

Current methods and the ones in perspective for the determination of biogenic amines in food

Gıdalarda biyojenik aminlerin belirlenmesindeki mevcut yöntemler ve bakış açıları

Review Article

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ABSTRACT

Biogenic amines are organic compounds, present in living organisms and they can be a responsibility for many essential processes. Naturally, they can be also in fruits and vegetable and all foods that contain free amino acids or proteins. In a high amount they can be produced by microorganism through the enzymatic reaction. Histamine, putrescine, cadaverine, tyramine, tryptamine, β -phenylethylamine, spermine and spermidine are considered to be the most important biogenic amines occurring in foods. Excessive consumption of these amines can inflict health concern and analysis of biogenic amines is important based on their toxicity and their usage as indicators of the degree of freshness or spoilage of food. Several methods exist for isolation, identifying and determination of biogenic amines in food. They are mainly based on chromatographic methods: thin layer chromatography (TLC), gas chromatography (GC), capillary electrophoresis (CE) and high-performance liquid chromatography (HPLC). Due to the low volatility and lack of chromophores of most biogenic amines, UV-spectrometric detection is limited. A new challenge is electrochemical determination of those amines based on oxidative reaction. This review shows different methods which allow quantitative determination of biogenic amines in different food stuffs.

Key Words

Biogenic amines, food stuffs, chromatographic methods, electrochemical methods.

ÖZET

Biyojenik aminler, canlı organizmalarda bulunan organik bileşiklerdir ve birçok temel işlemlerden sorumlu olabilirler. Meyve, sebze ve serbest amino asit veya protein içeren her gıdada doğal olarak bulunabilirler. Enzimatik tepkimeler yoluyla mikroorganizmalar tarafından yüksek miktarlarda üretilebilirler. Histamin, putresin, kadaverin, tiramin, triptamin, β -feniletilamin, spermin ve spermidin, gıdalarda en sık bulunan önemli biyojenik aminler olarak değerlendirilir. Bu aminlerin aşırı kullanımı, sağlık sorununa yol açabilir ve biyojenik aminlerin analizi, toksik etkilerinin ve tazelik veya bozulma derecelerinin bir göstergesi olarak oldukça önemlidir. Gıdalarda biyojenik aminlerin izolasyonu, tanımlanması ve tayini için çeşitli yöntemler mevcuttur. Bu yöntemler temel olarak kromatografik yöntemlerdir: ince tabaka kromatografisi (TLC), gaz kromatografisi (GC), kapiler elektroforez (CE) ve yüksek performans sıvı kromatografisi (HPLC). Birçok biyojenik aminlerin düşük uçuculuğu ve kromofor gruplarının olmaması dolayısıyla, UV-spektrometrik tayinleri sınırlıdır. Bu aminlerin tayini için yeni bir yöntem ise oksidatif tepkimelerinin elektrokimyasal izlenmesidir. Bu derlemede; farklı gıda numunelerinde biyojenik aminlerin kantitatif tayininde kullanılan çeşitli yöntemler gösterilmektedir.

Anahtar Kelimeler

Biyojenik aminler, gıda maddeleri, kromatografik yöntemler, elektrokimyasal yöntemler.

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INTRODUCTION

Biogenic Amines are nitrogenous compounds which are usually formed by decarboxylation of corresponding amino acids (Figure 1). Their structure may be aliphatic (putrescine, cadaverine, sperimine, sperimidine), aromatic (tyramine, -phenyl ethylamine) or heterocyclic (histamine, tryptamine). They are the source of nitrogen and initiate the synthesis of hormones, alkaloids, proteins and nucleic acids [1, 2]. They can also affect various organism processes such as the adjustment of body temperature, lack of nutrient, increase or decrease in blood pressure, etc. Histamine, putrescine, cadaverine, tyramine, tryptamine, -phenyl ethylamine, sperimine and sperimidine are considered as the most important biogenic amines which are found in food. Their presence or even their molding in food is applied as an indicating parameter to food quality because the consumption of food that has high content of them represents potential health risk. The presence of biogenic amines as microbial metabolite is associated with food fermentation process. In the case of processed food, high amounts of certain biogenic amines can be found in the final product as a result of the low quality of basic material, microbial contamination and inadequate conditions during production and

storage. Biogenic amines also can be endogenic origin, mainly in fresh food such as fruits, vegetables, fresh meat, milk and fish [3].

One can say that biogenic amines in food are being studied intensively; more information can be found in several recent reviews [4-7]. Chemical structures of some biogenic amines are given in Figure 2.

Their presence and impact in food

The recent trends in food quality have increased the level of research for compounds in low concentrations that may affect human health. Biogenic amines belong to this group of compounds, which otherwise can be called natural amines. Their amount usually increases during controlled or spontaneous microbiological fermentation of food during the breakdown of food. Biogenic amines in food products are created mainly by decarboxylation of amino acids

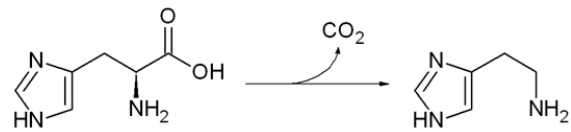


Figure 1. Formation of histamine from histidine with decarboxylation.

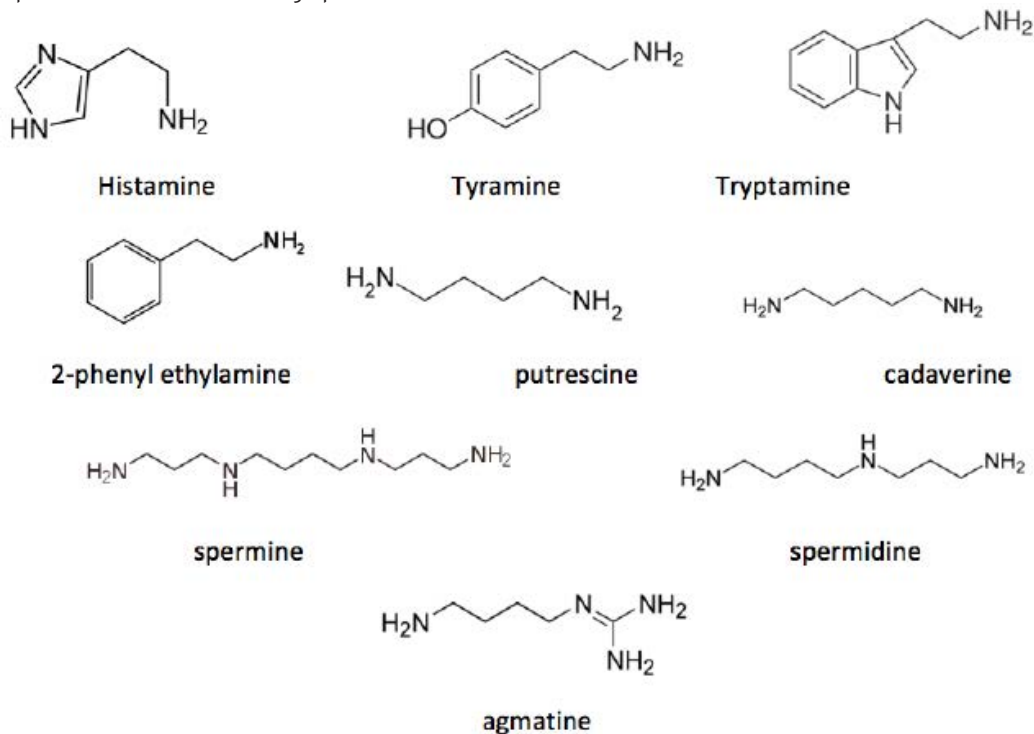


Figure 2. Chemical structures of biogenic amines that are found mainly in food.

known as bacterial decarboxylase. In order to form biogenic amines this is required:

- The active presence of free amino acid, but not always results in the formation of the corresponding amines,
- The presence of appropriate enzymes,
- Conditions that allow bacterial growth, synthesis and activity of the corresponding enzyme.

Some types of microorganisms on a high enzymatic protolithic activity are able to increase the risk of formation of biogenic amines in food systems, increasing the presence of free amino acids. Decarboxylase activity is bigger in acidic environment with an optimum pH in between 4.0 and 5.5. The bacteria are able to produce this enzyme as part of their defense mechanism against acidity. It is given attention to the impact of glukono-delta-laktonit (GDL) in the production of biogenic amine in processed foods (sausages). Glukono-delta-laktoni causes reduction of pH in the sausage which results in increased activity of decarboxylases of the bacteria. Under these circumstances, the bacteria produce more decarboxylase as part of their defense mechanism, which then increases the concentration of histamine, putrescine and tyramine [8, 9]. The temperature affects the formation of amines. The temperatures between 20°C and 37°C is optimal for the growth of most bacteria that contain decarboxylase, whereas the decrease of the temperature stops their growth. Biogenic amines mainly are present in the fermented products, such as cheese (5 - 4500 mg/kg) wine (5 - 130 mg/L), beer (2.8 to 13 mg/L), and sauerkraut (110-300 mg/kg) and in meals which are stored in inadequate manner, such as fish (2400-5000 mg/kg), beef liver (340 mg/kg), processed meats (10-700 mg/kg). These compounds are useful in foods that are not fermentable as an indicator of food decomposition. Rotten food is rich with biogenic amines and usually contains high levels of putrescine and cadaverine. The presence of biogenic amines in milk is low and is around 1 mg/L, but their cheese content reaches approximately 1 g/kg. Cheese contains proteins, enzymes, water, salt and bacteria and therefore represents an ideal environment for the production of biogenic amines from the free amino acids which can decarboxylase by enzymes

of microorganisms during cheese processing. Large amounts of biogenic amines in cheese, from the hygienic point of view, indicate the poor quality of the milk that is used to produce cheese or because of inadequate storage.

The fresh and processed pig meat contains high levels of adrenaline, spermidine and spermine and low levels of noradrenaline, putrescine, histamine, tyramine and cadaverine. The presence of large amounts of cadaverine in calf meat is followed by a big contamination from the Enterobacteriaceae. High production of tyramine (100 mg/kg) in sausage is accompanied with contamination from lactic acid bacteria. The presence of biogenic amines in fermented sausages may have originated from basic unprocessed material but contaminated by the process of fermentation. For instance, Carnobacterium diverges is responsible for the formation of tyramine in vacuum packaged meat, the formation of putrescine and cadaverine is caused by Enterobacteriaceae or Pseudomonas strains. There are three possible sources of biogenic amines in wine. They can be present from the beginning; can be formed by living during the malolaltic fermentation or can result from the engagement of bacteria involved in malolaltic fermentation. Dominant biogenic amines in wine are histamine, tyramine, putrescine, izofenilamine and β - phenylethylamine [10].

Recently, maximum levels have been reported as high as 16.6 mg/L histamine, 20.2 mg/L tyramine, and 76 mg/L putrescine in the wines from different European countries. Average levels for histamine were 3.63 mg/L for French wines, 2.19 mg/L for Italian wines and 5.02 mg/L for Spanish wines [11].

Toxicological effects

Biogenic amines are organic substances that are present in food and cause toxicological and health problems. The most frequent intoxications caused by biogenic amines include histamine. A quantity of 5-10 mg of histamine can be considered harmful and can cause health problems for sensitive people, where 10 mg histamine is considered tolerable limit, 100 mg histamine causes a medium toxic effect and the amount of 1000 mg is considered very toxic.

USA, Sweden, Austria and the Netherlands have set rules and legal requirements for the maximum permissible limit for biogenic amines in various foods and mainly for histamine.

European Union (EU) has also set rules for levels of histamine, which should be below 100 mg/kg for unprocessed fish meat and below 200 mg/kg in salted fish meat, for the species belonging to the families Scombridae and Clupeidae.

The Netherlands Institute for Food Research from the Czech Republic proposed the highest limit recommended from 100 to 200 mg/kg for histamine in meat products.

Biogenic amines such as tyramine and α -phenyl ethylamine are suggested as initiators of hypertensive crisis and migraine at some patients. Putrescine, spermine, cadaverine and spermidine do not have undesirable high effects on health, but they favor the intestinal absorption and reduce catabolism of amines. Tryptamine has toxic effects on human health by raising blood pressure, thus causing hypertension. Regardless of this, some states yet have not outlined rules for the maximum amount of tryptamine allowed in processed and canned meat.

Histamine poisoning is associated with allergy symptoms that usually are associated with the consumption of different types of fish that might have high level of histamine concentration.

It is hard to determine the exact toxicity of biogenic amines because the toxic dose depends on the efficiency of intoxicating mechanisms for each amine separately.

Analytical methods for determination of biogenic amines

Over the years, several methods have been proposed for isolating, identifying and determining biogenic amines in foods and biological systems, including spectrophotometry [12,13], high performance liquid chromatography [14-15] gas chromatography-mass spectrometry [16], double or single-isotope radio enzymatic assays [17], capillary zone electrophoresis [18], immunoanalysis [19], ion-selective electrode methods [20-23].

Those electrodes may be divided into two classes:

In the first group of histamine analysis are generally simple procedures with short analysis time although the chromatographic aspects are fraught with problem with selectivity and sensitivity.

Histamine analysis by means of pre - or post - column derivatization with fluorometric detection, and in this case fluorescent compounds are accompanied by good sensitivity and specificity but long analysis, non-reproducibility and problems of derivatization stability.

There are two reasons related to determining the significance of amines in food: the first is their toxicity potential, the second is the possibility to use them as indicators of food quality. The analysis of biogenic amines in most cases is used for: quality control of unprocessed products, intermediate and final products, fermentation process monitoring, process control, research and development. Due to the complex nature that samples may have, the potential presence of interfering compounds and the presence of biogenic amines are some typical problems that may be encountered during their analysis.

Pre clean-up method includes sample extraction, extracting more suitable reagents. Some of appropriate reagents that can be used for the extraction of biogenic amines are: 0.6 M perchloric acid, 5-10% trichloroacetic acid and 0.1 M chlorhydric acid. There are also several parameters that significantly affect the efficient extraction of biogenic amines, such as pH and the degree of saturation of extractive solution of salts. The extracting relative effect of these solvents also depends on the nature of biogenic amines and the type of food that they are extracted from. Solid Phase Extraction (SPE) can be considered a better choice than the classical liquid-liquid extraction for the fact that there is a wide range of absorb materials and furthermore the need to use various organic solvents is eliminated. Various chemical reagents are used while using these methods as: ninhidrina and o-phthalaldehyde as derivative reagents after column, benzyl chloride, fluorescein, and 9-fluorethylmetil chloroform as a derivate pre - column. Some of the methods of pre-arrangements as well as they have some necessary conditions of HPLC for determination of histamine and other biogenic amines are shown in Table 1.

Table 1. Pre-separation procedures and HPLC conditions for determination of histamine and other biogenic amines in food stuffs [4, 24].

Biogenic amines	Food samples	Sample pretreatment	Stationary phase	Mobile phase flow rate (mL/min)	Derivatization/detection
Histamine, tyramine, tryptamine, phenylethylamine, putrescine, cadaverine spermina, spermidina	Meat products	5% Trichloroacetic acid	For o-phthalaldehyde derivatives Zorbax Eclipse XDB C8. For dansyl derivatives Zorbax Eclipse XDB C18 column	For o-phthalaldehyde derivatives: gradient elution 100 mM acetate buffers (A; pH 5.8) and acetonitrile FR: 0.6. For dansyl derivatives: gradient elution H ₂ O/CAN FR:0.8	dansylchloride and o-phthalaldehyde/ 254V/VIS For o-phthalaldehyde: 330 and 440 as excitation and emission wavelengths
Histamine, tyramine, tryptamine, phenylethylamine, putrescine, cadaverine, spermine, spermidine	Wines	-	Waters Nova-Pak C18	Gradient elution. Eluent A: Na ₂ HPO ₄ and 12H ₂ O (3.6 mg/l, 10 mM). Eluent B: 1% 2-octanol in acetonitrile and eluent A (70:30 v/v). FR:0.8	o-phthalaldehyde /340 and 425 as excitation and emission wavelengths, respectively
Histamine	Tuna fish	HClO ₄ 1M	Luna C18	Gradient elution. Eluent A: 85% of buffer solution (pH 6.9) and 15% of methanol. Eluent B:acetonitrile	diode array detector (DAD)
Histamine, tyramine, tryptamine, putrescine, cadaverine spermine, spermidine, agmatine, phenylethylamine, dopamine, oktopamine, serotonin, creatinine	Alcoholic beverage	-	Nova-Pak C18	Gradient elution eluent A: 0.1M sodium acetate and 10 mM sodium octanesulfonate (pH 5.3). Eluent B: mixture of solvent B-acetonitrile (6.6:3.4), where solvent B was a solution of 0.2M sodium acetate and 10 mM sodium octanesulfonate solution adjusted to pH 4.5 FR:1	Post-column derivatizing with o-phthalaldehyde /fluorimetric detection, 340 and 445 as excitation and emission wavelengths, respectively
Tyramine	Cheese	HClO ₄ 5% (w/v)	Luna Fenomenex RP-18	Isocratic elution MeOH:H ₂ O (70:30) FR:1	Derivatization with 4-chloro-7 nitrobenzofurazan UV detection at 458 nm
Histamine, putrescine, tyramine, cadaverina, sperimine, sperimidine, serotonin	Coffee	Trichloroacetic acid	Kromasil C18	Gradient elution 0.5 mM Phosphoric acid = acetonitrile = Methanol FR:1	Diode array detector at 254 nm, connected in series with a fluorimetric detector programmed for excitation at 252 nm and emission at 500 nm (derivatization with dansylchloride)
Histamine, tyramine and phenylethylamine	Cheese	Solid phase extraction with CN bonded silica	A Luna C18	Gradient elution mixture of 0.1% TFA(v/v) aqueous solution (eluent A) and methanol (eluent B) FR: 0.2	Tandem mass spectrometry

Table 1. Continued.

Biogenic amines	Food samples	Sample pretreatment	Stationary phase	Mobile phase flow rate (mL/min)	Derivatization/detection
Histamine, tyramine, phenylethylamine, serotonin, creatinine sulfate, tryptamine, octopamine, dopamine, cadaverine, putrescine, agmatine, sperimine, sperimidine, methylamine, ethylamine	Spinach, hazelnut, banana, potato, and milk chocolate	0.6 M perchloric acid	A Nova-Pak C18	Gradient elution. Eluent A: a solution of 0.1M sodium acetate and 10 mM sodium octanesulfonate (pH 5.23), eluent B: mixture of solvent B-acetonitrile (6.6:3.4), where solvent B was a solution of 0.2 M sodium acetate and 10 mM sodium octanesulfonate solution adjusted to pH 4.5 with acetic acid FR:1:2	Derivatization with o-phthalaldehyde, fluorimetric detection 340 and 445 nm as the excitation (ex) and emission (em) wavelengths, respectively
Tryptamine, phenylethylamine, putrescine, cadaverine, histamine, tyramine, sperimine, sperimidine	Cheese	0.1 M hydrochloric acid	A reversed phase Kromasil KR 100-5 C18	Gradient consisting of eluents: (A) acetonitrile and (B) water FR:0.8	Spectrophotometric detector at 254 nm
Histamine, tyramine, tryptamine, putrescine, cadaverine	Beer	-	SGX-C18	Gradient elution 71 % (v/v) methanol in water for HI and TYR 63.5% (v/v) methanol in water for CAD, PUT and TRP FR: 0.5.	UV-VIS 254 nm
Putrescine, cadaverine, sperimidine, histamine, tyramine	Fish and fishery products	Trichloroacetic acid 5% (w/v)	C-18 ↔ Bondapak RP-column	Gradient elution methanol/water FR:1	UV detector at 254
Agmatine, cadaverine, histamine, tyramine, tryptamine, putrescine, octopamine, phenylethylamine, serotonin, sperimine, sperimidine	Fermented cabbage juices, soy sauces	HCl 0.1M or n-hexane	Grom-Sil a ODS-3 CP120 RP-18 encapsulated polymer coated column	Gradient elution. Eluent A: 100 mM NaOAc, pH 7.0; eluent B: 100 mM NaOAc, pH 4.3; eluent C: acetonitrile	UV-absorption at 260 nm
Histamine, putrescine, cadaverine, sperimidine	Fish tissues	Methanesulfonic acid	IonPac CS17 column	Gradient elution methanesulfonic acid gradient FR:1	Electrochemical detection
Histamine, putrescine, cadaverine, sperimine, sperimidine, tyramine and free amino acids amino acid et e lira	Dry-cured hams	0.4 M perchloric acid	LiChrospher 100C18	Not available	Derivatized with dansyl chloride reagent UV absorbance at 254 nm

As can be seen from the table dansyl chloride has been the most frequent reagent in HPLC, used for derivation of the main biogenic amines. However, the sensitivity and instability of this reagent has forced some authors to find other alternatives such as benzyl chloride, as fairly cheap reagent, stable and satisfactory pure, benzamide as reagents resistant to light, convenient to work in aggressive basic environments at room temperature. Fluorescent methods, UV and electrochemical detectors are used as detector, which are based on the oxidation of amine groups.

Thin layer chromatography is also well known in plant biochemistry. TLC procedures are important when have to deal with semi quantitative food. Thin layer chromatography in combination with the method of sample pre clean-up and derivation of biogenic amines can be used to detect the chloride of 3,5 dinitrobenzamide dansyl and fluorescent derivate of biogenic amines.

Dansyl chloride groups react with primary and secondary amines while fluorescent derivatives react only with primary amine groups. Dansyl products of biogenic amines are emitting energy as fluorescent light which is absorbed in wavelength (360 nm) in the UV and determines these compounds with the chromatography, at low levels. The thin one-dimensional layer chromatography has developed techniques that enable a satisfactory separation of biogenic amines that eliminates interference to some extent of other similar compounds, such as amino acids which are also able to move with analyzed biogenic amines. Multidimensional developed techniques have improved resolution of biogenic amines from each other and from interfering material, and in this case more compact and intense signs are achieved.

Gas chromatography often is not applied in determining biogenic amines. Due to the prolonged problems, derivatization is usually used. Biogenic amines are determined in the derived form as trifluoroacetyl or 2,4-dinitrophenyl derivatives. Columns used in the gas chromatography are capillary or loaded. Capillary columns provide better separation of biogenic amines. Detectors used in gas chromatography for the determination

of biogenic amines can be conductometric, ionium on fire, the electron capture detector or mass spectrometer. Reports related to biogenic amine separation from electrophoresis capillary (CE), are not many in number. There are three possible ways to solve the problem of division:

1. Aromatic biogenic amines or heterocyclic can be divided into buffer selective systems without derivatization.
2. The determination of polyamines is also possible in the derivate form (usually in the form of electrokinetic capillary chromatography) or
3. Their determination should be made indirectly.

Capillary electrophoresis has some advantages: it is fast, cheap and realizable becoming a very useful method in order to have an analytical overview of a large number of samples in a short period of time. Fluorometric methods are used when it is possible to obtain a fluorescent product of biogenic amine during a reaction with a suitable reagent. Positively, histamine can be determined using O-phthalaldehyde as derivative reagent and tyramine- with naftol. Determination of biogenic amines is also possible using an amino acid analyzer, but the determination is not very selective because at the same time all the amino acids are determined that are usually the forerunner of biogenic amines.

Fluorometric methods are used when it is possible to obtain a fluorescent product of biogenic amine during a reaction with a suitable reagent.

Electroanalytical methods

All the methods mentioned above that are reported as methods for determining biogenic amines generally suffer from several weaknesses such as the need for successive derivations that take more time, low reproducibility of results and the method in general, interference and problems associated with derivative product stability. Moreover, the necessary equipment's are expensive and to work with them costs too much. Alternatively, an enzyme-based electrodes (biosensor) using amine oxidases and dehydrogenases for determination of histamine by means of amperometric [25,26] detection methods have also been carried out to solve these drawbacks.

In this context, biosensors offer low price, rapid and short time analysis methods [27] which are mainly based on the use of amine oxidases, which convert the analyte to the corresponding aldehyde, NH_3 and H_2O_2 (Eq.(1)).



The consumption of O_2 [28] or the generation of H_2O_2 [29, 30] are usually monitored by measuring the reaction product which is than equivalent to the quantity of histamine. Nevertheless, the detection of hydrogen peroxide requires the application of high potential which may lead to have other compounds that can act as interferences. Sometimes using redox mediators [31] it is possible to detect H_2O_2 at lower applied potential, which is a common strategy to construct an amperometric biosensor. However, enzyme immobilization is tedious process which can lead to decreasing of enzyme activity, shift of the enzyme's optimal conditions or even to complete loss of the activity. Biosensor preparation is time-consuming and very often poorly reproducibility response.

Also are reports some of applied electrochemical methods for histamine quantification [32] including derivatization of histamine with *o*-phthalaldehyde and 2-mercaptoethanol which yielded complex products that could be electrochemically oxidized. There are not so many reports [33-38] about direct electrochemical oxidation of histamine on conventional bare electrodes such as platinum, gold, glassy carbon or heterogeneous carbon modified electrodes. One report describes cyclic voltammetry and flow injection analysis using boron-doped diamond and glassy carbon electrodes for the characterization of the histamine electrochemical behavior but not for its quantitative analysis [39].

The previous electrochemical methods used for the determination of histamine in the most cases the surface of the working electrode were modified (Table 2).

Using chemical modification or biological modification of the surface was achieved improvements at the limit of detection and in some cases the selec-

tivity of the sensor. These methods described so far enable a quick determination, sensitive and simple in real samples, while it remains a challenge for these methods the most effective selectivity in cases where the composition of the samples is complicated.

CONCLUSION

Biogenic amines that are present in different types of food have been subject of study for many authors because of their toxicity and because it can be used as an indicator of the degree of freshness or disrupting food. Histamine, putrescine, cadaverine, tyramine, tryptamine, phenylethylamine, spermidine and spermine are the most important biogenic amines. These amines can be found in meat, milk, chocolate, cheese, fish and some types of drinks. It is very crucial the monitoring of the amount of these amines in food products and drink regarding their importance for human health and safety and quality of food. Several methods have been described for the determination and analysis of biogenic amines in food products, which are based mainly in the thin layer chromatography, liquid chromatography, gas chromatography, biochemical analysis and capillary electrophoresis. Biogenic Amines are produced by bacteria decarboxylation of amino acids. Hence, the food products which during their processing are fermented or are contaminated during processing or preserving may contain biogenic amines. Analytical determination of biogenic amines is not easy because of the real sample which is very complex that needs to be analyzed. Amine extraction of real samples is very important in terms of obtaining adequate results for all amines. Huge part of analyzes are done with highly derivative steps that take a lot of time during the analysis process. It is necessary to develop sensitive methods which spend less time and are very useful analytical methods for the determination of biogenic amines. Electrochemical methods are promising methods due to their simplicity, lower cost, sensitivity and short time analyses. Further studies are in progress towards the application of the developed methods for biogenic amines determinations in several real samples.

Table 2. Listed previous electrochemical methods used for determination of histamine.

Technique	Working electrode	Working potential	Modifier	Ref.
Amperometric detection in FIA	Platinum electrode	+700 mV vs. Ag/AgCl	Diamine oxidase (DAO)	[21]
Cyclic Voltammetry	Au Ultramicroelectrode	+900 mV vs. Ag/ AgCl	Bare	[28]
Chronopotentiometric determination	Glassy carbon electrode	0 - 500 mV	Nickel film	[27]
Chronopotentiometry	Gold electrode	-0.2 - 1350 mV	Bare	[26]
Chronopotentiometry	Glassy carbon planar disc electrode	+400 mV vs. Ag/AgCl	Thin film of mercury	[29]
Amperometric detection in FIA	Glassy carbon electrode	+200 mV vs. Ag/AgCl	Immobilized histamine dehydrogenase	[40]
Potentiometric detection	Solid contact electrode (ion - selective electrode)		Polymeric membrane	[24]
Amperometric detection	Screen printed carbon electrodes	-50 mV vs. Ag/AgCl	Immobilization of diamine oxidase (DAO) and horseradish peroxidase (HRP)	[17]
Amperometric detection	Screen printed carbon electrodes	+400 mV vs. Ag/AgCl	MnO ₂ and pea seedling amine oxidase	[41]

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