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Importance of Quantitative Analysis of Toxic Biogenic Amines in Food Matrices

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Biogenic amines (BAs) are basic low molecular weight nitrogenous compounds. According to their chemical structure, these compounds can be distinguished into aliphatic (putrescine, cadaverine, spermine and spermidine), aromatic (tyramine and 2-phenylethylamine), and heterocyclic (histamine and tryptamine) variants (Figure 1). Another way to classify BAs is related to the number of amino groups in their molecular structure: monoamines, diamines and polyamines.

BAs are present in a wide variety of food products, such as fish, cheese, meat as well as alcoholic beverages. At low concentrations, BAs may be of endogenous origin, while high concentrations are typically present as a result of food decomposition.

BAs are mostly formed by microbial decarboxylation of free amino acids during fermentation, storage or in food spoilage. For example, BAs can be generated in cheese by the action of a broad variety of microorganisms, including *Bacillus*, *Clostridium*, *Hafnia*, *Klebsiella*, *Morganella* morganii, Proteus, *Lactobacillus* buchneri and *Lactobacillus* delbrueckii. Instead, Enterobacteriaceae and Enterococcus typically grow up in fish, meat and their products [1], to cite but a few.

When present at low concentrations, BAs are essential for many human and animal physiological functions but they can cause toxicological effects to human health when large amounts are ingested.

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histamine for the same catabolic enzymes, thus ultimately inhibiting the efficacy of the histamine detoxification process and leading to the accumulation of toxic compounds in plasma [3].

Recent studies have demonstrated a synergistic action of ethanol and BAs. Ethanol is able to inhibit some intestinal enzymes such as monoamine oxidases that are involved in the detoxification of BAs. Moreover, alcohol and acetaldehyde can increase the permeability of the intestinal wall leading to increased toxic effects promoted by BAs [2]. This is primarily important for wine consumers that are sensitive to these compounds [4-5].

As mentioned above, the study of BAs is gaining growing interest mainly for their relation to food hygiene. Accordingly, the amount of



Some of the most common aromatic amines (that is, tyramine, tryptamine, and 2-phenylethylamine, Figure 1) display vasoconstrictor action while others (such as histamine, Figure 1) induce a vasodilator effect. Tyramine and 2-phenylethylamine seem to be involved in the hypertensive crisis and are recognised to be responsible for the dietary-induced migraine [1]. Aliphatic BAs have shown no adverse health effect, but they can react with nitrites (usually added as preservatives in meat) to form nitrosamines which are known to have, *inter alia*, carcinogenic, teratogenic and mutagenic activity [1-3]. Putrescine and cadaverine (Figure 1) are able to compete with

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BAs is an important parameter of degree of freshness and quality of food preservation, therefore it can be considered as a marker of the level of its microbiological contamination [6].

Human health implications of BAs have stimulated governments and related regulatory agencies to establish legal limits and recommendations for these compounds in specific food products [3]. For these reasons, it is important to avail of analytical techniques and methods suited for accurate monitoring BAs levels in food matrices. In this framework, chromatographic techniques revealed the most appropriate means to fulfil the scope. Gas-chromatography (GC)based methods are especially useful for the determination of BAs in alcoholic beverages such as beer [7,8] and wine [9]. However, capillary electrophoretic (CE) [10] and high-performance liquid chromatography (HPLC) methods are usually preferred for the analysis of food matrices after either pre-column or post-column derivatization procedures. Indeed, detection of amines is rather difficult as a result of their weak absorbance in the UV region. Therefore, many methods based on derivatization of free amines with detectable label groups have been developed so far. Different chemical reagents for pre-column derivatization, including o-phthalaldehyde (OPA) [11], benzoyl chloride [12], dansyl chloride [4,13], dabsyl chloride [5,14], and fluorenylmethyl chloroformate (FMOC) [15] have been proposed over the years by several authors. For postcolumn derivatizations, chemical reagents as ninhydrin [16,17] and OPA [18] are usually employed.

Over the last decade, liquid chromatography coupled with mass spectrometry (LC-MS) is gaining increasing importance in this field due to its high specificity and sensitivity. Ultra-performance liquid chromatography with quadrupole time-of-flight mass spectrometry (UPLC/Q-TOFMS) clearly demonstrated to be an excellent platform for the analysis of BAs in food samples [19].

The ever-increasing awareness of the intimate connection between food quality and human health continuously leads scientists to face stimulating research challenges aimed at gaining further insight into this matter. In this scenario, the advancement in technologies will undoubtedly multiply the quality and quantity of analytical information.

Competing Interests

The Authors declare no conflict of interest with regard to this manuscript.

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