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Review

Recent trends in the determination of biogenic amines in fermented beverages – A review

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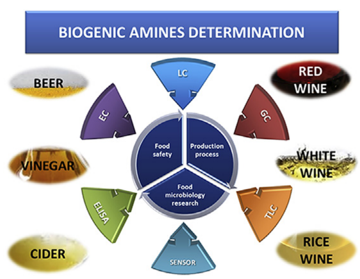
HIGHLIGHTS

- A critical review on analytical methods for BA in fermented beverages is presented.
- Recent sample treatments and analytical techniques are described and discussed.
- A previous derivatization is needed in most liquid chromatographic methods.
- BA determination is related to food safety, production process or microbiology research.

GRAPHICAL ABSTRACT



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ABSTRACT

Biogenic amines (BA) are generally considered as a food hazard, even though there is not a threshold for these biomolecules in the European legislation, except for histamine in fishery products. These compounds are formed during the storage and processing of certain foods through microbiological activity, and when present in high concentrations, could have toxicological effects, causing health problems in consumers, especially to sensitive persons. This fact, in addition to the economical concern involved, makes it necessary to control the amounts of biogenic amines in foods. For all these reasons, literature on biogenic amines in different food products, especially in fermented beverages, is extensive. This review provides an overview of the most recent trends in the determination of biogenic amines in fermented beverages focusing on novelty, improvement and optimization of analytical methods. Hence, the different sample treatment procedures (including derivatization), the most important analytical techniques and the most frequent applications are described and discussed. Although biogenic amines have been determined in wine and other fermented beverages for decades, new advancements and technical possibilities have allowed to increase the accuracy and sensitivity of analytical methods, in order to overcome the challenges posed by the complex matrices and their high intrinsic variability. Thus, the different purposes of BA determination (food safety, production process or food microbiology research) and the most widely employed analytical techniques have been reviewed.

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1. Introduction

The control of biogenic amines in foods is gaining importance in order to monitor production processes or to know their quality and freshness, but mainly to monitor food safety [1,2]. Thus, the number of analyses of these compounds has increased during the last years. They are mainly synthetized in foods and beverages by decarboxylation of amino acids, although some amines can be formed by amination and transamination of aldehydes and ketones [3].

The concentrations (mg kg^{-1} or L^{-1}) of the main BA in a wide range of products are summarized in Table 1. In general, the highest concentrations of these compounds have been found in fermented products, which show a significantly higher amount than non-fermented foods. Thus, histamine reached high levels in sufu, fish sauce, sausages and ripened cheeses (Table 1). Specially, a concentration of histamine of 10000 mg kg^{-1} was detected in spoiled fish [1]. Tyramine has been detected in high amounts in cheese samples, mainly in ripened cheese (Table 1). This could have an effect on health, due to its capacity to potentiate sympathetic cardiovascular activity by releasing noradrenaline, which is named 'cheese reaction' [53]. Regarding putrescine and cadaverine, they have been detected in significant concentrations in fermented meat and fish (Table 1). BA presence in foods is closely related to microbial activity. Thus, lactic acid bacteria are the main producers, although some species of yeast or bacteria of the family *Enterobacteriaceae* could synthetize them [54].

BA can produce a wide range of toxicological effects [1] being histamine and tyramine the main BA, regarding their toxic effect. Histamine is the most widely studied amine due to its ability to produce headaches, hypotension and digestive problems, while tyramine is often associated with migraine and hypertension [54]. Recently, Linares et al. [55] proved that tyramine was more cytotoxic than histamine on an *in vitro* model of the human intestinal epithelium. Thus, they observed that tyramine caused a cell necrosis, whilst histamine induced apoptosis. On the other hand, other polyamines such as putrescine and cadaverine have a lower pharmacological activity; however, they could interact with the amine oxidases and potentiate the effects of histamine and tyramine. Besides, these polyamines can react with nitrite to form carcinogenic nitrosamines [56].

Although BA have been described as having a certain potential toxicity, the maximum histamine level is only regulated in fishery products, at 50 mg kg^{-1} by the US Food and Drug Administration (FDA), and at 100 mg kg^{-1} by the European Community [57].

However, the European Food Safety Authority (EFSA) has released a scientific opinion where it remarks the risks associated with the increase of BA in fermented products [1]. This document concluded by stating the importance of controlling these compounds in food, as well as validating analytical methods for different types of matrices. On the other hand, some countries in Europe recommended establishing limits for histamine in wine [Germany (2 mg L^{-1}), Belgium (5–6 mg L^{-1}), and France (8 mg L^{-1})] [58,59]. Switzerland also established a legal threshold of 10 mg L^{-1} for histamine, which was rejected afterwards [41]. In this context, the International Organization of Vine and Wine (OIV) published, in the Compendium of International Methods of Analysis of Wines and Musts, two chromatographic methods to determine BA in order to standardize methods of analysis, thus helping to facilitate international trade [60]. Regarding beer, the *Nutritional codex* of the *Slovak Republic* recommended a maximum tolerable limit for histamine of 20 mg kg^{-1} [61].

According to Scopus database, a significant number of papers dealing with BA determination in food have been published since 2010. Thus, there are 1037 articles related to agricultural and microbiology areas. As shown in Fig. 1, the main food items analyzed were meat, fish, cheese and wine. Taking the fermented beverages and condiments as a group (wine, beer and vinegar), and together with fruit juices, they accounted for a 22% of the total research articles published in the aforementioned period.

Specifically, fermented beverages are constituted by a complex matrix that increases the difficulty of analyses and interferes with the results. The complexity of the varied food matrices is a critical aspect to be taken into account when obtaining adequate recoveries for all BA [1]. Regarding analytical determination, an array of methods such as high performance liquid chromatography (LC), ultra performance liquid chromatography (UPLC), gas chromatography (GC), thin-layer chromatography (TLC), ion-pair liquid chromatography (IPLC), capillary electrophoresis (CE), sensors and ELISA, among others, have been used for these compounds.

The literature includes some review articles focused on biogenic amines in foods, but none of them considers thoroughly the sample preparation, as well as all the analytical techniques employed for the determination of these compounds in food products – most of them only consider chromatographic methods. On the other hand, despite the number of works regarding biogenic amines in wine, beer and other beverages, there is currently no review article which compares and discusses the analytical methods for determining biogenic amines in these matrices.

For all the above, this review provides an overview of the most recent trends in the determination of BA in wine, beer, cider, fermented beverages and condiments, focusing on novelty, improvement and optimization of analytical methods from 2010 to present. Hence, the different sample treatment procedures (including derivatization), the most important innovations and improvements in the analytical techniques and the most frequent applications are