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Review

Recent analytical approaches to the analysis of biogenic amines in food samples

F. Bedia Erim *

Istanbul Technical University, Department of Chemistry, Maslak, Istanbul, Turkey

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ABSTRACT

Biogenic amines (BAs) are formed in certain food products during storage and processing, causing serious health problems, especially to sensitive persons. This review provides an overview on the studies published between 2011 and 2012, focusing on novelty, improvement, and optimization of analytical methods for the determination of BAs and on their applications to the important groups of food products.

Contents

1. Introduction

Biogenic amines (BAs) are small molecular compounds that form in certain food compounds and that are detrimental to human health. These compounds form under unhygienic conditions, by the decarboxylation of food amino acids (AAs) by microorganisms. Histamine, putrescine, cadaverine, tyramine, tryptamine, β-phenylethylamine, spermine, and spermidine are accepted to be the most important BAs occurring in foods [1]. Since the formation of BAs is used as an indication of food spoilage, the determination of their amounts in various foods is an important food-control activity.

Analyses of BAs are also the subjects of numerous scientific articles. In the past two years, several hundred Science Citation Index (SCI) journal articles have directly dealt with BA analysis in foods. Fig. 1 shows the distribution of food products in articles published in 2011 and 2012. As seen in Fig. 1, fish products head the list of foods most studied from the point of view of BAs. Scombroid poisoning is a type of fish poisoning caused by eating spoiled fish. Since most fish species are rich in free histidine, scombroid poisoning is accepted as mainly caused by elevated histamine levels in fish, generated by bacterial enzymatic conversion of free histidine [2]. The presence of other amines has been found to enhance histamine toxicity [1,3]. Currently, histamine is the only BA having official limits in fish products. Histamine is regulated as 50 mg/kg by the US Food and Drug Administration [4] and as 100 mg/kg by the European Community [5]. Since fish is a food product that readily spoils, the consumer is inclined to judge the freshness of the fish to be purchased visually and to be mindful of the hygienic and refrigeration conditions of the establishment selling the fish. Accordingly, BA-analysis studies have concentrated on processed fish products rather than fresh fish. In processed fish products, in the waiting duration and conditions before processing, any unhy-

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* Tel.: +90 212 2853151.
E-mail address: erim@itu.edu.tr

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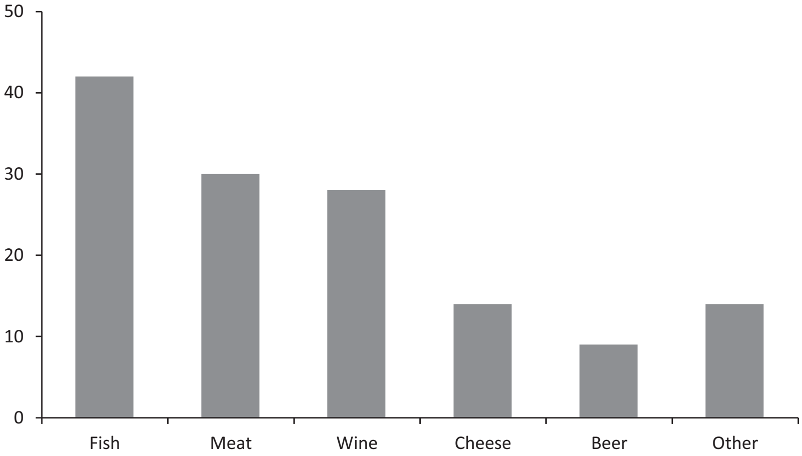

Fig. 1. Distribution of food products in articles published concerning biogenic amine analysis in 2011 and 2012.

gienic condition during fermentation may cause substantial BA accumulation in these products. The belief that microbiological spoilage cannot occur in salted products is incorrect, since BA accumulation can occur before salting. Moreover, if sea or rock salt contains nitrate and nitrite as impurities, BAs in salted fish products may react with nitrites to form potentially carcinogenic nitrosamines [1,3].

BAs are also present in meat and meat products, and are considered markers of freshness and hygiene during storage. Tyramine, cadaverine, putrescine, and histamine are the most common BAs in meat and meat products. The concentration of histamine is usually quantitatively lower than that found in fish [6]. Therefore, histamine poisoning is less common for meat products. However, the potential for forming carcinogenic nitrosamines in some meat products with high BA levels and added nitrates and nitrites as preservatives is particularly important [6]. Thus, in the past two years, the emphasis in BA studies of meat products has been on processed meat products, such as sausage products from different types of meat from different regions.

BAs have also been detected in wines of all kinds. BA formation is considered an indicator of lack of hygiene during the winemaking process. Red wines generally contain larger amounts of BAs than white wines, due to the difference of the vinification processes [7]. The formation of BAs in wines is of concern not only from the point of view of health, but also from the point of view of the taste of the wines. The formation of BAs causes a taste in the wine that is disliked by the consumers. Thus, the reduction of BA amounts is an important challenge for the wine producers.

Other food products that are the subjects of BA studies include cheeses, beers, various beverages, and traditional sauces.

When we generally consider studies of BAs in foods, we note different purposes:

(1) developing new analysis methods or improving the current methods for BA analyses;
(2) reporting the BA contents of products from different countries and regions, using known methods;
(3) using BA analyses to control the effectiveness of methods developed in food preparation, storage, and packaging in order to reduce BA production; and,
(4) dealing with the connection between the contents of BAs and BA-producing microorganisms.

The analysis, with rapid, trustworthy methods, of the BA contents in foods is important from the points of view of human health and food quality. The current review aims to cover reports on BA analyses in 2011 and 2012. The review focuses on analytical methods. Included in this review are studies that report newly developed analytical methods, improvements in current methods, and applications of current methods to a large number of products, along with method validation. The aim of this review is to note the difficulties and recent progress in BA analyses.

In 2011 and 2012, a significant number of reviews were published on the BA contents of food products. BAs were reviewed in fish, fish products, and shellfish by Prester [8], and in dairy products by Linares et al. [9]. BAs in wines were reviewed by two groups: Hernández-Cassou and Saurina [10] and Peña-Gallego et al. [7]. Biosensors for BAs were reviewed by Kivirand and Rinken [11]. Chromatographic methods for BAs, together with methylxanthines and water-soluble vitamins, were reviewed by Płonka [12]. The review article published by Gomez et al. on the analytical characterization of wine by capillary electrophoresis (CE) covered BAs [13]. The Cifuentes group included BAs in their last biannual review of articles on recent advances in the application of capillary electromigration methods to food analysis [14].

2. Biogenic amine analysis in food samples

The quantification of BAs in food samples has mainly been performed by chromatographic techniques, such as LC, GC and TLC, CE techniques, and sensors developed for BA analysis. The chromatographic and electrophoretic methods reviewed in this study are shown in Table 1. BA analyses using sensors are shown in Table 2.

2.1. Chromatographic and electrophoretic methods

Classical reversed-phase HPLC has been the most generally used technique for the determination of BAs in different kinds of food. Very similar procedures for the extraction of BAs from the food matrix were employed before HPLC analysis. Solid samples are extracted with acidic solvents, such as trichloroacetic acid (TCA), perchloric acid or hydrochloric acid. Acid treatment also deproteinizes extracts. Wine samples are used directly or after a simple polyvinylpolypyrolidone (PVPP) treatment and then filtration in order to remove phenolic components.

Pre-column or post-column derivatization of BAs is often needed in order to increase the sensitivity of UV and fluorescence detection. Moreover, since BAs are polar molecules, derivatization reduces their polarity and improves resolution in reversed-phase

Table 1
Biogenic amine analyses by LC/TLC/GC and capillary electrophoresis

Sample	Analytes	Sample treatment	Derivatization Reagent	Separation Method	Detection	LOD and LOQ	Ref.
Wine	His, Tyr, Spr, Spm, Put, Cad, Phe	PVPP pretreatment	Dns-Cl	HPLC, C18 column (150 × 4.6 mm, 5 μm) A: water, B: acetonitrile	UV-254 nm	LOD:0.09–0.3 mg L^{-1} LOQ:0.3–1 mg L^{-1}	[15]
Wine	His, Tyr, Spr, Spm, Put, Cad, Phe	PVPP pretreatment	Dns-Cl	HPLC, C18 column (150 × 4.6 mm, 5 μm) A: methanol, B: water	Fluorescence λex/ λem = 330/ 520 nm	LOD: 0.001–0.09 mg L^{-1} LOQ: 0.003–0.3 mg L^{-1}	[16]
Fish and fish products	His, Try, Put, Phe, Cad, Tyr, Spr, Spm	5% TCA	Dns-Cl	HPLC, C18 column (250 × 4.6 mm, 5 μm) A: Ammonium acetate, B: Acetonitrile, C: Distilled water	Fluorescence λex/ λem = 350/ 520 nm	LOD:0.02–0.24 mg kg^{-1}	[17]
Fish products	Try, Phe, Put, Cad, His, Tyr, Spr, Spm	0.4 M perchloric acid	Dns-Cl	HPLC,C18 column, (250 × 4.6 mm,3.5 μm) A: Ammonium acetate, B: Acetonitrile	UV 254 nm	LOD: 0.567-1.80 mg kg^{-1} LOQ:1.71-5.46 mg kg^{-1}	[18]
Orange juice	Try, Phe, Put, His, Tyr, Spr	μ-SPE with hydrazone based ligands after dansylation	Dns-Cl	HPLC, C18 column, (250 × 4.6 mm) A: acetonitrile:water (70:30)	UV 254 nm	LOD: 3.82–31.3 ng L^{-1} LOQ: 12.7–104 ng L^{-1}	[19]
Wine, Yellow wine	Try, Phe, Put, Cad, Tyr, Spm	Extraction with ionic liquids after dansylation	Dns-Cl	HPLC, C18 column, (250 × 4.6 mm, 5 μm) A:acetonitrile:water (gradient)	UV 254 nm	LOD: 1–2 μg L^{-1}	[20]
Fish and fish products	Agm, Phe, Cad, His, Put, Spr, Spm, Tyr, Try	0.4 M HClO$_4$	Dns-Cl	HPLC, C18 column, (50 × 4.6 mm, 1.8 μm) A: ammonium acetate, B: acetonitrile	UV 254 nm	LOD: 0.2–1.2 mg kg^{-1} LOQ: 0.4-2.4 mg kg^{-1}	[21]
Bokbunja wines	Try, Put, Cad, His, Phe, Spr, Tyr	SPE clean-up after dansylation	Dns-Cl	UPLC, BEH C18 column, 2.1 × 50 mm, 1.7 μm A: 0.1% formic acid in water, B:0.1% formic acid in acetonitrile	Q-TOFMS	LOD:3–15 ng mL^{-1} LOQ: 20 ng mL^{-1}	[22]
Beer, cheese, sausage	Try, Put, Cad, His, Phe, Tyr, Spr Together with 23 amino acids	0.1 M HCl	Dns-Cl	UPLC, BEH C18 column, (2.1 × 100 mm, 1.7 μm) A: 0.1% formic acid in water, B: 0.1% formic acid in acetonitrile	Q-TOFMS	LOD:0.005–0.02 μg/mL LOQ: 0.02–0.05 μg/mL	[23]
Fish	Agm, Phe, Cad, His, Put, Spr, Spm, Tyr, Try	75 g L^{-1} TCA	OPA post - column	HPLC, C18 column, (100 × 3 mm, 3 μm) A: sodium acetate, octane sulfonate (pH 4.5), B: sodium acetate, octane sulfonate (pH.4.5), acetonitrile	Fluorescence λex/ λem = 354/ 430 nm	LOD: 0.2–1.2 mg kg^{-1} LOQ: 0.4–2.4 mg kg^{-1}	[21]
Wine	His, Tyr, Cad, Try, Put, methylamine, ethylamine, ethanolamine Together with 17 amino acids	–	OPA	HPLC, C 18 column, (3,9 × 150 mm) A: phosphate buffer solution (pH 7.3), methanol, tetrahydrofuran B: phosphate buffer (pH 7.3), methanol	Fluorescence λex/ λem = 340/ 425 nm	LOD: 0.05–0.35 mg L^{-1} LOQ:0.17–1.18 mg L^{-1}	[24]
Fermented meat samples	Try, Phe, Put, Cad, His, Ser, Tyr, Spm, Spr	0.4 M HClO$_4$ SPE purification after derivatization	Dbs-Cl	HPLC, C18 column, (100 × 3 mm) A: methanol: acetonitrile: water, B:methanol:acetonitrile	UV 450 nm	LOD:0.1–0.96 mg kg^{-1} LOQ:0.32–3.21 mg kg^{-1}	[25]
Wine	Put, Cad, Phe, His, Tyr	–	Benzoyl chloride	HPLC, C18 column, (250 × 4.6 mm, 5 μm) A:water, B:acetonitrile	UV 254 nm	LOD: 0.045–0.057 mg L^{-1} LOQ: 0.15–0.19 mg L^{-1}	[26]
Salami, cheese, wine, canned tuna, sauerkraut, cheese	Phe, Trp, His, Put, Spr, Spm, Cad, Tyr, β-alanine, and 5 amine compounds	10% TCA	Benzoyl chloride	HPLC, C18 column, (1.5 × 0.2 cm), 5 μm A: water, B: acetonitrile + 0.1% formic acid	Triple-quadrupole tandem mass	LOQ:0.05 μg kg^{-1}	[27]
Rice wine	His, Try, Phe, Tyr, Put, Cad, Spr, Spm	–	CNBF	HPLC, C18 column, (250 × 4.5 mm), 5 μm A: acetonitrile, B: HAc–NaAc buffer, pH: 6.2	UV 254 nm	LOD: 0.1–2 μM (0.0102–0.405 mg L^{-1})	[28]
Beer	Oct, Tyr, Phe	Ultrasound-assisted micro-extraction with ionic liquids after derivatization	DMQC-OSu	HPLC, C18 column, 150 × 4.6 mm, 5 μm A: methanol–water	Fluorescence λex/ λem = 326/ 412 nm	LOD:0.25–50 ng mL^{-1} LOQ: 0.83–167 ng mL^{-1}	[29]
Milk, yogurt, lake water	His, Tyr, Try, Spm, Phe, Spr, Put, Cad	Deproteiniza-tion with acetonitrile	TMBBSu BODIPY	HPLC,C8 Column, (250 × 4.6 mm, 5 μm) A : THF/methanol, B: H$_3$PO$_4$/Na$_2$HPO$_4$ buffer solution (pH:7.4)	Fluorescence λex/ λem = 490/ 510 nm	LOD: 0.1–0.2 nM (8.82–40.4 ng L^{-1})	[30]

(*continued on next page*)

Table 1 (*continued*)

Sample	Analytes	Sample treatment	Derivatization Reagent	Separation Method	Detection	LOD and LOQ	Ref.
Fish	Put, Cad, His, Phe,Spr, Spm, Tyr, Try	5% TCA, SPE	–	HPLC, C18 column, (250 × 4.0 mm, 5 μm) A: ammonium formate, formic acid, water, pH 3.3, B: methanol	MS/MS	LOD:0.02–0.25 mg kg^{-1} LOQ:0.07–0.75 mg kg^{-1}	[31]
Fish	Put, Cad, His, Tyr, and three volatile amines	0.6 M HClO$_4$	–	UHPLC, BEH C18 column, 100 × 2.1 mm, 1.7 μm A: methanol, B: formic acid solution	MS/MS	LOQ: 25 μg/kg for all, 60 μg kg^{-1} for trimethylamine	[32]
Fish and fish products	Agm, Cad, His, Phe, Put, Try, Tyr, urocanic acid	Matrix solid-phase dispersion CN-silica sorbent/ammonium formate, acetonitrile eluent	–	UHPLC-HILIC, BEH-HILIC column, (150 × 2.1 mm,1.7 μm) A: ammonium formate buffer B:acetonitrile	Orbitrap mass spectrometry	LOD: 0.0237–2.58 ppm LOQ:0.0791–8.61 ppm	[33]
Cheese	His, Spm, Spr, Tyr, Put, Phe	0.1 M HCl, SPE	–	HPLC, RP cation exchange column, 5 μm A: acetonitrile/water , trifluoroacetic acid (0.05%) B:acetonitrile/water, trifluoroacetic acid (0.35%)	Evaporative light scattering detection	LOD: 1.4–3.6 mg L^{-1} LOQ: 3.6–9.3 mg L^{-1}	[34]
Beer, herb tea, dairy beverage, vinegar	Spr , Spm, Phe, Dopamine, Serotonin, Octopamine, His, Agm, Tyr, Try, γ-aminobutyric acid, Put, Cad, β-alanine	–	–	Ion-pair LC, Silica-Phenyl-Hexyl column, (150 × 2 mm, 3 μm) Perfluorocarboxylic acids as ion-pair reagents A: Nonafluoropentanoic acid (NFPA) in water, B: NFPA in methanol	Chemi-luminescent nitrogen detector	LOD: 0.1–0.4 μg mL^{-1}	[35]
Wine	His, Tyr, Put, Cad	PVPP treatment Extraction with iso-hexane after derivatization	Dns-Cl	TLC, silica gel 60 TLC glass plates, without fluorescent indicator Eluent: 4/1 chloroform/triethylamine	Densitometry 312 nm	LOD: 0.6–0.7 mg L^{-1} LOQ: 1–1.2 mg L^{-1}	[36]
Beer	Put, Cad, Tyr, His, Together with 14 amine compounds	Liquid-liquid microextraction simultaneous with derivatization dispersive solvent: acetonitrile, extractive solvent: toluene	Isobutyl chloro-formate	GC, capillary column, (20 m × 0.18 mm, 0.18 μm film thickness) Carrier gas: Helium	MS	LOD: 0.3–2.9 μg L^{-1} LOQ: 1–9.5 μg L^{-1}	[37]
Wine	Tyr, Phe, Try, Cad, Spr, His, Put	–	FITC	Non-ionic micellar electrokinetic chromatography, Silica capillary 58 × 50 cm, 50 μm i.d. Separation electrolyte: Brij 35, borate buffer, pH:9.6	LIF λex/λem = 488/520 nm	LOD: 0.416–1.26 nM (0.0576–0.113 μg L^{-1})	[38]
Beer	Ethanolamine Try, tryptophan	–	–	Microchip capillary electrophoresis, Glass microchannel chips, Effective length: 75 mm 20 mM phosphate buffer (pH 2.5)	Amperometric detection Ruthenium-coated glassy carbon electrodes	LOD: 1.4–6.8 mg L^{-1}	[39]
Wine	His, Phe, Tyr	–	–	CITP-CZE, ITP column 140 mm, 800 μm, CZE column: 160 mm, 300 μmITP: Leading electrolyte: Potassium, pH:6 ; Terminating electrolyte: ε-aminocaproic acid pH:4.3 CZE: Background electrolyte: ε-aminobutyric acid (GABA), HEC; pH:4.1	UV- 280 nm	LOD: 0.33–0.37 mg L^{-1} LOQ: 0.49–0.55 mg L^{-1}	[40]

Biogenic amines: His, Histamine; **Tyr**, Tyramine; **Try**, Tryptamine; **Spr**, Spermidine; **Spm**, Spermine; **Put**, Putrescine; **Cad**, Cadaverine; **Phe**, Phenylethylamine; **Agm**, Agmatine; **Oct**:, Octopamine
Derivatization agents: Dns-Cl, Dansyl chloride; **OPA**, o-phthalaldehyde; **Dbs-Cl**, Dabsyl chloride; **CNBF**, 4-chloro-3,5-dinitrobenzotrifluoride; **DMQC-OSu**, 2,6-dimethyl-4-quinolinecarboxylic acid N-hydroxysuccinimide ester; **TMBBSu**, 1,3,5,7-tetramethyl-8-(N-hydroxysuccinimidyl butyric ester)-difluoroboradiaza-s-indacene; **FITC**, Fluorescein isothiocyanate; **Detectors: MS/MS**, Tandem quadrupole mass spectrometer; **Q-TOFMS**, Quadrupole-time of flight mass spectrometer ; **LIF**, Laser-induced fluorescence
All derivatization processes are pre-column, and post-column processes are indicated.

Table 2
Biogenic amine analysis by sensors

Sample	Analytes	Sample treatment	Analysis Method	LOD and LOQ	Ref.
Meat and Fish	Total biogenic amine content Responses of Cad, Put, Spr, Him, Try, Tym, Phe	Liquor of pork and fish meat was obtained by a special centrifugal separator	Biosensor, amperometric Graphite electrode/Monoamine oxidase(MAO)-Diamine oxidase(DAO)-Putrescine oxidase (PUO)	LOD: 5 μM His (DAO) LOD: 5 μM Put (PUO) LOD: 2 μM Tyr (MAO)	[41]
Wines and beers	Total biogenic amine content	–	Biosensor/amperometric Au screen-printed electrode/ diamine oxidase (DAO), polyazetidine prepolymer	LOD: 0.2 mg L^{-1} as putrescine eq.	[42]
Fish	Histamine (quantitative) The response patterns of Spr, Spm, Try, Cad, Phe, 5 amine compounds	Hexane/ dichloro-methane-ultrasonic	Fluorescence sensor, λex/λem = 350/480 nm Aggregation-induced emission of carboxylic acid modified tetraphenylethenes with biogenic amines	Linear range: 0–100 ppm for His	[43]
Fish	Total biogenic amine content Responses of Tyr, His, Spr, Put, Spr, 1-tetradecylamine, benzylamine	Methanol	Fluorescence sensor, λex/λem = 485/620 nm Microplate wells containing a pyrylium dye The dye shows a visible color change with biogenic amines	LOD: 0.16–0.59 μg/mL	[44]
Fish	Total biogenic amine content Responses of histamine, putrescine, spermidine	Gaseous vapor of the fish is injected into ethanolic solution of Ru(II)–Eu(III) complex	Fluorescence sensor, λex/λem = 365/624 nm Luminometric responses Ru(II)-Eu(III) complex with biogenic amine vapors	LOD: 10–30 ppb	[45]

columns. For this reason, a derivatization step for BAs has been employed in some HPLC-MS/MS applications, even though the mass detector is adequate for the direct detection of underivatized amines.

Amongst several derivatization agents, dansyl chloride is one of the most used. Dansylation and chromatographic conditions were optimized using a central composite design in order to evaluate the BA content in a large number of Chilean young and reserved wines. The dansylated amines were detected by UV [15] and by fluorescence [16]. From the results of two consecutive studies using the same protocol in the same laboratory, an obvious increase can be seen in the sensitivities of BAs when a fluorescence detector is used instead of UV for dansylated amines.

In the following two studies, dansyl derivatization and HPLC separation of BAs were optimized for a large number of fish products. In the first study, the BA contents of 13 species of fish and 49 fish products from southern China were separated by HPLC and detected with a fluorescence detector [17]. In the second study, 65 traditional fish products from Turkey and 11 European countries were analyzed applying dansyl derivatization, HPLC separation and UV detection [18].

In a novel micro-solid-phase extraction (μ-SPE) technique, the synthesized hydrazone ligands are physically trapped in the sol–gel network and used for extraction of the dansyl-derivatized BAs. The technique was applied to the preconcentration of BAs in orange juice, before HPLC determination. High enrichment factors were obtained (94–460 fold), due to the high affinity between the sol–gel sorbent that contained benzophenone 2,4-dinitrophenylhydrazone ligand and the target analytes. The mechanism of extraction was interpreted as due to π–π interactions. Consequently, significantly low limits of detection (LODs) were obtained for BAs using UV detection [19].

Room-temperature ionic liquids (ILs) have been used as novel media for derivatization, extraction and preconcentration of BAs in wines. Dansyl chloride was selected as the derivatizing reagent. The derivatizations of BAs were conducted in a water-IL two-phase system and the dansylated amines were separated by HPLC and detected with UV. The use of IL significantly improved the efficiency of both the derivatization reaction and the preconcentration [20].

An HPLC method with column particles of 1.8 μm in diameter has been modified and compared to classical methods using 5-μm column particles for the separation of dansylated BAs. Both eluent consumption and elution time were reduced considerably using smaller particle sizes in separation columns. Backpressures were below 170 bar and this allowed the use of classical HPLC systems rather than costly ultra-high-pressure liquid chromatography (UHPLC) equipment. This method was applied to analyze BAs in lean canned tuna and fatty frozen herring samples [21].

In all of the above studies, dansyl chloride was used as pre-column derivatization agent. Dansylation gives stable products. However, the derivatization process with this agent is time consuming and needs heating. In the above-mentioned studies, the time for the derivatization process was 45–60 min and the temperature applied 40–60°C [15–17,21]. Exceptionally in one study, 70°C and 10 min were reported as reaction temperature and time, respectively [19]. A novel improvement in dansylation step was observed in the study reported by Jiang et al. [20], who performed dansylation in an IL-water two-phase system at room temperature under ultrasound for 20 min. The IL phase was taken out and injected into the HPLC system for the analysis.

In the following two studies, dansylated BAs were separated by ultra-performance LC (UPLC). The UPLC technique with columns packed with smaller particles and high flow rates provides a significant decrease in the separation time of BAs. An ultra-UPLC/quadrupole-time of flight mass spectrometry (UPLC/Q-TOFMS) method was developed for the detection of BAs in Korean Bokbunja (a perennial shrub belonging to the *Rosaceae* family) wines. An SPE cartridge was used for clean-up and extraction after dansyl-chloride derivatization. Less analysis time than the conventional HPLC methods was needed with UPLC. The analysis of all BAs was achieved within 6 min [22], much less than the 20–60 min separation times in classical HPLC.

A UPLC/Q-TOFMS method was developed for dansylated BAs together with 23 amino acids. Separation of all analytes was performed in 25 min. The developed method was applied to the analysis of AAs and BAs in beer, cheese, and sausage samples [23].

O-phthalaldehyde (OPA) is another well-known derivatization agent for BAs. OPA reacts rapidly with BAs at room temperature and forms a fluorescent product. OPA can be used as both pre-column and post-column derivatization agent due to its short reaction time.

The post-column derivatized BAs by O-phthalaldehyde were separated by HPLC with column particles 3 μm in diameter. Reduced analyses time and eluent consumption were obtained with the modified HPLC method compared to classical methods using 5-μm column particles. In addition, the modified method used 50% less post-column derivatization solution than the classical method. In spite of the smaller sizes of column particles, the maximum pressures remained below 170 bar and a classical HPLC system was used in applying the method to the analysis of lean canned tuna and fatty frozen herring samples [21].

An analytical methodology for the simultaneous determination of free AAs and BAs by RP-HPLC with fluorimetric detection was optimized using a pre-column derivatization by O-phthalaldehyde. Eight BAs and 17 AAs were eluted within 70 min. The optimized method was applied to the simultaneous analysis of BAs and AAs in 14 Spanish Monastrell wines [24].

The commonly applied HPLC method to determine BAs in dry fermented meat after dansylation has been compared with an alternative dabsylation procedure. The derivatization temperature in the dabsylation procedure was raised to 70°C, without any loss of the analytes. Since severe decomposition of dansylated amines was observed at the temperatures higher than 65°C, the use of dabsyl chloride at 70°C resulted in a 25-min reduction in derivatization time in comparison with dansylation at 40°C. Furthermore, the use of irritating ammonia to remove the excess of dansyl chloride was avoided. Dabsyl derivatives were detected at 450 nm and it was claimed that, in that way, interferences from UV-absorbing biological compounds present in the meat extracts were mostly avoided [25].

Derivatization of BAs with benzoyl chloride gives stable reaction products with a short derivatization procedure. The benzoylation method has been used to quantify BAs by HPLC in wine samples. The incubation time for wines and benzoyl chloride was 20 min at room temperature. In this work, the presence of BAs was correlated via chemometric analysis with the type of cultivation of the wine grape (traditional or organic) and their concentration in the different stages of winemaking (must, alcoholic fermentation and malolactic fermentation) [26].

Novel stable-isotope-dilution assays have been developed for the quantization of BAs in several foods (salami, cheese, Italian wine, canned tuna, and sauerkraut) by LC-MS/MS. In this method, isotopically-labeled BAs were added as internal standards to the food suspensions in trichloroacetic acid in order to reduce erroneous results due to extraction and uncertainty in the degree of derivatization. The sample was equilibrated for 30 min and the filtrate was derivatized with benzoyl chloride for 2 h at room temperature before HPLC analysis [27].

The effects of storage temperature and time on biogenic contents in rice wines were investigated using an HPLC method. In this method, 4-chloro-3,5-dinitrobenzotrifluoride was used as derivatization agent and the derivatization process took 30 min at 60°C [28].

IL-based ultrasound-assisted liquid–liquid microextraction (UALLME) has been developed for the BAs before HPLC analysis. A fluorescence probe of 2,6-dimethyl-4-quinolinecarboxylic acid N-hydroxysuccinimide ester was used for the derivatization of BAs. The derivatized amine solution was then extracted with an IL under ultrasound. This study mainly concentrated on the factors affecting extraction efficiency, such as type and volume of IL, pH, ultrasonication time and centrifugation time. The method developed was applied to the determination of three BAs in beer samples. The sensitivity of the UALLME method for BAs was compared with some other extraction techniques applied for BAs, such as micellar, solid phase, liquid phase, and cloud point, and was found more sensitive [29].

A newly synthesized fluorescence dye, 1,3,5,7-tetramethyl-8-(N-hydroxysuccinimidyl butyric ester)-difluoroboradiaza-s-indacene (TMBB-Su) was proposed as derivatization agent before HPLC separation for the trace determination of BAs in milk, yoghurt and lake-water samples. This dye was reported as independent of pH. Due to its strong fluorescence quantum, the LODs obtained for BAs using the proposed method were found significantly lower than those of existing HPLC methods with chemical derivatization [30].

Coupling of HPLC with MS detectors can eliminate the derivatization step and reduce analysis time and chemical consumption. An analysis method for underivatized BAs in fish tissues using SPE followed by LC–MS/MS analysis was developed. The MS/MS method was validated and compared with a method based on the analysis of dansyl derivatives by LC and a fluorescence detector (FD). The analysis results of underivatized BAs with MS/MS showed higher sensitivity and precision than the analysis of dansyl derivatives by FD [31].

An analysis method for the simultaneous determination of BAs and volatile amines in anchovy samples by UHPLC-MS/MS has been developed. The main advantage of the selection of UHPLC was the significantly fast elution time of less than 8.5 min. In the study, the contents of amines in anchovy were monitored at different storage times [32].

Tuna samples were dispersed in a CN-silica sorbent and eluted with a mixture of aqueous ammonium formate buffer and acetonitrile. After the matrix-solid-phase-dispersion process, BAs and urocanic acid in the eluent were separated and detected by ultra-high-performance hydrophilic interaction chromatography and Orbitrap MS detection. The last peak, putrecine, was eluted in 11 min and the total separation time (with equilibration) of 18 min was sufficiently short and comparable to that of classical HPLC columns [33].

A novel detection method for BAs has been proposed. An HPLC method with evaporative light-scattering detection (ELSD), for the separation and determination of BAs, was validated and the results were compared with those obtained through LC–UV determination, based on a pre-column dansyl-chloride-derivatization step. The ELSD response was based on the amount of light scattered by analyte particles created by evaporating a solvent as it passed through a light beam. In this methodology, no chromophores needed to be present in target molecules and no derivatization was required during the analytical process. ELS detectors were reported as more affordable than mass spectrometers having the same advantages. Although the LC-UV method applied in the same study for comparison showed higher sensitivity than the LC–ELSD method, the sensitivity of the LC-ELSD method was still found suitable to quantify BAs in cheese samples [34].

Another detection method has been developed for a direct detection of BAs to eliminate the derivatization step. BAs were separated by an ion-pair LC method using perfluorocarboxylic acids as ion-pair reagents and detected by a chemiluminescent nitrogen detector (CLND). The relative response factors determined by this detector were proportional to the numbers of nitrogen atoms in each compound. The performance of the LC-CLND was compared with HPLC–UV (post-column derivatization with ninhydrin) and HPLC-charged aerosol detector (CAD) methods for 14 BAs in the same study. The HPLC–CLND technique provided narrower peaks and the resolutions were dramatically improved. The samples of beer, dairy beverage, herb tea, and vinegar were analyzed by the proposed LC–CLND method [35].

A TLC/densitometry method has been validated for BAs as an economic alternative to HPLC. The method was based on the dansylation of BAs followed by TLC separation. The TLC method developed was applied to the determination of BAs in wine samples [36].

For analysis of BAs, GC is rare compared to HPLC due to the lack of volatility of BAs. A dispersive liquid-liquid microextraction (DLLME) GC-MS method was developed for the determination of BAs together with other small amine compounds in beers. BAs were derivatized by isobutyl chloroformate. In this study, special attention was paid to optimizing the DLLME procedure, which was performed simultaneously with a derivatization process [37].

CE is the second most reported separation and analysis technique for BAs after HPLC. The main advantages of CE are speed, high separation efficiency, low sample consumption, and inexpensive separation columns. However, UV-detection sensitivities in CE are lower than those of HPLC. Detection sensitivity of BAs in CE can be increased by on-line preconcentration techniques or coupling CE with isotachophoresis (ITP). Recently, a combination of laser-induced fluorescence (LIF) detector with CE separation provided a remarkable improvement in LODs of fluorescently-labeled BAs.

A non-ionic micellar electrokinetic chromatography method coupled to LIF detection has been developed for the quantitative determination of BAs. In this study, a non-ionic surfactant, Brij 35, was used for BA separation instead of the commonly used surfactant, sodium dodecylsulfate (SDS) in CE. The use of Brij 35 in the separation electrolyte enhanced the fluorescent intensity of fluorescein isothiocyanate (FITC)-labeled BAs considerably and shortened their separation time. Separation was completed in less than 10 min. A combination of LIF with CE separations provided remarkably low LODs. The method was applied to the analysis of BAs in wine and pomegranate-molasses samples [38].

The use of a mixed-valent ruthenium oxide/hexacyanoruthenate polymeric film electrochemically deposited onto glassy-carbon electrodes has been proposed for the amperometric detection of BAs and their AA precursors, following their separation by microchip CE. In this study, attention was paid to optimizing the modified working electrode. The electrochemical detector cell was placed at the end of the separation channel of the microchip. The separation method did not allow separation of single amines and AAs, and all assayed aliphatic amines, heterocyclic amines and AAs were coeluted in groups. The method was applied to the determination of the total amount of different classes of these amine compounds in beer samples [39].

Increase in the UV sensitivity of BAs in CE separation has been the aim of on-line coupling of capillary zone electrophoresis (CZE) with capillary isotachophoresis (cITP). In this way, BAs were on-line pre-concentrated in the ITP step and separated and detected in the CZE step. The method was applied to the determination of three selected BAs in wine samples [40].

2.2. Sensors

In recent years, many sensors for BA analysis have been developed as alternatives to the expensive instrumentation of chromatographic methods. Biosensors for BAs comprise various combinations of different enzymes for the bio-recognition of BAs. The most common signal transducers for the construction of biosensors for BAs are electrochemical sensors [11]. However, chemical sensors developed are generally based on the fluorescence response of the interaction between BAs and sensor molecules.

Three enzyme-based biosensors for BAs were developed for meat-spoilage monitoring. The enzymes were separately co-immobilized on graphite electrodes with peroxidase and Os mediator. The modified graphite working electrodes were used for amperometric detection of BAs. With diamine oxidase (DAO), the total BA content was measured. Monoamine oxidase (MAO) was used for the determination of tyramine, tryptamine and phenylethylamine content. Putrescine was selectively detected with putrescine oxidase (PAO). The suitability of the DAO and PAO biosensor methods for monitoring the freshness of fish and pork meat was demonstrated. However, the MAO sensor proved to be less suitable for monitoring the freshness of meat. The method was compared with an HPLC method and the results correlated with total BA content measured by the HPLC method [41].

An amperometric biosensor was based on DAO immobilized using polyazetidine prepolymer on the surface of screen-printed gold electrodes. The sensor developed was applied to the analysis of the total BA contents of wine and beer samples. The results were compared with those obtained by a GC-MS method. The results showed better suitability for wine samples, but the method was less efficient for beer samples [42].

Carboxylic-acid-modified tetraphenylethenes (TPEs) have been synthesized and used as fluorometric sensors for BAs. These active molecules showed no emission in solution, but a mixture of the carboxylic-acid-substituted TPE and BAs displayed a blue emission on aggregation. The chromic responses were utilized to distinguish the amines. The response patterns were systematically classified by using linear discriminant analysis. Based on the state (aggregation)-dependent fluorescence, 10 different amines, including BAs, were qualitatively identified. Histamine content in tuna fish was quantified. The assay showed impressive detection sensitivity to histamine in tuna-fish samples [43].

A chameleon dye (Py-1) has been developed as a sensor for BAs. The dye in a polymeric cocktail was placed to the bottom of the wells of a standard microplate. This sensing microplate enabled a semi-quantitative readout of analyte concentration by eye and fluorescence readout of 96 samples. On reaction with BAs for a 10-min incubation time, the dye shows a significant visible color change from blue over green to red. The close similarity of the linear ranges of all amines suggests determination of the total amount of BAs in real samples. A standard addition method of histamine was used to quantify amines in seafood. Fish samples were extracted with methanol. Proteins were denatured and precipitated in methanol and removed with filtration [44].

A heterobimetallic Ru(II)–Eu(III) complex was synthesized and used as a chemodosimeter for BAs in their vapor form. The naked-eyed luminometric responses of the complex towards different vapors and gaseous were observed. Real-time monitoring of gaseous BAs was applied to real fish samples by studying the spectrofluorimetric responses of the Ru(II)–Eu(III) complex toward different BA concentrations. A linear spectrofluorimetric response was found toward BA concentration in real fish samples. GC/MS studies were also used as a reference for the studies [45].

2.3. Overview of the analytical methods

As seen from Tables 1 and 2, the LOD values of analytical methods for BAs are generally at the level of ppm. The application of liquid extraction or SPE processes before chromatographic analysis decreases the LOD values to ppb levels. ILs seem effective in this respect [20,29]. There were exceptional LOD values at ng/L levels by HPLC analysis in two studies. In one, the synthesized hydrazone-based ligands were trapped in a silica sol–gel matrix and used for micro-SPE of BAs before HPLC analysis [19]. In the other, the use of a newly synthesized difluoroboradiaza-s-indacene (BODIPY)-type fluorophore, 1,3,5,7-tetramethyl-8-(N-hydroxysuccinimidyl butyric ester)-difluoroboradiaza-s-indacene(TMBB-Su), was reported as the derivatization agent for BAs [30].

Significantly low LODs down to 0.06 $\mu g\,L^{-1}$ were reported for CE–laser-induced-fluorescence (CE–LIF) detection. The use of a non-ionic surfactant as the separation medium increased detection sensitivities of BAs in the micellar electrokinetic mode together with LIF detection [38].

A remarkable LOD was reported down to 0.01 $\mu g\,L^{-1}$ with a fluorescence sensor based on the luminometric responses of the Ru(II)–Eu(III) complex with BA vapors [45].

3. Conclusion

This review has reported on the analytical techniques applied to monitoring BAs in different food samples in 2011 and 2012. Classical reversed-phase HPLC seems to be the method applied most to the analysis of BAs in food samples. A derivatization step is needed before the separation process for UV or fluorescence detection of BAs. The innovations in HPLC analysis are to the extraction and derivatization steps rather than the separation process. Novel tools for SPE or liquid-phase extraction have been developed in order to concentrate BAs and to increase their sensitivities. Novel derivatization processes or derivatization agents have been proposed to decrease the derivatization time and to increase derivatization efficiency. The use of UHPLC markedly reduces the elution times of BAs to less than 10 min compared to the 20–60 min separation time of HPLC. The use of MS/MS detectors with HPLC can eliminate the derivatization step. However, derivatization can still be preferred because derivatization also improves the resolutions of polar amines in reversed-phase columns.

CE is a good alternative to HPLC. CE has high separation efficiency and low running costs, and provides the same high-speed separation as UHPLC. A combination of LIF detector with CE separations provides remarkable improvements in the LODs of BAs.

Improper extraction and derivatization due to the complexity of food samples may cause erroneous results, so strict validation of separation methods, especially recovery studies, is necessary to be sure of the accuracy and the precision of the sample-preparation processes.

The development of novel sensors for BA analysis appears to provide alternative methods to separation techniques. The advantages of sensors are their low cost, very short analysis times and the possibility of their use on site. However, they are not selective to all individual amines. Generally, total BA contents are obtained via sensors. Due to the lack of selectivity, they are sensitive to the food matrix and the accuracy of the results should be checked with a reliable method before using a sensor on a new food sample.

Due to the current importance of food BAs in quality control and consumer safety, there is still a challenge to develop new methods for their fast, reliable analysis in samples of different foods in the market.

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