# BREWING ON AN INDUSTRIAL AND A CRAFT SCALE – IMPACT ON THE PHYSICOCHEMICAL PROPERTIES AND VOLATILE COMPOUNDS PROFILE OF THE PALE PILSENER-STYLE LAGER BEER ANALYSED WITH HS/GC-MS

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# Highlight

Volatile compounds profile of a craft and industrial beer analysed using headspace gas chromatography-mass spectrometry method.

# Abstract

The pale Pilsener-style lager beers produced on a massive and craft scale were taken to analyse their basic physicochemical properties (alcohol content, pH, haze, real degree of fermentation) and volatile compounds profiles. The research was carried out using a beer analyser equipment and a headspace gas chromatographymass spectrometry method (HS/GC-MS). The findings showed that in terms of physicochemical and flavour attributes, the quality of craft beers differed to a higher degree from the standard Pilsener beer quality than in the case of industrial beers.

# Keywords

Industrial and craft beer; pilsener; volatile compounds; off-flavours; HS/GC-MS, physicochemical properties

# Introduction

It is believed that the process of making beer represents the world's oldest biotechnology, which helps to account for the fact that the brewing industry is currently the most established on the alcoholic beverages market with beer being nearly the most consumed beverage in the world [1,2]. In generic terms, there are two main types of beer being produced both on an industrial and a craft (artisanal) scale, namely (1) ale – top fermenting styles of beer and (2) lager - bottom fermenting styles of beer, which refers to the type of yeast used in the fermentation process. Although the craft beer industry in Poland, as distinct from the industrial one, is primarily focused on producing *ale* beers rather than *lagers*, it is the production of the bottom fermenting style that has been found to grow faster recently (c. 3.5-fold faster than ale craft beers in 2019) [3]. Overall, there are three to five main commercial companies brewing on an industrial scale in Poland, being distinguished by the annual beer production exceeding 200 000 hL, with their combined market share reaching 98%, and these are particularly: Kompania Piwowarska, Grupa Żywiec and Carlsberg Polska [2,4]. Throughout the years, the prime objective of such large industrial breweries has been aimed at providing highly standardised product, designated "for everybody", so that the producers can meet the demands of the average consumer and at the same time maximise their profits [5,6]. As a consequence of this policy, the pale pilsener type of lager beer due to its mild and generally not very characteristic flavours has become ubiquitous on the market and is considered now the most dominant and widely brewed single beer style all over the world [7]. Nevertheless, as the noticeable change in consumer attitudes and preferences towards beer did occur in Poland in the beginning of the second decade of the 21st century, the number of microbreweries (craft breweries, contract breweries and brew pubs), offering products with enhanced sensory characteristics or new beer styles whatsoever, have been steadily increasing ever since then (it passed from 107 to 308 in the years 2010-2015) [4,7,8]. This phenomenon associated with opposition to standardisation of beer brewing and beer consumption is called "the craft beer revolution" [5,9]. Despite the popularity of this slogan and craft breweries in themselves among beer consumers in Poland these days, it has to be pointed out that there is no official, common shared

and agreed definition of craft beer and craft breweries as well. It is of note, however, that there are many regional and national brewers associations all over the world, which represent independent microbreweries and simultaneously supply us with some working definitions in terms of craft brewing striving to safeguard their member's interest [8,10]. As far as Poland is concerned, it seems reasonable to invoke PSBR ("Polskie Stowarzyszenie Browarów Rzemieślniczych"), since according to its 2019 annual report, this microbrewers association was incorporating 25 craft breweries throughout the country at the time, with their combined beer production volume making up to 50% of the total production volume of craft beer in Poland [3]. Although PSBR's regulations as to what craft brewery is do not strictly refer to brewery's annual production, it is declared that for all of the associated breweries it does not exceed 18 000 hL. Apart from that, according to PSBR, a craft brewery is innovative as well as economically and personally independent of another (not artisanal) brewery. Moreover, it essentially uses traditional raw materials, i.e. water, barley malt, yeast and hops and thus theoretically provides a high-quality product being sold at a relatively high price [10].

#### Brewing on an industrial and a craft scale

Concerning the scale of production, the quality of even the same style of beer made following industrial and artisanal manufacturing methods might vary significantly, which opens up discussions which scale is favourable for providing better quality of beer [11]. In fact, one of the reasons for the change in consumer preferences for beer in favour of craft was the desire for new taste experiences provided by particular flavours, which were not being found in industrial beers [8]. On the other hand, in contrast to common belief, craft beer may turn out to be of inferior quality to industrial one due to the lack of such steps of production as pasteurisation and filtration processes as well as poor quality control in the production chain. The exclusion of microfiltration phase prior to, and heating-process after beer bottling may result in generating undesirable flavours induced by incompletely removed yeast and microbial contamination respectively [11]. Further, the ability of a small brewery to follow the quality of semi-finished product and contents of various beer compounds, and thus to maintain a steady production is limited because of small budget and resultant lack of investment in accurate analytical instruments like those based on chromatographic analysis, being vital for brewery's development and competition [12]. For apparently this reason, the SWOT analysis made by Wojtyra and Grudzień characterises the difficulty in providing consistently high-quality of beer as one of the weaknesses of the craft beer industry in Poland [4]. It is worth mentioning on an industrial beer, however, that in order to minimise production costs it is common nowadays for macrobreweries to brew with unmalted cereals (barley, maize, wheat or rice) as partial substitution of barley malt, which is by no means irrelevant for the quality and can have potentially negative effects on beer foam or flavour, for instance [11]. In fact, it is the latter that is considered of the greatest importance with regard to the sensory profile of the beer, and consequently beer's subsequent market performance [1,2].

# Volatile compounds

Beer flavour is contingent on presence and intensity of positive and negative taste and aroma characteristics, the latter being determined by many classes of volatile compounds derived from raw materials [2]. Furthermore, the ultimate volatile compounds profile of the beer is influenced by the production technologies (e.g. pasteurisation, microfiltration) and process conditions (wort aeration level, fermentation temperature, conditioning time), yeast strain (secondary metabolites), as well as storage conditions (light and oxygen contribution) and last but not least by microbial contamination [1,11-14]. Hence, In order to provide a highquality product, it is necessary to keep good manufacturing practice (GMP) and obtain the balance of the beer aroma through maintaining a proper concentration of volatiles such as esters, higher alcohols, carbonyl compounds (aldehydes and ketones), sulphur compounds and organic acids, which at concentrations above their sensory thresholds are perceived either detrimental or beneficial to beer flavour depending on its style [4,14]. In this way, the volatile profile is one of the unique characteristics of each beer style, determining its quality [15]. Pilsener, also commonly known as pils, represents the group of lager beers, which are generally brewed with the use of pale barley malts and fermented in relatively low temperatures (6-12°C) by bottomfermenting yeast Saccharomyces pastorianus. Despite the fact that there are many variants of pilseners on the market throughout the world, which might stem from slight differentiation in choice of raw materials and methods of production, it is preferred that this style of beer be characterised by clean, crisp and refreshing hoppy taste, delicate fruity aroma, lean body (well attenuated beer), as well as clarity and colour intensity at the level of: 0-1 and 4-8°EBC respectively [16]. As opposed to the top-fermented beers, the volatile profile of the bottom-fermented ones is highlighted by aldehydes and ketones, rather than by esters and higher alcohols and this, by all means accounts for less intense taste sensations when consuming beers of pilsener style [17].

It is of note, however, that all of the abovementioned volatiles should be subject to control in order to obtain a clean flavour profile of the pilsener beer, since not only esters introducing fruity aromas and higher alcohols causing harshness negatively affect the flavour of lager, but also carbonyl compounds, i.e. aldehydes (acetaldehyde) and vicinal diketones (diacetyl) due to their very low sensory thresholds induce off-flavours such as grassy and buttery ones respectively [18]. Amongst other volatiles determining the quality of the pilsener beer, the sulphur compounds such as dimethyl sulphide (DMS) or methanethiol (methyl mercaptan) play a significant role, introducing at high concentrations unpleasant notes of cooked or rotten vegetables (e.g. maize, cabbage) [19]. According to the literature, however, subthreshold-levels of DMS (c.  $30 \mu g/L$ ) or even slightly higher concentrations, below  $100 \mu g/L$ , are considered acceptable and beneficial to the flavour of lager [20,21].

#### Gas chromatography

Given the fact that beer volatile organic compounds (VOCs) are present in beer at relatively very low concentrations (from ng to mg L<sup>-1</sup>), the need for accurate analyses of VOCs with the use of sensitive and modern techniques becomes apparent [12,19]. One of the most suitable and sophisticated analytical systems designed for both qualitative and quantitative analysis of extracted VOCs from beer is based on headspace gas chromatographic method coupled to mass spectrometry (HS/GC-MS). In generic terms, the identification is done by partitioning followed by MS (Mass Spectrometry) detection of analytes, being initially carried through a very thin capillary column by helium or another inert gas such as nitrogen or hydrogen, which is in contact with a stationary phase, i.e. an absorbent (e.g. porous polymers) covering the inner side of the column. Owing to different affinities of analytes to the stationary phase, the retention times will also be diverse, making it possible to identify individual compounds [12,19,22–24] (Figure 1). For more details on investment calculations with regard to GC-MS, especially meant for a craft brewery, refer to the source [12].

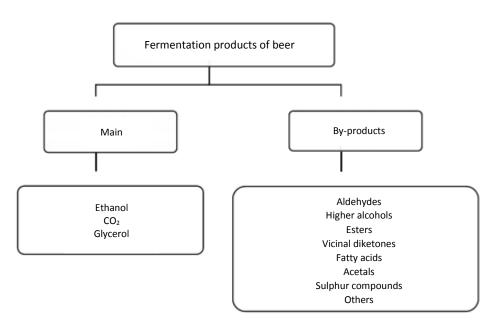


Figure 1. Ingredients of beer produced during fermentation and maturation. Source: The author's own modification on the basis of Kucharczyk et. al (2017) [22].

#### Research purpose

The aim of this study was to examine the volatile compounds profiles of craft and industrial (commercial) beers of pale Pilsener-style by the use of HS/GC-MS, with respect to beers' flavour attributes developed following industrial and artisanal manufacturing methods, along with pointing out potentially resulting quality defects. Given a significant contribution of volatiles to beer sensory characteristics and concomitantly consumer acceptance, as well as the influence of different manufacturing practises on the issue, studies might be useful for brewers in terms of identification the reasons for off-flavours, showing the need for both having at their disposal of sophisticated analytical instruments and maintaining high-quality production standards at each stages of brewing, so that consumers can be supplied with beers of appropriate flavour character for specific style. Further, the physicochemical characterisation of beers will enable to determine if the basic beer parameters, as alcohol content, are in accordance with these specific properties included on the labels, as well as the analysis

of other physicochemical attributes like beer haze or colour intensity will provide a better insight into the impact of the manufacturing scale on the quality of beer. Those results along with determined volatile compounds profiles of beers might also be of particular interest to consumers.

#### Methods

#### <u>Materials</u>

A total of 12 Pilsener-style lager beers produced on a craft (6 beers – group I: A-F) and a massive (6 beers – group II: G-L) scale in Poland were collected for the study. The beers were purchased from the supermarkets or specialised craft beer shops, depending on their availability. The samples of commercial (industrial) beers were selected amongst beers being produced by the largest beer companies in Poland according to the literature [4]. Craft beer samples were chosen based on the affiliation of a brewery to one of the biggest Polish microbrewers association (PSBR). Beers produced by such brewery are distinguished by having the legally protected mark with the information "craft beer" claimed on their label.

#### Analysis of volatile compounds through HS/GC-MS

The analysis of volatile compounds from the hypersurface phase of the tested beers was carried out using the gas chromatography technique coupled with mass spectrometry and headspace attachment (HS-GC-MS). Beer samples with a volume of 10 ml were placed in a glass vial with a capacity of 20 ml containing approx. 4g of sodium chloride. The vial was then closed tightly with an aluminium cap with silicone/PTFE sept. After mixing, sample was analysed using the Agilent 7820A gas chromatograph, the Agilent 5977B GC/MSD mass detector (mass spectrometer) and the 7697A Agilent headspace phase sample feeder. The separation was made on a Restek Rtx-5 column with a length of 60m, a diameter of 0.32 mm and a film thickness of 1  $\mu$ m. Helium was used as a carrier gas and the flow rate was 1.1 ml/min. The temperature of the ion source was 230°C and the quadrupole was 150°C, ionisation energy was 70eV. Mass acquisition mode in the range of masses 20-400. The identification of individual compounds was based on a comparison of the spectrum with that available in the NIST library. The content of dimethyl sulphide (DMS) and 2,3-butanedione was also measured by quantitatively comparing its retention time with the retention time of the standard for which the calibration curve was prepared. Each sample was analysed in 3 repetitions. Identification of volatiles was verified using linear retention indices (LRI) – calculated and found in the literature [25–29]. In gas chromatography method, the area of a peak generated is proportional to the amount of the compound that is present in the sample. The volatile compounds profile of the analysed samples was defined as the percentage of the surface area under the peak of a specific compound in relation to the sum of the surface areas of all identified compounds on the chromatogram.

# Physicochemical analysis of beer

The basic physicochemical properties of commercial and craft beers were tested with the beer analyser equipment. The DMA 4500 M (Anton-Paar) density measuring instrument combined with the Alcolyzer Beer ME and Turbidity meter Haze QC ME modules were used for determination of beer's: density (g/cm<sup>3</sup>), alcohol content (%v/v), original and final extract (°Plato), real degree of fermentation (RDF%), haze (°EBC), colour intensity (°EBC) and pH. All the measurements were performed in triplicate, by injection into the Beer Analyzer 50 mL of each sample previously decarbonated by the use of laboratory shaker.

# Statistical analysis

Data collected from triplicate beer samples were subjected to statistical analysis using the STATISTICA 13 (Dell, StatSoft) [30]. In order to compare values, one-way analysis of variance (ANOVA) and Tukey HSD at significance level of  $\alpha$  = 0.05 was performed.

#### **Results and discussion**

# Physicochemical characterisation

The most important physicochemical properties of examined beers are shown in Table 1. Statistically significant differences with respect to all measured parameters between the group of craft (group I: A-F) and the group of industrial (group II: G-L) beers were observed (P < 0.05) (Figure 2: a-g). These parameters influence beer sensory quality as well as its microbiological stability.

	Sample											
Parameter	Group I – craft	t beers				Group II – industrial beers						
	Α	В	с	D	E	F	G	н	I	J	к	L
Alcohol content (% v/v)	$3.99 \pm 0.01^{h}$	5.38 ± 0.01 <sup>b</sup>	5.34 ± 0.05 <sup>bc</sup>	$5.04 \pm 0.04^{e}$	$4.93 \pm 0.04^{ef}$	$3.90\pm0.01^{h}$	$4.83 \pm 0.01^{fg}$	4.78 ± 0.11 <sup>g</sup>	$5.24\pm0.02^{cd}$	$5.42 \pm 0.04^{ab}$	5.53 ± 0.02ª	$5.20\pm0.01^d$
Final extract (°P)	2.51 ± 0.01 <sup>c</sup>	1.78 ± 0.01 <sup>b</sup>	1.97 ± 0.03 <sup>e</sup>	$2.26 \pm 0.02^{d}$	2.54 ± 0.02°	2.71 ± 0.00ª	2.63 ± 0.01 <sup>b</sup>	$1.48 \pm 0.04^{i}$	1.72 ± 0.02 <sup>g</sup>	1.51 ± 0.01 <sup>hi</sup>	$0.82 \pm 0.01^{j}$	1.54 ± 0.01 <sup>h</sup>
Colour intensity (°EBC)	$8.43 \pm 0.02^{j}$	13.63 ± 0.05 <sup>c</sup>	15.13 ± 0.16 <sup>b</sup>	$12.30 \pm 0.12^{d}$	$11.05 \pm 0.02^{f}$	17.32 ± 0.06ª	11.88 ± 0.01 <sup>e</sup>	7.95 ± 0.03 <sup>k</sup>	9.03 ± 0.01 <sup>i</sup>	10.51 ± 0.04 <sup>g</sup>	$9.84 \pm 0.01^{h}$	7.08 ± 0.01 <sup>1</sup>
Haze (°EBC)	1.06 ± 0.02 <sup>ef</sup>	1.35 ± 0.01 <sup>e</sup>	10.35 ± 0.58ª	$6.65 \pm 0.21^{b}$	2.95 ± 0.08 <sup>d</sup>	5.64 ± 0.03°	0.79 ± 0.01 <sup>fg</sup>	0.24 ± 0.02 <sup>h</sup>	0.38 ± 0.01 <sup>gh</sup>	0.39 ± 0.02 <sup>gh</sup>	0.53 ± 0.02 <sup>gh</sup>	0.38 ± 0.03 <sup>gh</sup>
Original extract (°P)	10.09 ± 0.01 <sup>g</sup>	11.92 ± 0.02 <sup>ab</sup>	12.02 ± 0.06ª	11.75 ± 0.07 <sup>bcd</sup>	11.82 ± 0.06 <sup>bc</sup>	10.11 ± 0.01 <sup>g</sup>	11.72 ± 0.02 <sup>cd</sup>	10.56 ± 0.15 <sup>f</sup>	11.61 ± 0.02 <sup>d</sup>	11.74 ± 0.07 <sup>cd</sup>	11.30 ± 0.03 <sup>e</sup>	11.38 ± 0.01 <sup>e</sup>
рН	4.53 ± 0.01ª	5.23 ± 0.00 <sup>a</sup>	$4.80 \pm 0.01^{b}$	4.65 ± 0.01 <sup>d</sup>	$4.61 \pm 0.00^{e}$	4.57 ± 0.00 <sup>f</sup>	4.79 ± 0.00 <sup>b</sup>	4.27 ± 0.00 <sup>j</sup>	4.72 ± 0.01 <sup>c</sup>	4.57 ± 0.01 <sup>f</sup>	$4.42 \pm 0.00^{i}$	4.45 ± 0.01 <sup>h</sup>
DMS (µg/l)	54.40 ± 6.23 <sup>bc</sup>	65.61 ± 5.37 <sup>b</sup>	136.29 ± 20.18ª	137.49 ± 13.66ª	43.15 ± 4.04 <sup>bcd</sup>	$0.00 \pm 0.00^{d}$	37.80 ± 32.73 <sup>cd</sup>	38.15 ± 33.07 <sup>bcd</sup>	$0.00 \pm 0.00^{d}$	$0.00 \pm 0.00^{d}$	$0.00 \pm 0.00^{d}$	$0.00 \pm 0.00^{d}$
Density (g/cm3)	1.0080 ± 0.00°	$1.0051 \pm 0.00^{f}$	$1.0058 \pm 0.00^{e}$	$1.0070 \pm 0.00^{d}$	1.0081 ± 0.00°	1.0088 ± 0.00ª	1.0084 ± 0.00 <sup>b</sup>	$1.0039 \pm 0.00^{i}$	$1.0048 \pm 0.00^{g}$	$1.0040 \pm 0.00^{hi}$	$1.0014 \pm 0.00^{j}$	1.0042 ± 0.00 <sup>h</sup>
Real degree of fermentation (RDF%)	$60.60 \pm 0.06^{i}$	68.71 ± 0.05 <sup>d</sup>	67.58 ± 0.27 <sup>e</sup>	$65.25 \pm 0.16^{f}$	$63.639 \pm 0.1^{g}$	59.05 ± 0.04 <sup>j</sup>	62.64 ± 0.06 <sup>h</sup>	69.48 ± 0.49°	68.86 ± 0.11 <sup>d</sup>	70.46 ± 0.04 <sup>b</sup>	75.00 ± 0.07ª	69.89 ± 0.05°

Table 1. Physicochemical properties of examined beers. *Source: Results of the authors' research.* 

letters (a-I) within the same line (horizontally) differ significantly with a p value < 0.05

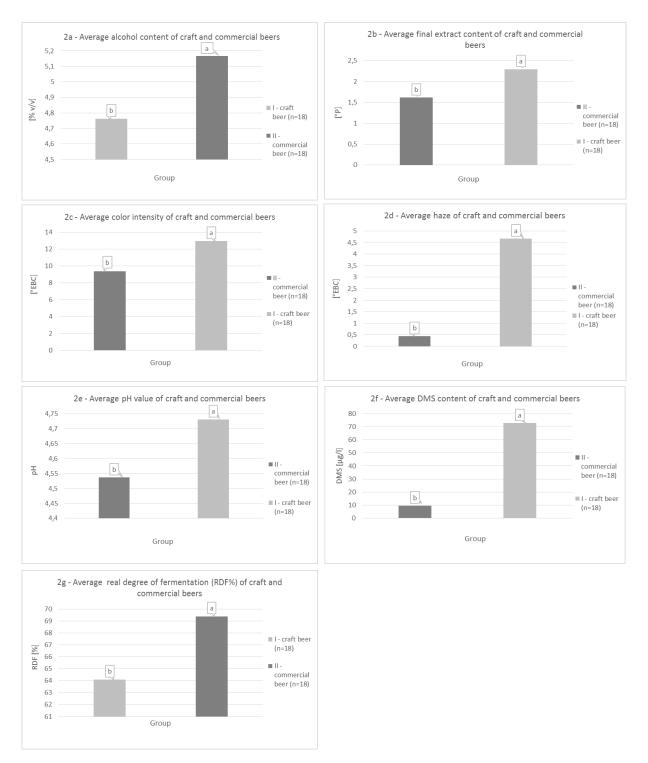


Figure 2 (a, b, c, d, e, f, g). Statistically significant differences between craft (I) and commercial (II) group of beer. Source: Results of the authors' research.

Sensory evaluation of beer covers four different aspects such as beer's appearance, aroma, flavour, and mouthfeel [31]. The assessment of beer's appearance incorporates, amongst others, colour intensity and clarity, which both significantly affect hedonic response, while drinking beer. If the expectation and the visual experience during drinking differ, then beer quality may be rated negatively right from the beginning [32]. In this way, regardless of the manufacturing scale, it is generally best to produce beer with appearance attributes that match the typical characteristics of a specific beer style. According to the literature, lager beer (principally

the pale Pilsener-style) is usually expected to not exceed 1°EBC haze, which is considered a brilliant (clear) beer [33]. In the twelve beers studied, haze values were in the range of 0.24 to 10.35°EBC (Table 1). Thus, a considerable variation in beer haze among samples was observed. It is of note that only beers made by industrial processes were characterised by a desirable haze for lager beer, i.e.  $< 1^{\circ}EBC (0.45^{\circ}EBC on average)$ , while all craft beer samples exhibited higher values (4.67°EBC on average) (Table 1 and Figure 2d). The formation of haze is influenced by a lot of factors, including raw materials used in the process as well as mash, wort and beer production technology [34]. Craft beers, as opposed to industrial beers, are usually made without the addition of chemical adsorbents removing haze-active compounds during filtration (proteins and polyphenols) such as PVPP or silica gel, or by completely eliminating the process of beer filtration. It is probably the main cause of increased haze values measured in craft beers in comparison to beers brewed on an industrial scale. Similarly, colour intensity measured was also significantly higher among craft beers than among industrial beers (Figure 2c) (P < 0.05). In the Doorn et. at. (2019) study it was confirmed that, as the colour intensity of beer increased its rated ability to quench one's thirst decreased [32]. Given that thirst-quenching quality of Pilsener-style lager beer is of great importance to consumers due to their wish to drink refreshing beer, it should be concluded that industrial beers in terms of colour intensity are of superior quality to craft ones. On the other hand, only two out of six commercial beers (samples H and L) had a colour of proper intensity for pilsener style, i.e. in the range of 4-8°EBC (Table 1) [16]. In contrast to parameters of beer haze and colour intensity, the average real degree of fermentation (RDF), and thus also the average alcohol content were significantly lower for the group of craft beers than for the group of industrial beers (P < 0.05) (Figure 2a, 2g). RDF determines the rate of real attenuation, that is the actual percentage of sugars consumed by yeast and converted into alcohol and carbon dioxide during the fermentation process. Hence from a sensory point of view, that parameter influence the textural attributes (so-called mouthfeel), as a lower RDF percentage gives rise to beers with higher levels of sweetness and syrupy taste, whereas the higher RDF%, the more refreshing, lighter and drier the beer [35]. Andrade et al. (2016) [36], when evaluating the quality of different brands of Pilsner-style beer, reported RDF between 59.02 and 69.44%. Overall our findings regarding RDF% are in accordance with findings reported by Andrade et al., except for four samples of industrial beers, namely H, J, K and L, which exhibited higher RDF% (Table 1). It has to be pointed out, however, that sugar syrups were used as malt adjuncts (partial substitutes of barley malt) when producing K and L beers, which significantly increased the content of easily fermented sugars in worts, hence also RDF% (information with respect to raw materials composition was claimed on the label). The labelling of beers must also indicate the alcoholic strength by volume. Considering that the tolerance allowed in terms of the indication of the alcoholic strength by volume for beers featuring alcoholic content below 5.5% v/v is 0.5% v/v [37], only three samples (two industrial beers – I and J, and one craft beer – B) fell short of that specific requirement (table 2). Tozetto et al. (2019) [38] when analysing 28 Pilsener-style lager beers, reported average alcohol content at the level of 4.7% v/v, which is more consistent with the results obtained for the group of craft beers (4.75%v/v on average) than for the group of industrial beers (5.15% v/v on average) (Figure 2a). The pH of the beers studied was in the range of 4.27-5.23. It is generally stated that lager beer should be characterised by a pH of around 4.0-5.0. Sample B of craft beer had the highest (5.23), whereas sample H of industrial beer the lowest pH (4.27) (Table 1). Also the average pH of craft beers was significantly higher than average pH of industrial beers (Figure 2e). To sum up, the results show that the manufacturing scale does seem to impact the physicochemical properties of the pale Pilsener-style lager beer. The average values of the basic characteristics of beers produced on a craft scale (by artisanal processes) deviates from standards for Pilsener-style beer to a higher degree than in the case of beers made following industrial processes. In this respect, from the point of view of the average consumer, industrial beers may be perceived of superior quality to craft beers.

#### Volatile compounds identification

The HS/GC-MS analysis of the pale Pilsener-style lager beers provided the information about volatile profile of each sample (Table 3), which paved the way for the characterisation of the flavours of individual beers as well as the comparison of the volatile compounds' profiles between the groups of industrial and craft beers. The analysis of volatile compounds in craft and industrial beers of Pilsener-style with the use of HS-SPME/GC-MS made by Giannetti et. al. (2019) [5] showed that manufacturing scale has a substantial impact on the beer volatile compounds profiles, as only 13 out of 111 volatiles identified were simultaneously present in all 79 beers analysed (42 craft and 37 industrial products purchased on the Italian market). Based on the evaluation of average concentrations, expressed as TIC area, 6 out of 13 identified compounds were subsequently assigned to the group of craft beers, whereas the rest of them to the group of industrial beers, giving the discrimination as to which group of beers was characterised by a higher content of an individual compound. The authors

concluded their study with the encouragement for other scientists to further characterise quality marker compounds of craft beers, underlining the need for quantification of the identified markers by analysis of the pure standard. Therefore, in this study beers purchased on the Polish market were analysed in order to determine their volatile compounds profiles (qualitative analysis) with additional focus on quantitative analysis of dimethyl sulphide (DMS) and 2,3-butanedione (diacetyl), by using respective standards. These two volatile compounds are potentially present in beer and introduce, at high concentrations, unpleasant notes of cooked vegetables and butter respectively.

In the analysed batch of samples a total of 57 volatile compounds were identified by using NIST spectrum library and literature LRI values (Table 4). Those compounds can be classified into 6 groups, namely: esters (29), alcohols (14), carboxylic acids (3), carbonyl compounds (6), terpenes (4) and sulphur compounds (1). The volatile compounds profiles of 12 beers, 6 from craft group (A-F) and 6 from commercial group (G-L), are shown in Table 3. From the results, it is clear that the volatiles production was higher in the beers made by artisanal processes (especially in sample B) than in the industrial beers (Table 3). On average, the craft beers featured higher quantities of all identified compounds from 6 mentioned groups, for instance, an average of 14 esters and 7 alcohols were identified in the craft beers, whereas an average of 9 esters and 6 alcohols were identified in the industrial beers. These basic results are consistent with previous literature reports [11] and highlight just how standardisation procedures being implemented in commercial breweries (filtration and pasteurisation) as well as a better control of manufacturing processes in the case of industrial beers may contribute to a flattening or a complete elimination of a specific volatile compounds from the finished product. On the one hand, based on the results obtained it might be argued that craft beers retain more flavour attributes or nutritional properties, nevertheless, as far as the pale Pilsener-style lager beer is concerned, it must be stressed that too intense aromas disturb the clean profile desired for this style of beer and consequently negatively affect the beer quality.

Parameters	Sample													
	Group I – craft beers							Group II – industrial beers						
	Α	В	С	D	E	F	G	н	I	J	К	L		
Alcohol content measured (% v/v)	3.99	5.38	5.34	5.04	4.93	3.90	4.83	4.78	5.24	5.42	5.53	5.20		
Alcohol content labelled (% v/v)	4.40	4.70	5.00	5.00	4.80	4.10	5.00	5.00	6.00	6.00	5.70	5.50		
IΔ <sub>A</sub> I	0.41	0.68	0.34	0.04	0.13	0.20	0.17	0.22	0.76	0.58	0.17	0.30		

Table 2. Comparison of alcohol content measured and labelled for studied beers. Source: Results of the authors' research.

IΔ<sub>A</sub>I – the absolute value of a difference between alcohol content measured and labelled for specific beer

	Sample												
Compound	Group I – craf	t beers				Group II – industrial beers							
	A	В	с	D	E	F	G	н	I	J	к	L	
Acetaldehyde	$0.039 \pm 0.002^{f}$	0.063 ± 0.002 <sup>e</sup>	0.155 ± 0.009 <sup>b</sup>	$0.129 \pm 0.003^{cd}$	$0.109 \pm 0.004^{d}$	$0.118 \pm 0.003^{cd}$	0.131 ± 0.007 <sup>c</sup>	$0.109 \pm 0.002^{d}$	0.167 ± 0.011 <sup>b</sup>	$0.258 \pm 0.017^{a}$	0.071 ± 0.003 <sup>e</sup>	0.160 ± 0.002 <sup>b</sup>	
Ethanol	86.881 ± 0.455 <sup>ab</sup>	82.359 ± 0.383 <sup>d</sup>	84.730 ± 0.781 <sup>c</sup>	85.708 ± 0.468 <sup>bc</sup>	87.367 ± 0.185ª	87.032 ± 0.504 <sup>ab</sup>	86.971 ± 0.499 <sup>ab</sup>	82.996 ± 0.468 <sup>d</sup>	86.081 ± 0.614 <sup>abc</sup>	85.711 ± 0.536 <sup>bc</sup>	82.949 ± 0.242 <sup>d</sup>	87.206 ± 0.175ª	
Acetone	0.000 ± 0.000 <sup>c</sup>	0.126 ± 0.017 <sup>a</sup>	$0.040 \pm 0.008^{b}$	0.101 ± 0.021 <sup>a</sup>	0.046 ± 0.010 <sup>b</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>				
2-Propanol	$0.000 \pm 0.000^{b}$	0.459 ± 0.003 <sup>a</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	
2-Nitroethanol	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	$0.030 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	0.000 ± 0.000 <sup>a</sup>	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	
Ethyl formate	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.029 \pm 0.004^{a}$	0.011 ± 0.009 <sup>b</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	
Dimethyl sulphide	0.025 ± 0.003 <sup>b</sup>	$0.020 \pm 0.000^{b}$	0.047 ± 0.005 <sup>a</sup>	$0.049 \pm 0.004^{a}$	0.015 ± 0.002 <sup>bc</sup>	$0.014 \pm 0.012^{bc}$	0.007 ± 0.012 <sup>bc</sup>	0.012 ± 0.011 <sup>bc</sup>	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{c}$	
1-propanol	0.348 ± 0.005 <sup>fg</sup>	0.598 ± 0.004 <sup>c</sup>	0.308 ± 0.001 <sup>hi</sup>	$0.511 \pm 0.009^{d}$	0.365 ± 0.020 <sup>f</sup>	$0.364 \pm 0.006^{f}$	0.336 ± 0.005 <sup>gh</sup>	1.398 ± 0.018ª	0.410 ± 0.011 <sup>e</sup>	$0.538 \pm 0.004^{d}$	0.663 ± 0.006 <sup>b</sup>	$0.300 \pm 0.002^{i}$	
Acetic acid	0.127 ± 0.016 <sup>a</sup>	0.041 ± 0.007 <sup>bcd</sup>	0.059 ± 0.002 <sup>b</sup>	0.107 ± 0.011 <sup>a</sup>	0.055 ± 0.008 <sup>bc</sup>	0.129 ± 0.026 <sup>a</sup>	0.031 ± 0.003 <sup>bcd</sup>	0.045 ± 0.006 <sup>de</sup>	0.023 ± 0.003 <sup>ae</sup>	0.025 ± 0.004 <sup>cde</sup>	0.000 ± 0.000 <sup>e</sup>	0.032 ± 0.010 <sup>bcd</sup>	
Ethyl acetate	2.960 ± 0.146 <sup>ef</sup>	4.168 ± 0.122 <sup>b</sup>	$4.660 \pm 0.267^{a}$	3.260 ± 0.113 <sup>de</sup>	3.035 ± 0.088 <sup>ef</sup>	$2.630 \pm 0.128^{f}$	3.757 ± 0.220 <sup>bc</sup>	2.702 ± 0.115 <sup>f</sup>	3.2648± 0.153 <sup>de</sup>	$2.775 \pm 0.171^{f}$	5.063 ± 0.063 <sup>a</sup>	3.477± 0.052 <sup>cd</sup>	
Isobutanol	0.826 ± 0.007 <sup>d</sup>	0.578 ± 0.009 <sup>f</sup>	$0.823 \pm 0.030^{d}$	0.889 ± 0.026 <sup>cd</sup>	0.958 ± 0.021 <sup>bc</sup>	0.924 ± 0.023 <sup>c</sup>	0.717 ± 0.010 <sup>e</sup>	1.401 ± 0.032 <sup>a</sup>	1.002 ± 0.045 <sup>b</sup>	1.402 ± 0.037 <sup>a</sup>	0.942 ± 0.013 <sup>bc</sup>	$0.828 \pm 0.008^{d}$	
3-Methyl-2-butanone	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.029 \pm 0.002^{a}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	
1-butanol	0.000 ± 0.000 <sup>c</sup>	$0.080 \pm 0.000^{b}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	0.337 ± 0.006 <sup>a</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.080 \pm 0.000^{b}$	$0.000 \pm 0.000^{c}$	
Methyl isobutyrate	0.000 ± 0.000 <sup>b</sup>	0.067 ± 0.006 <sup>a</sup>	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	
Ethyl propionate	0.027 ± 0.006 <sup>de</sup>	0.073 ± 0.006 <sup>b</sup>	0.027 ± 0.006 <sup>de</sup>	0.037 ± 0.006 <sup>d</sup>	$0.020 \pm 0.000^{e}$	$0.020 \pm 0.000^{e}$	$0.040 \pm 0.000^{d}$	0.057 ± 0.006 <sup>c</sup>	$0.080 \pm 0.010^{b}$	$0.030 \pm 0.000^{de}$	0.096 ± 0.003 <sup>a</sup>	$0.040 \pm 0.000^{d}$	
Propyl acetate	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{\rm b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.025 ± 0.001 <sup>a</sup>	0.000 ± 0.000 <sup>b</sup>	
1-Butanol. 3-methyl-	4.773 ± 0.041 <sup>ef</sup>	5.715 ± 0.045 <sup>b</sup>	$4.563 \pm 0.134^{fg}$	5.080± 0.118 <sup>cd</sup>	4.494 ± 0.057 <sup>fg</sup>	5.168± 0.119 <sup>cd</sup>	4.323 ± 0.053 <sup>g</sup>	6.405 ± 0.128 <sup>a</sup>	4.947 ± 0.166 <sup>de</sup>	5.317± 0.128 <sup>cd</sup>	4.391 ± 0.059 <sup>g</sup>	3.940 ± 0.036 <sup>h</sup>	
1-Butanol. 2-methyl-	1.770 ± 0.024 <sup>def</sup>	$1.615 \pm 0.031^{f}$	1.706 ± 0.075 <sup>ef</sup>	1.885± 0.054 <sup>cd</sup>	2.038 ± 0.037 <sup>bc</sup>	1.810 ± 0.065 <sup>de</sup>	1.839 ± 0.029 <sup>de</sup>	1.921 ± 0.049 <sup>bcd</sup>	2.046 ± 0.096 <sup>b</sup>	2.448 ± 0.070 <sup>a</sup>	1.778± 0.040 <sup>de</sup>	1.694 ± 0.030 <sup>ef</sup>	
2-Pentanone. 4-methyl-	0.027 ± 0.001 <sup>c</sup>	0.066 ± 0.002 <sup>a</sup>	0.000± 0.000 <sup>d</sup>	0.045 ± 0.003 <sup>b</sup>	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	$0.000 \pm 0.000^{d}$	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	$0.000 \pm 0.000^{d}$	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	
Ethyl isobutyrate	$0.000 \pm 0.000^{\circ}$	$0.204 \pm 0.012^{a}$	$0.000 \pm 0.000^{\circ}$	$0.073 \pm 0.004^{b}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{c}$	
Isobutyl acetate	$0.020 \pm 0.000^{cd}$	$0.000 \pm 0.000^{e}$	0.037 ± 0.006 <sup>b</sup>	$0.010 \pm 0.009^{d}$	0.020± 0.000 <sup>cd</sup>	0.020± 0.000 <sup>cd</sup>	$0.020 \pm 0.000^{cd}$	0.030± 0.000 <sup>cb</sup>	$0.000 \pm 0.000^{e}$	0.020± 0.000 <sup>cd</sup>	$0.060 \pm 0.000^{a}$	0.027 ± 0.006 <sup>bc</sup>	
Methyl isovalerate	0.000 ± 0.000a	0.020 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	0.000 ± 0.000a	
2.3-Butanediol	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.020 ± 0.000a	0.020 ± 0.000a	0.000 ± 0.000b	0.000 ± 0.000b	0.023 ± 0.006a	0.027 ± 0.006a	0.030 ± 0.010a	0.020 ± 0.000a	

Table 3. Average volatiles profiles (n=3) of 12 beers, 6 from commercial group and 6 from craft group. Source: Results of the authors' research.

	Sample													
Compound	Group I – craf	t beers				Group II – industrial beers								
	A	В	с	D	E	F	G	н	I	J	к	L		
Ethyl butanoate	0.047 ± 0.006 <sup>bc</sup>	0.057 ± 0.006 <sup>bc</sup>	0.077 ± 0.006 <sup>a</sup>	0.053 ± 0.006 <sup>bc</sup>	$0.060 \pm 0.000^{b}$	0.043 ± 0.006 <sup>c</sup>	0.000± 0.000 <sup>d</sup>	$0.047 \pm 0.006^{bc}$	0.057 ± 0.006 <sup>bc</sup>	0.053 ± 0.006 <sup>bc</sup>	0.077 ± 0.006 <sup>a</sup>	$0.060 \pm 0.000^{b}$		
Furfural	0.117 ± 0.091 <sup>a</sup>	$0.000 \pm 0.000^{b}$	0.057 ± 0.015 <sup>ab</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.017 ± 0.015 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		
Butanoic acid. 2-methyl ethyl ester	0.000 ± 0.000 <sup>b</sup>	$0.022 \pm 0.002^{a}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$		
Butanoic acid. 3-methyl ethyl ester	$0.000 \pm 0.000^{b}$	$0.026 \pm 0.001^{a}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		
1-Hexanol	0.000 ± 0.000 <sup>b</sup>	$0.045 \pm 0.002^{a}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$		
Isoamyl acetate	0.840± 0.092 <sup>d</sup>	$0.202 \pm 0.012^{f}$	1.479 ± 0.165 <sup>b</sup>	0.521 ± 0.031 <sup>e</sup>	0.723 ± 0.031 <sup>de</sup>	0.893± 0.065 <sup>d</sup>	1.133 ± 0.110 <sup>c</sup>	1.583 ± 0.098 <sup>b</sup>	0.862± 0.075 <sup>d</sup>	0.697 ± 0.061 <sup>de</sup>	2.677 ± 0.053 <sup>a</sup>	1.239 ± 0.031 <sup>c</sup>		
2-Methylbutyl acetate	0.067 ± 0.006 <sup>de</sup>	$0.000 \pm 0.000^{f}$	0.116 ± 0.013 <sup>b</sup>	$0.051 \pm 0.004^{e}$	$0.080 \pm 0.000^{cd}$	0.076± 0.007 <sup>d</sup>	0.107 ± 0.012 <sup>b</sup>	0.097 ± 0.06 <sup>bc</sup>	0.073± 0.006 <sup>d</sup>	0.077 ± 0.006 <sup>cd</sup>	0.233 ± 0.009 <sup>a</sup>	0.108 ± 0.002 <sup>b</sup>		
Isobutyl isobutyrate	0.023 ± 0.006 <sup>b</sup>	0.079 ± 0.005 <sup>a</sup>	0.000 ± 0.000 <sup>c</sup>	$0.081 \pm 0.006^{a}$	$0.000 \pm 0.000^{c}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{c}$	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>		
Amyl propionate	$0.000 \pm 0.000^{\circ}$	$0.040 \pm 0.003^{a}$	0.000 ± 0.000 <sup>c</sup>	0.032 ± 0.001 <sup>b</sup>	$0.000 \pm 0.000^{c}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{c}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>		
β-Myrcene	$0.000 \pm 0.000^{b}$	$0.564 \pm 0.014^{a}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		
Ethyl caproate	0.193 ± 0.031 <sup>bc</sup>	$0.000 \pm 0.000^{e}$	0.292 ± 0.043 <sup>a</sup>	0.187 ± 0.015 <sup>bc</sup>	$0.147 \pm 0.006^{cd}$	0.187 ± 0.012 <sup>bc</sup>	$0.140 \pm 0.017^{cd}$	0.117± 0.006 <sup>d</sup>	0.117± 0.015 <sup>d</sup>	0.147 ± 0.015 <sup>cd</sup>	0.183 ± 0.006 <sup>bc</sup>	0.203 ± 0.006 <sup>b</sup>		
Butyl 2-methylbutyrate	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.020 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$	$0.000 \pm 0.000^{a}$		
1-Hexyl acetate	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	0.023 ± 0.003 <sup>a</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$		
Isobutyric acid. isopentyl ester	0.000 ± 0.000 <sup>c</sup>	$0.108 \pm 0.007^{a}$	0.000 ± 0.000 <sup>c</sup>	0.037 ± 0.006 <sup>b</sup>	$0.000 \pm 0.000^{c}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>		
2-Methylbutyl isobutyrate	0.030 ± 0.000 <sup>c</sup>	0.115 ± 0.007 <sup>b</sup>	0.000± 0.000 <sup>d</sup>	0.197 ± 0.013 <sup>a</sup>	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	0.000± 0.000 <sup>d</sup>	$0.000 \pm 0.000^{d}$	0.000± 0.000 <sup>d</sup>	$0.000 \pm 0.000^{d}$		
Hexanoic acid. 4-methylene methyl ester	0.037 ± 0.006 <sup>b</sup>	0.103 ± 0.006 <sup>a</sup>	0.027 ± 0.006 <sup>b</sup>	0.034 ± 0.007 <sup>b</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{c}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>		
Ethyl heptanoate	0.000 ± 0.000 <sup>c</sup>	$0.063 \pm 0.006^{a}$	0.000 ± 0.000 <sup>c</sup>	0.013 ± 0.011 <sup>b</sup>	$0.000 \pm 0.000^{c}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>		
2-Nonanol	0.000 ± 0.000 <sup>c</sup>	$0.067 \pm 0.006^{a}$	0.000 ± 0.000 <sup>c</sup>	$0.012 \pm 0.011^{b}$	$0.000 \pm 0.000^{c}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	$0.000 \pm 0.000^{\circ}$	0.000 ± 0.000 <sup>c</sup>	0.000 ± 0.000 <sup>c</sup>		
Linalool	0.103 ± 0.006 <sup>c</sup>	$0.647 \pm 0.040^{a}$	0.063± 0.006 <sup>d</sup>	0.332 ± 0.021 <sup>b</sup>	$0.020 \pm 0.000^{e}$	0.027 ± 0.006 <sup>de</sup>	$0.000 \pm 0.000^{e}$	$0.000 \pm 0.000^{e}$	0.000 ± 0.000 <sup>e</sup>	$0.000 \pm 0.000^{e}$	$0.000 \pm 0.000^{e}$	0.000 ± 0.000 <sup>e</sup>		
2-Phenylethanol	0.112 ± 0.010 <sup>de</sup>	$0.196 \pm 0.004^{bc}$	0.152 ± 0.023 <sup>bcde</sup>	0.100 ± 0.007 <sup>e</sup>	0.137 ± 0.038 <sup>de</sup>	0.111 ± 0.002 <sup>de</sup>	0.140 ± 0.012 <sup>cde</sup>	$0.278 \pm 0.040^{a}$	$0.210 \pm 0.017^{b}$	0.147 ± 0.015 <sup>cde</sup>	0.167 ± 0.015 <sup>bcd</sup>	0.130 ± 0.010 <sup>de</sup>		
Octanoic acid (Caprylic acid)	0.050 ± 0.003 <sup>a</sup>	0.021± 0.002 <sup>d</sup>	0.057 ± 0.007 <sup>a</sup>	0.028 ± 0.002 <sup>cd</sup>	0.054 ± 0.006 <sup>a</sup>	0.032 ± 0.003 <sup>bc</sup>	0.021± 0.002 <sup>d</sup>	$0.040 \pm 0.001^{b}$	0.000 ± 0.000 <sup>e</sup>	$0.000 \pm 0.000^{e}$	$0.000 \pm 0.000^{e}$	$0.020 \pm 0.002^{d}$		
Ethyl caprylate	0.300 ± 0.045b	0.606 ± 0.030a	0.289 ± 0.046b	0.189 ± 0.016de	0.158 ± 0.008def	0.195 ± 0.013de	0.113 ± 0.018f	0.220 ± 0.008cd	0.343 ± 0.025b	0.133 ± 0.012ef	0.313 ± 0.006b	0.343 ± 0.009b		
2-Decanol	0.000 ± 0.000b	0.021 ± 0.003a	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b		
α-Terpineol	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.013 ± 0.012a	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b	0.000 ± 0.000b		
5-Hydroxymethylfurfural	0.057 ± 0.006ab	0.043 ± 0.006ab	0.027 ± 0.006bcd	0.030 ± 0.000bcd	0.017 ± 0.015de	0.033 ± 0.006bcd	0.037 ± 0.006bc	0.030 ± 0.000bcd	0.000 ± 0.000e	0.020 ± 0.000cd	0.020 ± 0.000cd	0.020 ± 0.000cd		

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	Sample													
Compound	Group I – craft beers							Group II – industrial beers						
	A	В	с	D	E	F	G	н	I	1	к	L		
Linalyl iso-valerate	0.000 ± 0.000 <sup>b</sup>	0.063 ± 0.006ª	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$		
Phenethyl acetate	$0.033 \pm 0.006^{d}$	0.000 ± 0.000 <sup>e</sup>	0.063 ± 0.006 <sup>c</sup>	$0.000 \pm 0.000^{\rm e}$	$0.033 \pm 0.006^{d}$	$0.030 \pm 0.000^{d}$	0.063 ± 0.006 <sup>c</sup>	0.123 ± 0.006 <sup>b</sup>	$0.060 \pm 0.000^{\circ}$	$0.040 \pm 0.000^{d}$	$0.143 \pm 0.006^{a}$	0.070 ± 0.000 <sup>c</sup>		
Ethyl pelargonate	0.000 ± 0.000 <sup>b</sup>	0.034 ± 0.008 <sup>a</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$		
2-Undecanol	0.000 ± 0.000 <sup>b</sup>	0.049 ± 0.007 <sup>a</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{\rm b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		
Methyl geranate	0.000 ± 0.000 <sup>b</sup>	0.126 ± 0.011 <sup>a</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{\rm b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		
Capric acid (Decanoic acid)	0.020 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>	0.000 ± 0.000 <sup>a</sup>		
4-Decenoic acid. ethyl ester. (Z)	$0.000 \pm 0.000^{b}$	0.027 ± 0.006 <sup>a</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		
Ethyl caprate	0.073 ± 0.006 <sup>c</sup>	0.137 ± 0.015 <sup>b</sup>	0.047 ± 0.012 <sup>cde</sup>	$0.020 \pm 0.000^{\rm e}$	$0.020 \pm 0.000^{ef}$	0.043 ± 0.006 <sup>de</sup>	$0.000 \pm 0.000^{f}$	0.030 ± 0.000 <sup>de</sup>	0.197 ± 0.023 <sup>a</sup>	0.047 ± 0.006 <sup>cde</sup>	0.033 ± 0.006 <sup>de</sup>	0.057 ± 0.006 <sup>cd</sup>		
Humulene	$0.000 \pm 0.000^{b}$	0.027 ± 0.006ª	0.000 ± 0.000 <sup>b</sup>	$0.000 \pm 0.000^{\rm b}$	$0.000 \pm 0.000^{\rm b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{\rm b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{\rm b}$	$0.000 \pm 0.000^{b}$	$0.000 \pm 0.000^{b}$		

Values marked by different letters (a-i) within the same line differ significantly with a p value  $\leq 0.05$ 

Apart from ethanol that constituted the major volatile compounds, in all 12 samples the largest share in the profile belonged to two esters: ethyl acetate (2.63 - 5.06%) and isoamyl acetate (0.20 - 2.68%) as well as two alcohols: 3-methyl-1-butanol (3.94 - 6.41%) and 2-methyl-1-butanol (1.62 - 2.45%), which is also in accordance with findings reported in the literature [23,39]. Volatile esters give the beer fruity character, so in generic terms our results demonstrated that craft beers might be characterised by fruity flavours to a higher degree than industrial beers. Nevertheless, it should be highlighted that the industrial beers showed a greater presence of isoamyl acetate. This volatile ester is characterised by a "banana flavour". The sample K of industrial beer featured also significantly higher ethyl acetate content in comparison to other beers (P < 0.05) (Table 3 on the basis of results received from [30]). In the case of that specific sample (K), it may be assumed that such results may have stemmed from the addition of sugar syrups being added to wort when high gravity brewing technology is implemented (information about the addition of sugar syrups was included on the label of the beer marked with K letter). It has previously been shown that high-gravity brewing (>16°Plato) is associated with disproportionate higher levels of esters, particularly ethyl acetate and isoamyl acetate [39]. According to the literature, many commercial brewing companies and only some large craft breweries use HGB [40]. The results of present study also share a few of similarities with Giannetti's et. al. (2019) [5] and Giannetti's et. al. (2018) [11] findings in terms of other esters being detected in craft and industrial beers. Similarly, 2-methylbutyl isobutyrate was not detected in any of the industrial beers studied, whereas it was detected in 3 out of 6 craft beers (samples A, B and D). Isobutyl isobutyrate was also detected only in those three samples of craft beers. There is evidence to support the hypot

was only detected in craft beers. Giannetti et. al. (2019) [5] have also found that phenethyl acetate (characterised by a rose-like flavour) is more concentrated in industrial beers, which is in good agreement with our findings (table 3). Also higher alcohols play a crucial role in the flavour of beer. Of particular importance is 2-phenylethanol characterised as possessing "rose flavour" [44]. In line with previous studies [5], the highest content of 2-phenylethanol was in the industrial beers (sample H and I), which made them have a better fragrance, taste and rose like aroma.

Giannetti et. al. (2019) [5] noted that industrial beers featured a higher acids content. Our results do not seem to confirm their observation, since carboxylic acids identified, i.e. acetic acid, octanoic acid and decanoic acid were either present at significantly higher levels in the craft beers (P < 0.05) (acetic and octanoic acid – samples A, D, F) or were not detected in the industrial beers whatsoever (decanoic acid) (Table 3). The control of both acetic acid and octanoic acid production during brewing is crucial since at concentrations above their taste thresholds (200 and 5 ppm for Pilsener-style respectively) they impart off-flavour [45–47]. Acetic acid contributes with vinegary odour, whereas octanoic acid with rancid notes [47]. The level of carboxylic acids in beer is mostly contingent on the yeast strain, however, it was also shown that beers obtained with a low level of wort saturation with oxygen were characterised by exceeding contents of octanoic acid and consequently by rancid flavours [46]. Beer volatiles from the group of carbonyl compounds are ketones and aldehydes. According to the literature, some specific compounds such as furfural or 2,3-butanedione (diacetyl) may be considered important markers of beer flavour deterioration [11,17]. Furfural is formed during beer ageing by Maillard reaction [11,17]. It was found that the industrial beers did not contain furfural, whereas 3 out of 6 craft beers contained that substance (sample A, C, F). On the other hand, 2,3-butanedione was not detected in any sample of the beer analysed in the study. One of the main purposes of the study was to investigate whether the manufacturing scale affect dimethyl sulphide (DMS) content in the finished product. DMS was the only sulphur compound detected in the beers. Through the evaluation of average concentration, expressed in µg/l, of dimethyl sulphide, it is clear that the craft beers are characterised by a significantly higher content of DMS than industrial beers (P < 0.05) (Table 1 and 3, Figure 2f). DMS was not detected in 4 out of 6 industrial beers, whereas the volatile compounds profile of all the craft beers included the presence of DMS. Additionally, in the case of the samples C (136.3  $\mu$ g/l) and D (137.5  $\mu$ g/l) the concentrations of DMS exceeded the limit values (100  $\mu$ g/l) established for lager beer [20,21]. Therefore, it may be assumed that DMS adversely affect the aroma of the beers C and D and may lead to undesirable flavour impressions, while drinking them by consumers. DMS concentration in beer is dependent on the wort boiling technology (vigour of the boil) as well as on the wort aeration level prior to fermentation.

#### Table 4. Comparison of obtained LRI values with literature data.

Compound	RT average	LRI calc	LRI <sub>lit</sub>	Literature
Acetaldehyde	4.73			
Ethanol	5.41			
Acetone	5.80			
2-propanol	5.89			
2-Nitroethanol	5.90			
Ethyl formate	6.11			
DMS	6.21			
1-propanol	6.77			
Acetic acid	7.24			
Ethyl acetate	7.77			
Isobutanol	8.05			
1-butanol	8.79			
3-Methyl-2-butanone	8.78			
Methyl isobutyrate	9.27			
Ethyl propionate	9.79	710	696	[25]
Propyl acetate	9.85	713		
1-Butanol. 3-methyl-	10.32	735	718, 747	[25,26]
1-Butanol. 2-methyl-	10.41	739	728, 744, 744	[25,27,28]
2-Pentanone. 4-methyl-	10.49	743		
Ethyl isobutyrate	10.82	759	756	[27]
Isobutyl acetate	11.14	774	776	[27]
Methyl isovalerate	11.23	778		
2.3-Butanediol	11.28	780	796	[25]
Ethyl butanoate	11.70	800	806, 800	[25,27]
Furfural	12.61	842	829, 845	[27,29]
Butanoic acid. 2-methyl ethyl ester	12.78	850	846	[27]
Butanoic acid. 3-methyl ethyl ester	12.83	852	854	[27]
1-Hexanol	13.17	868	880, 880	[25,27]
Isoamyl acetate	13.33	876	876, 871	[27,29]
2-Methylbutyl acetate	13.39	878	877, 873	[19,29]
Isobutyl isobutyrate	14.17	914		
Amyl propionate	15.43	970		
β-Myrcene	16.00	996	988, 991	[19,29]
Ethyl caproate	16.01	997	996, 1000, 996, 1000, 1003	[25–29]
Butyl 2-methylbutyrate	16.18	1004		
1-Hexyl acetate	16.31	1010	1006	[25]
Isobutyric acid. isopentyl ester	16.35	1012	1014	[29]
2-Methylbutyl isobutyrate	16.45	1017		
Hexanoic acid. 4-methylene methyl ester	16.77	1031		
Ethyl heptanoate	18.19	1096	1095, 1097, 1097, 1101	[25,27–29]
2-Nonanol	18.32	1102	1107, 1098, 1102, 1103	[25,27–29]
Linalool	18.44	1108		
2-Phenylethanol	19.10	1138	1119, 1135, 1118, 1112, 1113	[25–29]
octanoic acid (Caprylic acid)	19.48	1156	1169, 1179, 1192, 1180	[26–29]
Ethyl caprylate	20.34	1196	1196, 1193, 1198, 1198, 1202	[25–29]
2-Decanol	20.49	1203	1211	[29]
α-Terpineol	20.84	1220	1195	[25]
5-Hydroxymethylfurfural	21.21	1238		
Linalyl iso-valerate	21.75	1264		
Phenethyl acetate	22.02	1277	1260, 1260, 1255, 1257	[25,27–29]
Ethyl pelargonate	22.41	1296	1295, 1297, 1296, 1297	[25,27–29]
2-Undecanol	22.60	1305	1309	[25]
Methyl geranate	23.17	1334	1320	[29]
Capric acid (Decanoic acid)	23.61	1356	1387, 1382, 1373, 1366	[25–28]
4-Decenoic acid. ethyl ester. (Z)-	24.16	1384		
	-			1
Ethyl caprate	24.39	1396	1396, 1391, 1398, 1395, 1398	[25–29]

# Impact

The results might have significant implications for improving the chemical-technical quality control system in a craft brewery whereby it would be possible to provide an average consumer with a somewhat more standardised final product in terms of beer flavour and physicochemical attributes.

The Introduction of gas chromatography techniques in a brewery for the purpose of controlling the quality of wort and beer might have a positive impact on the efficiency of the overall brewing process, owing to easier evaluation and quicker identification of the reasons for obtaining an undesirable beer volatile profile and subsequent modification of brewing technology (regulation and proper setting of specific technological parameters).

# Conclusions

The conducted research has shown that the scale of production significantly affects the profile of volatile compounds and physicochemical parameters of the pale Pilsener-style lager beers. Therefore, it is concluded that there is a clear need to control the quality of Pilsener-style beers available on the market, produced both on an industrial and a craft scale.

Headspace gas chromatography coupled to mass spectrometry (HS/GC-MS) is a powerful and accurate diagnostic tool for determination of beer flavour attributes, including detection of potential off-flavours.

# Conflict of interest

There are no conflicts to declare.

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