Talanta 154 (2016) 134–140

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of tryptamine in foods using square wave adsorptive stripping voltammetry

Daniel J.E. Costa [a], Ana M. Martínez [b], Williame F. Ribeiro [c], Kátia M. Bichinho [a], María Susana Di Nezio [b], Marcelo F. Pistonesi [b], Mario C.U. Araujo [a,*]

[a] Universidade Federal da Paraíba, Departamento de Química, Laboratório de Automação e Instrumentação em Química Analítica/Quimiometria, Caixa Postal 5093, CEP 58051-970 João Pessoa, PB, Brazil
[b] Departamento de Química, Universidad Nacional del Sur, INQUISUR (UNS-CONICET), Av. Alem 1253, B8000CPB Bahía Blanca, Buenos Aires, Argentina
[c] Universidade Federal da Paraíba, Centro de Ciências Agrárias, Departamento de Ciências Fundamentais e Sociais, 58397-000 Areia, PB, Brazil

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form
19 March 2016
Accepted 19 March 2016
Available online 21 March 2016

Keywords:
Tryptamine
Adsorptive Stripping Voltammetry
Food analysis

ABSTRACT

Tryptamine, a biogenic amine, is an indole derivative with an electrophilic substituent at the C3 position of the pyrrole ring of the indole moiety. The electrochemical oxidation of tryptamine was investigated using glassy carbon electrode (GCE), and focusing on trace level determination in food products by square wave adsorptive stripping voltammetry (SWAdSV). The electrochemical responses of tryptamine were evaluated using differing voltammetric techniques over a wide pH range, a quasi-reversible electron-transfer to redox system represented by coupled peaks P_1–P_3, and an irreversible reaction for peak P_2 were demonstrated. The proton and electron counts associated with the oxidation reactions were estimated. The nature of the mass transfer process was predominantly diffusion-limited for the oxidation process of P_1, the most selective and sensitive analytical response (acetate buffer solution pH 5.3), being used for the development of SWAdSV method, under optimum conditions. The excellent response allowed the development of an electroanalytical method with a linear response range of from 4.7–54.5) $\times 10^{-8}$ mol L^{-1}, low detection limit (0.8×10^{-9} mol L^{-1}), and quantification limit (2.7×10^{-9} mol L^{-1}), and acceptable levels of repeatability (3.6%), and reproducibility (3.8%). Tryptamine content was determined in bananas, tomatoes, cheese (mozzarella and gorgonzola), and cold meats (chicken sausage and pepperoni sausage), yielding recoveries above 90%, with excellent analytical performance using simple and low cost instrumentation.

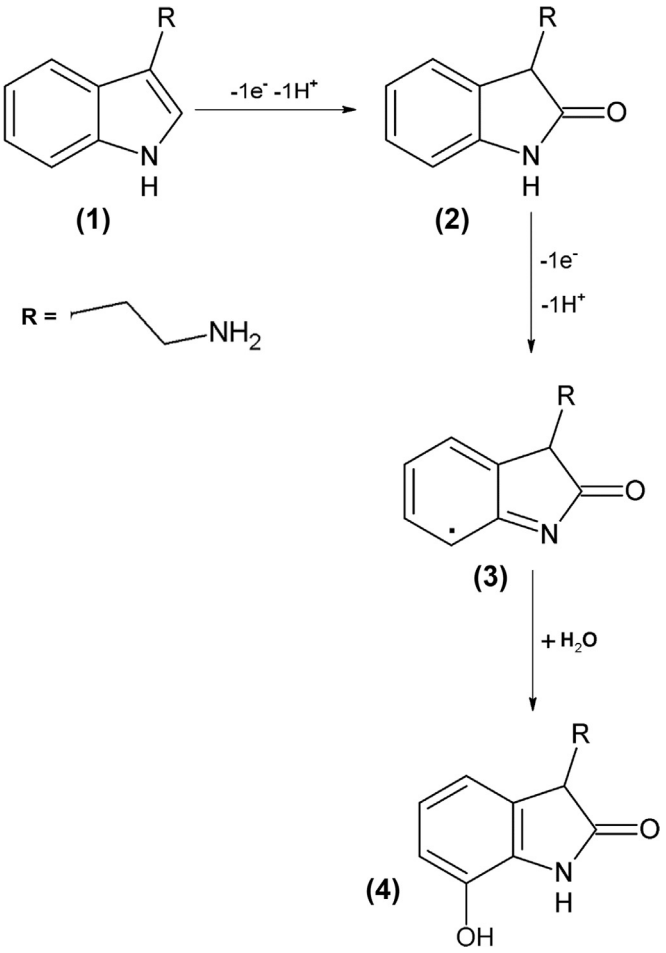
1. Introduction

Tryptamine (indole-3-ethylamine, Scheme 1) is an indole derivative with an electrophilic substituent at the C3 position of the pyrrole ring of the indole moiety [1]. This compound is a low molecular weight (160.2 g mol^{-1}) biogenic amine which can be formed by microbial decarboxylation of amino acids, or by amination and transamination of aldehydes and ketones [2]. It is formed by decarboxylation of the amino acid tryptophan, and is a precursor to serotonin, a neurotransmitter that acts in central nervous system and gastrointestinal tract [3,4]. Tryptamine is found in certain fruits and vegetables, meats, cheese, eggs, alcoholic drinks, beverages and other fermented foods, in a wide range of concentrations [5,6]. The concentration of amines in foods depends on the microorganisms present, the decarboxylase enzyme activity on specific amino acids, and the favorability of the enzymatic conditions. Once biogenic amines are formed, they are difficult to destroy either by pasteurization or cooking. Determination of biogenic amines in food products has received worldwide attention because of their hazardous effects on humans; such as rash, migraine, hypertension and hypotension. Biogenic amine (BA) content is a food quality marker [7].

Employing chromatographic techniques, several methods have been developed to analyze tryptamine [2,6,8–13]. These methodologies generally employ toxic reagents, derivatization agents, and they generate hazardous waste. Furthermore, sample treatment becomes necessary; steps such as ultra-sonication, centrifugation and filtration. To determine biogenic amines in food samples that involve sample preparation electrophoresis methods have also been employed [14,15]. The major disadvantages of such methodologies (chromatography and electrophoresis) are that they require expensive instrumentation, skilled labor, and in general, various steps for sample preparation. Voltammetric methods offer sensitive

* Corresponding author.
E-mail address: mariougulino@gmail.com (M.C.U. Araujo).

http://dx.doi.org/10.1016/j.talanta.2016.03.063
0039-9140/



Scheme 1. Proposed tryptamine oxidation mechanism.

analytical results, feature low costs, and short analyses times, and have proven to be very efficient in the determination of indole derivatives, such as: tryptamine, indole-3-acetamide, gramine, indole acetic acid, indole propionic acid, indole butyric acid and tryptophan [1]. Electrochemical oxidation of these substances (with a substituent at the C3 position) has been investigated by Enache and Oliveira-Brett in 2011, on a bare GCE over a wide pH range, using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV) [1].

Xing et al. in 2012 developed an electrochemical sensor based on polypyrrole-sulfonated graphene (PPy-SG)/hyaluronic acid-multi-walled carbon nanotubes (HA-MWCNTs) to determine tryptamine in cheese and lactobacillus beverage samples. The analytical method was carried out applying the standard addition method. The tryptamine linear range was from 9.0×10^{-8} mol L^{-1} to 7.0×10^{-5} mol L^{-1} [16]. An array of voltammetric chemically modified sensors with phthalocyanines was employed to determine biogenic amines in fish. The spoilage products, ammonia, dimethylamine, trimethylamine, cadaverine, and histamine were studied. However tryptamine was not included [17]. Alonso-Lomillo et al. determined total biogenic amines by using enzymatic biosensors with screen-printed carbon electrodes. The electrodes were modified by an aryl diazonium salt, using hydroxysuccinimide and carbodiimide. The method allowed total amine content determination in salted anchovy samples expressed in histamine equivalent units [18].

The goal of this study is to present tryptamine determination using square wave adsorptive stripping voltammetry (SWAdSV), on a glassy carbon electrode (GCE) without surface modification. GCE has traditionally been the substrate of choice for adsorptive stripping voltammetric measurements of organic compounds [19]; such as halosulfuron-methyl [20], triclocarban [21], norfloxacin [22], tamoxifen [23], and Adriamycin [24]. The adsorption process plays an important role in the accumulation process. When these compounds contain electrochemically reducible or oxidizable functional groups, they react with the oxidized electrode material, and the compound formed is adsorbed [19]. The methodology is fast, and sensitive, it requires little analysis time, and it was applied to determine tryptamine in cheese, fruits and cold meats. The electrochemical oxidation of the tryptamine was also studied using differing voltammetric techniques in a wide pH range.

2. Experimental

2.1. Apparatus and reagents

Tryptamine (99%) and all of the other chemicals were of analytical grade, and purchased from Sigma-Aldrich. Solutions and subsequent dilutions were prepared daily with ultrapure water in a Millipore Milli-Q System (conductivity ≤ 0.1 μS cm^{-1}). Stock solutions of tryptamine (1.0×10^{-3} mol L^{-1}) were prepared in water and stored under refrigeration. Buffer solutions 0.1 mol L^{-1} were prepared and employed as supporting electrolyte; following the procedure described by Oliveira et al. [25]: HCl/KCl (pH 1.5 and 2.1); HAc/NaAc (pH 3.6, 4.2, and 5.3); NaH_2PO_4/Na_2HPO_4 (pH 6.0, 7.0 and 8.0); borax/NaOH (pH 9.1 and 10.1); and NaOH/KCl (pH 11.9 and 12.7).

All voltammetric experiments were carried out at room temperature using an Eco Chemie, μAutolab® Type II, potentiostat, coupled to a Metrohm 663 VA Stand®, three-electrode module, and a 3 mL single-compartment electrochemical cell. A platinum wire, an Ag/AgCl electrode (3 mol L^{-1}, KCl), and a GCE (ϕ=3 mm) were employed as counter, reference, and working electrode, respectively.

2.2. Electrode preparation and measurement procedure

The GCE was polished on a mirror finish using filter paper with diamond spray (particle size 1.0 mm, purchased from Risitec), and then rinsed with plenty of water. The electrode was then conditioned in 0.1 mol L^{-1} sulphuric acid by 10 successive CV scans (from -1.2 to $+1.4$ V) at a scan rate of 1.0 V s^{-1}. In the SWV and DPV experiments, the electrode surface was always polished between measurements. The DP and SW voltammograms were smoothed and background-corrected using (respectively) the Savitzky–Golay smooth functions (level: 4), and a moving average with an available step window of 2 mV in the GPES version 4.9 software. The treatment provided a better and clearer identification of the peaks.

LSV and CV used scans rates (v) of 25–100 mV s^{-1}. DPV used a pulse amplitude (a) of 50 mV, a modulation time of 70 ms, and (v) of 10 mV s^{-1}. SWV used a frequency (f) of 25 s^{-1}, scan increment (ΔEs) of 2 mV, scan rate of 50 mV s^{-1}, and (a) of 50 mV. Under optimized operational conditions (see Table 1), SWV stripping mode used a f of 150 s^{-1}, ΔEs of 6 mV, and v of 900 mV s^{-1}, with an a of 50 mV. For the accumulation step, the electrode was kept immersed in 3 mL of a sample solution under stirring (1500 rpm), while leaving its potential at open circuit (potential window 0.7–0.95 V vs Ag/AgCl). An accumulation time of 10 s was used for the quantitative measurements.

2.3. Sample preparation

The analyzed samples were two varieties of cheeses (gorgonzola and mozzarella), chicken sausage, pepperoni, bananas, and