PRESENCE OF CARBONYL COMPOUNDS IN BEERS - A BRIEF REVIEW

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Abstract: This work aimed to perform a brief literature review on methodologies for the determination of carbonyl compounds in beer, their interference in the quality of the beverage and their effects on human health. Bibliographic materials were selected from different databases published between 2017 and 2021. About 50 titles were selected, of which 24 were chosen for this review considering their adherence to the topic. Derivatization was the most used treatment for sample preparation and chromatography the most used technique for measuring analytes. The identification of carbonyl compounds shows the relevance of analytical methods for monitoring these compounds in beer and its components.

Keywords: beer; carbonyl compounds; analytical methods; derivatization; chromatography.

PRESENÇA DE COMPOSTOS CARBONÍLICOS EM CERVEJAS - UMA BREVE REVISÃO

Resumo: Este trabalho teve como objetivo realizar uma breve revisão na literatura acerca de metodologias para a determinação de compostos carbonílicos em cerveja, a interferências destes na qualidade da bebida e seus efeitos na saúde humana. Os materiais bibliográficos foram selecionados em diferentes bases de dados publicados entre os anos de 2017 e 2021. Cerca de 50 títulos foram selecionados, dos quais, 24 foram escolhidos para esta revisão considerando a aderência ao tema. A derivatização foi o tratamento mais utilizado no preparo das amostras e a cromatografia, a técnica mais usada na medida dos analitos. A identificação dos compostos carbonílicos mostra a relevância dos métodos de análises para o monitoramento destes compostos na cerveja e em seus componentes.

Palavras-chave: cerveja; compostos carbonílicos; métodos analíticos; derivatização; cromatografia.

1. INTRODUCTION

Beer is an alcoholic beverage produced from the fermentation of cereals, whose main ingredients are, water, barley malt, hops and yeast, and up to 45% of the malt can be replaced by brewers adjuncts. In some types of beers, such as craft beers, ingredients such as: fruits, fruit juices, spices, among others, can be added as long as they do not change the original composition of the drink [1].

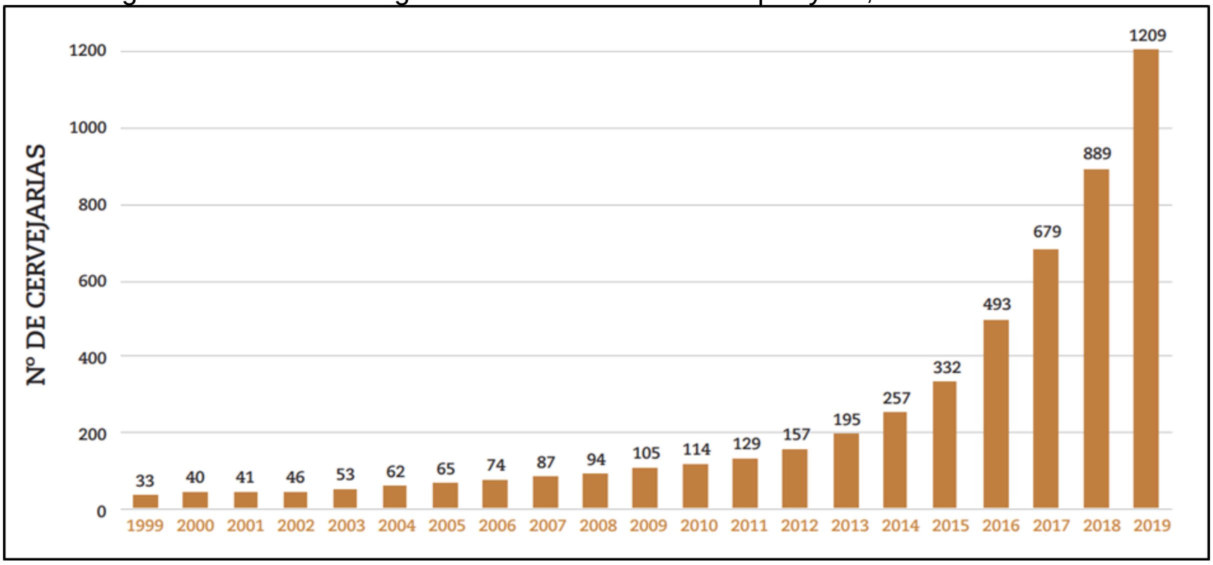
Brazilian legislation defines beer as the "drink resulting from fermentation, from brewer's yeast, malted barley must or malt extract, previously submitted to a cooking process added with hops or hop extract [1].

Beer is one of the most consumed alcoholic beverages in the world [2] and is lso the favorite among Brazilians [3]. 14 billion liters of the beverage are produced annually in Brazil. This production places the country as the third largest producer in the world market, only behind the United States and China, which occupy the second and first position respectively [4].

A growth in the brewing sector has been observed in recent years. According to the Ministry of Agriculture, Livestock and Supply (MAPA), 320 new breweries were registered in 2019. With these numbers, Brazil reached the mark of 1209 establishments distributed throughout the country [5]. The growth of which is related to the increase in the consumption of the drink, which has been occupying an increasing space on the Brazilian table [6].

Figure 1 shows the progress of the sector in terms of registered establishments, from 1999 to 2019.

Figure 1- Number of registration of establishments per year, in Brazil.



Source: [5]

In the search for a better quality product, breweries have been seeking to increasingly improve the quality control of their products and processes. These improvements involve several factors such as the use of methodologies involving more modern equipment and high quality raw material [7].

The composition of beer, as well as its production process, leads to the formation of some chemical compounds that can alter the flavor and stability of the final product. An example is the carbonyl compounds [8]. These compounds significantly contribute to the definition of the sensory properties of beer [9], and when degraded, they can give rise to enviable flavors, compromising the quality of the beverage. In addition, some carbonyl compounds from alcoholic beverages can be carcinogenic, such as formaldehyde and acetaldehyde, whose carcinogenicity has already been duly proven by the International Agency for Research on Cancer-IARC. [10].

In Brazil, beer quality standards are regulated by the Ministry of Agriculture Livestock and Supply (MAPA), through Normative Instruction 65/2019 that establishes the tolerance limits for some substances [1]. However, regarding carbonyl compounds, the brazilian legislation does not mention reference values these compounds individually.

To contribute to the process of improving the quality of beer, as well as monitoring the presence of carbonyl compounds in the beverage, this work aimed to conduct a literature review about methodologies used for the determination of carbonyl compounds in beers, the effects of these compounds in human health and their interference in the properties of the beverage.

2. METHODOLOGY

A search was carried out for scientific articles and other bibliographic materials published between 2017 and 2021 in the databases, Google Academic, Scielo, ScienceDirect and Web of Science. The terms beer; carbonyl compounds; analytical methods; derivatization; chromatography, were used as keywords for the research. After the research, 50 titles, including 4 from previous years, were selected. After reading the abstracts, 24 titles were included in this review, considering their adherence to the topic.

3. LITERATURE REVIEW

Carbonyl compounds are organic species that have in their structure a double bond between carbon and oxygen atoms and are represented by the carnonyl functional group ($R_2C=O$). These compounds can originate from various sources such as: contamination of oil and ethanol, raw materials from the alcohol-chemical and petrochemical industries, extrusion at high temperatures used in the polymer production process, photochemical reactions of hydrocarbons, natural sources (such as forest fires) and human action (such as vehicular emissions) [11].

Some carbonyl species, such as aldehydes, are widely used in textile, pharmaceutical, food and as preservatives in cosmetic industries. In foods, these compounds can be found in vegetables, fruits, dairy products and in a variety of beverages [12]. In beers, carbonyls compounds can be present in several stages of the process, with the alcoholic fermentation stage being the one with the greatest contribution [13].

The presence of carbonyl compounds in beers, in particular aldehydes and ketones, significantly influence the sensory properties of the beverage, especially flavor and smell, which are the result of mixtures of these compounds in different concentrations. [14]. In addition, in the human body, carbonyls can interact with DNA forming some types of compounds that can promote mutations, increasing the risk of cancer in some parts of the body, causing damage to human health [15].

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Formaldehyde and acetaldehyde ingested through alcoholic beverages are examples of carbonyls that are already on the International Agency for Research on Cancer (IARC) list of toxic agents. They are in group 1 (compounds with confirmed carcinogenicity to humans) of the IARC classification list [10].

Another toxic and very common effect caused by the presence of acetaldehyde in the body is veisalgia, known as “hangover”. After drinking alcoholic beverages, such as beer, ethanol can be converted to acetaldehyde and high levels of this compound in the body can cause headache, nausea, drowsiness, fatigue and vomiting. Which are some of the symptoms that indicate a hangover [16].

The identification and quantification of carbonyl compounds in beers and its components, as well as their effects on human health, are some of the factors that have motivated the scientific community to carry out several studies. A toanalysis of carbonyl compounds in beers, however, has been a challenge. Features such as: absence of chromophore properties, volatility and high reactivity make its detection difficult [17].

Another point is that the reference methods adopted in Brazil by the Ministry of Agriculture, Agriculture and Supply (MAPA) only identify total aldehydes [18], which makes it impossible to identify the analytes individually. As an alternative, methodologies involving the use of chromatographic techniques have been developed and applied in the beer analysis process [19].

In the literature, several studies have been carried out showing the analysis of carbonyl compounds in beers and the use of chromatography in the identification and quantification of compounds.

ZHAO et al., (2017) [17], analyzed formaldehyde in beer samples using the technique of liquid chromatography equipped with a diode array detector (HPLC-DAD). The aim of this work was to develop an easy method to analyze the compounds of interest and test the ethoxyamine hydrochloride (EAHC) reagent as a derivatizer. Acetonitrile was used as an extracting solvent. The limit of detection (LOD) and the limit of quantification (LOQ) were defined according to the baseline signal/noise ratio and the values found were 0.016 mg/L and 0.042 mg/L, respectively. The concentrations found in the samples ranged from 0.17 mg/L to 0.62 mg/L of formaldehyde. The authors concluded that the proposed method had moderate reaction conditions and lower detection limit when compared to the derivatization method using 2,4-dinitrophenylhydrazine (2,4-DNPH).

LIU et al., (2018) [20], analyzed acetaldehyde in beers with the aim of establishing an effective method by GC-HS. As a solvent, ethanol was used. The limit of detection was 0.05 mg/L. The acetaldehyde values found ranged from 1.42 to 8.16 mg/L. According to the authors, the results obtained showed that the proposed method provides an apt tool for improving the quality of beer flavor in the brewing industry.

DITRYCH et al., (2020) [21], analyzed 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, hexanal, furfural, phenylacetaldehyde, metional and *trans*-2-onenal in brewer's wort sample. The work aimed to understand the importance of fermentation in the instability of beer flavor. The technique used for analysing the carbonyl compounds was gas chromatography coupled to mass spectrometry (CG-MS). Limits of detection ranged from (0.1 to 5.6 µg/L), and from (0.1 to 16.9 µg/L) for the limit of quantification. The concentrations found were: 2-methylpropanal (33.4 to 471.2 µg/L); 2-methylbutanal (6.9 to 343.0 µg/L) ; 3-methylbutanal (65.0 to 865.8 µg/L); hexanal (7.7 to 71.3 µg/L); furfural (208.5 to 414.6 µg/L); phenylacetaldehyde (117.2 to 234.2 µg/L); metric (83.5 to 159.1 µg/L); and *trans*-2-onenal (T2N) (0.4 to 4.6 µg/L).

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HERNANDES et al.,(2019) [22], analyzed acetaldehyde, acrolein, formaldehyde and furfural, with the aim of developing and validating a method to simultaneously evaluate these compounds in beer samples. The technique used was gas chromatography coupled to a mass spectrometer (GC-MS-SIM). The 2,2,2-Trifluoroethylhydrazine (TFEH) reagent was used as a derivatizer. The values found for the limits of detection (LOD) and limit of quantification (LOQ) were: acetaldehyde (0.03 and 1.0 µg/L), acrolein (0.3 and 2.5 µg/L), formaldehyde (0.3 and 1.0 µg/L), furfural (0.1 and 1.0 µg/L), respectively. The concentrations found for the compounds analyzed were: acetaldehyde (1.3 to 1.63 µg/L), acrolein (2.6 to 5.4 µg/L), formaldehyde (2.6 to 385 µg/L), furfural (1.15 to 4264.3 µg/L).

The studies presented showed the effectiveness of chromatographic techniques for the identification and quantification of carbonyl compounds in beer and its components. In addition to being effective, these techniques have versatility, sensitivity and selectivity suitable for this type of analysis. Table 1 contains some information on methods and treatments already applied

Table 1 - Methods used for the determination of carbon compounds in beer samples

Carbonyl compounds	Sample preparation	Analysis	LOD	LOQ	Concentration range	Ref.
Acetaldehyde	Ethoxyamine hydrochloride (EAHC).	HPLC-DAD	0,016 mg/L	0,042 µg/L	0,17 a 0,62 mg/L	[17]
Furfural	2,4-DNPH	HPLC-DAD	91 µg/L	-	205 a 687 µg/L	[23]
Acetaldehyde Acrolein, Formaldehyde Furfural	2,2,2-trifluoroethylhydrazine (TFEH)	GC/MS-SIM	0,03 µg/L 0,3 µg/L 0,3 µg/L 0,1 µg/L	1,0 µg/L 2,5 µg/L 1,0 µg/L 1,0 µg/L	(1,3 a 1,63) µg/L (0,3 e 2,5) µg/L (0,3 e 1,0) µg/L (0,1 e 1,0) µg/	[22]
Formaldehyde	2,4-DNPH	HPLC-UV	0,6 ng/L	-	(172 a 388) ng/L	[24]

4. FINAL CONSIDERATIONS

Through the review, it was possible to observe that beer is considered one of the most consumed alcoholic beverages in the world and the favorite among Brazilians.

Some carbonyl compounds have carcinogenic characteristics proven by the IARC, which makes it important to monitor these compounds in the beverage.

Derivatization with 2,4-DNPH, EAHE and TFEH reagents are still the most used and chromatography the most used technique.

The toxic effects caused by the presence of carbonyl compounds in beer, as well as their influence on the sensory properties of beer, point to the need to monitor these compounds in the beverage, contributing to improve the quality of the beverage.

The development of innovative methodologies can positively contribute to the simultaneous analysis of different carbonyl compounds in beer and its components.

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