26 ± 1	5.59 ± 1.41	39.80 ± 8.99	ND[e]	35.23 ± 3.71	24.76 ± 1.44	128.03 ± 2.67
CB13	Belgian Dubbel	Ale	7.3 ± 0.8	86 ± 1	26 ± 1	7.85 ± 1.91	ND[e]	9.43 ± 0.69	46.02 ± 3.55	21.98 ± 2.35	140.66 ± 9.17
CB14	Belga / IPA	Ale	6.8 ± 0.3	29 ± 1	57 ± 1	3.40 ± 0.42	ND[e]	11.13 ± 1.01	46.56 ± 3.55	37.11 ± 1.75	115.02 ± 4.82
CB15	Quadrupel	Ale	9.1 ± 0.4	156 ± 1	26 ± 1	7.00 ± 0.42	ND[e]	ND[e]	57.89 ± 5.42	ND[e]	172.10 ± 8.61
CB16	Bock	Lager	6.7 ± 0.1	86 ± 1	23 ± 1	5.88 ± 0.51	42.33 ± 3.50	ND[e]	22.19 ± 3.28	18.76 ± 0.99	101.51 ± 6.22
CB17	American Lager	Lager	4.8 ± 0.2	9 ± 1	24 ± 1	4.46 ± 0.01	9.50 ± 0.05	4.52 ± 0.61	27.44 ± 0.03	28.01 ± 0.48	63.65 ± 0.05
CB18	American Pale Ale	Ale	6.2 ± 0.3	26 ± 1	62 ± 3	19.64 ± 5.11	42.16 ± 10.45	7.33 ± 1.39	44.81 ± 9.79	19.28 ± 4.23	71.03 ± 11.75
IB1	German Pils	Lager	5.0 ± 0.2	8 ± 1	9 ± 1	13.28 ± 0.27	15.94 ± 0.23	ND[e]	ND[e]	15.46 ± 0.83	74.23 ± 2.22
IB2	Premium American Lager	Lager	5.4 ± 0.2	10 ± 1	16 ± 2	5.38 ± 0.57	23.48 ± 3.69	ND[e]	15.31 ± 2.03	16.72 ± 2.02	87.01 ± 9.65
IB3	Standard American Lage	Lager	4.5 ± 0.1	9 ± 1	18 ± 1	2.91 ± 0.28	13.68 ± 1.99	ND[e]	13.41 ± 1.44	19.84 ± 1.83	85.51 ± 6.33
IB4	American Premium Lager	Lager	5.3 ± 0.2	9 ± 1	20 ± 1	7.66 ± 0.10	27.79 ± 0.67	ND[e]	17.99 ± 0.55	25.16 ± 0.76	90.27 ± 2.41
IB5	American Lager	Lager	4.6 ± 0.3	7 ± 1	8 ± 1	5.76 ± 0.29	15.31 ± 0.99	ND[e]	ND[e]	ND[e]	ND[e]
IB6	Standard American Lager	Lager	4.7 ± 0.1	8 ± 1	12 ± 1	3.24 ± 0.08	14.85 ± 0.93	ND[e]	13.70 ± 0.46	17.66 ± 0.57	78.30 ± 3.37
IB7	Pilsen	Lager	4.8 ± 0.9	6 ± 1	8 ± 1	3.24 ± 0.57	21.77 ± 4.01	ND[e]	16.91 ± 2.21	18.03 ± 2.38	79.15 ± 9.63
IB8	Pilsen	Lager	5.1 ± 0.0	8 ± 1	10 ± 1	8.71 ± 0.95	20.50 ± 2.17	ND[e]	17.24 ± 0.62	19.07 ± 1.11	98.22 ± 3.25
Mean		Craft beer	6.3 ± 1.3a[f]	46 ± 42a[f]	27 ± 16a[f]	7.05 ± 4.77a[f]	28.21 ± 12.35a[f]	6.52 ± 2.17	38.02 ± 10.64a[f]	25.93 ± 6.32a[f]	111.06 ± 32.29a[f]
		Industrial beer	4.9 ± 0.3b[f]	8 ± 1b[f]	13 ± 5b[f]	6.27 ± 3.54a[f]	19.16 ± 5.01a[f]	-	15.76 ± 1.92b[f]	18.85 ± 3.14a[f]	84.67 ± 8.18b[f]

Source: Authors. [a]Concentration in % (v/v). [b]EBC. [c]IBU. [d]Concentration in mg L^{-1}. [e]ND: Not detected. [f]Means followed by the same letter, in the column, do not differ by Student's, *t* test at the 95% confidence level (α = 0.05).

The result obtained for Student's t test for samples of industrial and craft beers did not present significant differences in terms of acetaldehyde, ethyl acetate and iso-butanol. The p values obtained were greater than $\alpha = 0.05$, at the 95% confidence level. The parameters bitterness, colour, ethanol, iso-amyl alcohol, methanol and propanol showed significant differences in samples of craft and industrial beers, since p values were lower than $\alpha = 0.05$, at the confidence level of 95 %. Methanol concentration was not evaluated by Student's t test, as it was not possible to detect the presence of this compound in industrial beer samples.

Besides, although chromatographic peaks of DMS, diacetyl and isoamyl acetate have appeared in some samples, as shown in the chromatographic profiles of Figure 1, their concentrations were not considered, since they were outside the studied analytical range and below the method's quantification limit. Anyway, the fact that diacetyl and DMS are not present in quantifiable concentrations guarantees the quality of the samples, since these are considered beverage defects when above the sensory perception limits, which are 0.10-0.15 mg L^{-1} and 0.009-0.069 mg L^{-1}, respectively (**Choi, Ahn & Kim, 2015; Kishnani, Barr & Speer, 2021**).

Considering esters, these are normally present in beers with high density worts, both for the Ales and Lagers family, noting that these compounds are important contributors to the beverage's flavor (banana, apple, solvent and ester) **(Baxter & Hughes, 2001; Saerens et al., 2008; Olaniran et al., 2017)**. Thus, special attention must be given to the preparation of the wort as to the guarantee of adequate density for these compounds formation, both for industrial and craft beers.

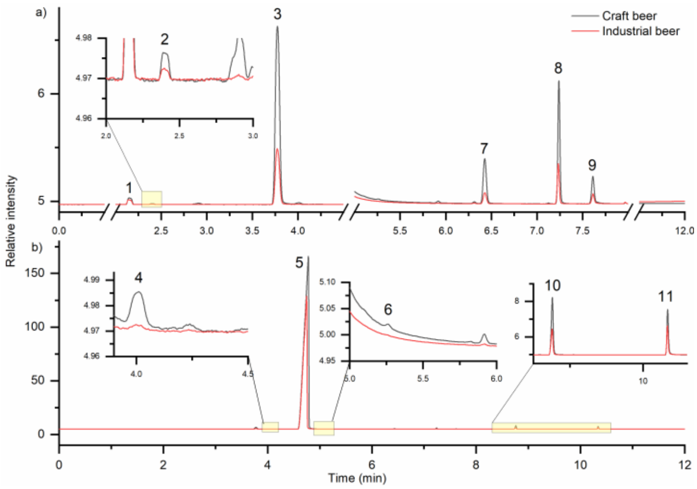

Figure 1 Chromatographic profile of samples of craft and industrial beers. Identified analytes: a) acetaldehyde (1), dimethylsulfide (2), ethyl acetate (3), propanol (7), iso-butanol (8) and isoamyl alcohol (9); b) methanol (4), ethanol (5), diacetyl (6), iso-amyl acetate (10) and n-hexanol (internal standard, 11).

Still considering the Table 3 results, it also was observed that the alcohol content in the industrial beer samples ranged from 4.5 to 5.3% (v/v), while in the craft samples the variation was from 4.4 to 9.1% (v/v), which suggests that the alcohol content tends to be higher in craft beer. The sensory threshold of ethanol is 1.77% (v/v), therefore, regardless of the type of beer, industrial or artisanal, they all enable the perception of this **compound (Baxter & Hughes, 2001; Tan & Siebert, 2004; Preedy, 2011; Pires & Brányik, 2015)**. Furthermore, all samples evaluated are in accordance with current legislation in Brazil, which states that the alcoholic strength of beers should vary from 0.5 to 54% (v/v) **(Brazil, 2019a; Brazil, 2019b)**.

About beer color, according to Baxter & Hughes (2001) the EBC scale ranges from 4.5 to 1550 and each color value will confer a beer flavor attribute. Lighter beers tend to have aromas of biscuity, sweet, nutty, cereal, and toffee, while darker beers will have malt, toffee, caramel, nutty, fruity, molasses, chocolate, smoky, coffee, and burnt flavors. The samples of industrial beers evaluated presented values from 6 to 10 EBC (Table 3) and uniformity in their color tending to present the flavor of biscuity, while the samples of craft beers showed values from 7 to 156 EBC (Table 3), that is a large variety in the possibility of flavors, demonstrating the complexity of this type of beer.

The bitterness values in the industrial beer samples ranged from 8 to 20 IBU, while in the craft beer samples the variation was from 6 to 62 IBU (Table 3). Bitterness is related to the presence of cis and trans isomers of α-acids and its intensity depends on the proportions of these compounds. Bitter beers, such as craft beers (Table 3), tend to have a higher concentration of isohumulone, while industrial beers tend to have a higher concentration of isocohumulone **(Hughes & Simpson, 1993; King & Duineveld, 1999; Schönberger , 2006; Silva & Faria, 2008; Rosales et al., 2021).**

Considering the different volatile organic compounds found in the beers, some notes will be present individually. The propanol, which has a sensory threshold of 800 mg L^{-1} and provides an alcoholic and sweet flavor to beers **(Baxter & Hughes, 2001; Pires & Brányik, 2015; Olaniran et al., 2017)** ranged from 22.19 to 57.89 mg L^{-1} in craft beers while the variation from 13.41 to 17.99 mg L^{-1} was detected in industrial beers (Table 3). Usually, craft beers tend to have a stronger alcoholic and sweet flavor than industrial beers, and in addition to other variables, the concentration of propanol must also be considered.

Analyzing the results for iso-myl alcohol, which has a sensory threshold of 70 mg L^{-1} and gives banana, wine and alcoholic flavor to beers **(Baxter & Hughes, 2001; Preedy, 2011; Pires & Brányik, 2015; Olaniran et al. , 2017)**, this showed concentrations of 63.65 to 172.10 mg L^{-1} and 74.23 to 98.22 mg L^{-1} in craft and industrial beers, respectively. Because of the found concentrations, it is possible to mention all beers of will confer these enhanced flavors in the analyzed beer, since they are above the sensory threshold. Furthermore, craft beers tend to have higher average concentrations than industrial beers (Table 3).

About methanol, the literature mentions that the concentration of this compound in beer can vary from 0.5 to 3 mg L^{-1}, that its sensory threshold is 10000 mg L^{-1} and its flavor is described as solvent and alcoholic **(Baxter & Hughes, 2001; Tan & Siebert, 2004; Preedy, 2011)**. In this work, only samples of craft beers presented this compound with concentrations ranging from 4.52 to 11.13 mg L^{-1}. The presence of methanol in craft beers can be a possible marker to differentiate industrial from craft beers. Furthermore, the analytical monitoring of this compound in craft beers is very important since methanol is an indicator of microbiological contamination in the process and has toxic characteristics to humans. Its presence may be linked to the use of mixed culture (yeasts, fungi and bacteria) which may possibly promote the production of methanol and other congeners. Furthermore, pectinmethylesterase-producing microorganisms will only be a problem when pectin sources are used, which is the case for only some types of beers **(Paine & Dayan, 2001; Dorokhov et al., 2015; Ohimain, 2016).**

The compounds acetaldehyde (green leaf, paint and fruity flavors), ethyl acetate (solvent, fruity and sweet flavors), and isobutanol (alcoholic and solvent flavors) have sensory thresholds of 25, 30 and 200 mg L^{-1}, respectively **(Baxter & Hughes, 2001; Preedy, 2011; Pires & Brányik, 2015; Olaniran et al., 2017).** Considering the results of the concentrations of these compounds in the different beers, it is possible to observe that they did not present a significant difference (Table 3), so the flavors derived from these compounds end up acting in a similar way in industrial and artisanal samples.

Statistical analysis

Considering all the parameters analyzed, it was used a multivariate analysis to evaluate data. PCA was used to search for correlation between the variables (acetaldehyde, bitterness, colour, ethanol, ethyl acetate, iso-amyl alcohol, iso-butanol, methanol and propanol) with the studied samples. PCA was generated by combining two criteria, the cumulative percentage variation and the Kaiser rule, which present cutoff points for the eigenvalues **(Wold, Esbensen & Geladi, 1987; Ferré, 1995; Valle, Li & Qin, 1999; Jolliffe, 2005; Tzeng & Berns, 2005)**. The eigenvalues selected were those that allowed greater data variance and allowed differentiation between industrial and craft beers. In Figure 2 it is possible to observe PCA generated with all variables obtained from samples of industrial and craft beers.

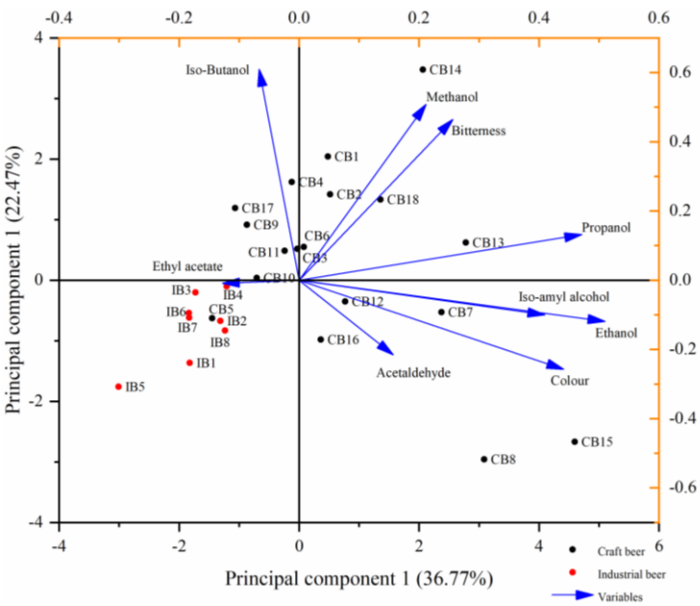

Figure 2 Biplot of the first two main components for samples of industrial beers (red color) and craft beers (black color) correlated with all studied variables.

The first two main components were selected because their eigenvalues were greater than 2 and because they were responsible for 59.24% of the total data variation (Figure 2). Two groups were formed, one grouping industrial samples (red color) and the other handmade samples (black color), and the variables that

allowed the characterization of the groups are associated with the main component 1.
Another interesting observation in Figure 2 is that the variables acetaldehyde, bitterness, colour, ethanol, iso-amyl alcohol, iso-butanol, methanol and propanol best represent craft beers (black), possibly due to the complexity of the flavors found in this type of beer. It is common for this type of beer to be made with greater amounts of hops, carbohydrates and be more bitter. Industrial beers (red) were better represented by only one variable, ethyl acetate, since this type of beer has a low flavor complexity, as it usually uses only traditional and cheaper raw materials in its production **(Baxter & Hughes, 2001; Buiatti, Guglielmotti & Passaghe, 2021; Habschied et al., 2021; Rosales et al., 2021).**

About the craft beer CB5, that is together with the industrials beers, as seen in Figure 2, the authors believe that is related to the fermentation process that is used to make this beer, that was a bottom fermentation. The caracteristics of this type of beer is a kind of a Lager beer that presents little complexity in flavors, since the concentration of compounds (Table 3) of this beer is very similar to industrial samples.
Considering the search for correlations between the variables analyzed in the samples of craft and industrial beers, the Table 4 shows the Pearson correlation coefficients obtained.

Table 4 Pearson correlation matrix between the chemical compounds obtained in the analyses.

Compounds	Ethanol	Colour	Bitterness	Acetaldehyde	Ethyl acetate	Methanol	Propanol	Iso-Butanol	Iso-amyl alcohol
Ethanol	1,00								
Colour	0,76	1,00							
Bitterness	0,36	0,13	1,00						
Acetaldehyde	0,23	0,14	0,03	1,00					
Ethyl acetate	-0,18	-0,26	0,00	0,23	1,00				
Methanol	0,22	-0,05	0,50	0,11	-0,21	1,00			
Propanol	0,69	0,58	0,51	0,24	-0,16	0,43	1,00		
Iso-Butanol	-0,29	-0,31	0,40	-0,40	0,13	0,46	0,02	1,00	
Iso-amyl alcohol	0,72	0,63	0,07	0,11	0,00	0,14	0,50	0,00	1,00

Source: Authors.

Considering the values of the correlation between ethanol-color (0.76), ethanol-propanol (0.69) and ethanol-iso-amyl alcohol (0.72), there is a moderate or strong correlation between the final alcohol content of the beer and the parameters color, propanol and isoamyl alcohol, regardless of whether the beer is industrial or craft. The correlations between the other parameters and ethanol in the beers were insignificant or weak, suggesting that the differences in parameters are not caused by differences in alcohol content.
As for the other coefficients obtained, many were presented as insignificant or weak. However, it is worth mentioning the value obtained for bitter-methanol (0.50), because, although methanol does not influence the flavor of beers, it is a component with toxic characteristics to humans **(Paine & Dayan, 2001).** Thus, beers with high bitterness, which is a characteristic of many craft beers, need more attention regarding the concentration of this analyte in the beverage.

CONCLUSION

When evaluating volatile organic compounds, and color and bitterness parameters in samples of industrial and craft beers, it was found that craft samples have greater complexity of aroma and flavor compared to industrial samples. Furthermore, it was observed that methanol can be a compound to differentiate craft samples from industrial ones, considering that this compound was not quantified in industrial samples.
From the multivariate statistical analysis of principal components, it was possible to differentiate the samples of craft beers from industrial ones, noting that craft beers are better explained by the parameters acetaldehyde, bitterness, color, ethanol, isoamyl alcohol, iso-butanol, methanol and propanol. It is due to the fact that this type of beer is produced with greater amounts of hops and carbohydrates and, normally, is more bitter. All these factors prove the greater chemical complexity of the flavor of craft beers compared to industrial ones.
Furthermore, the correlation matrix showed that the color, propanol and isoamyl alcohol parameters are correlated with the alcoholic content of the beer, regardless of whether it is craft or industrial. So, beers with high bitterness tend to have high methanol content, therefore, beers with high bitterness values should be evaluated for methanol content.

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