Talanta 117 (2013) 405–411

Contents lists available at ScienceDirect

Talanta

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

Simultaneous determination of cadaverine and putrescine using a disposable monoamine oxidase based biosensor

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ARTICLE INFO

Article history:
Received 2 September 2013
Accepted 22 September 2013
Available online 27 September 2013

Keywords:
Monoamine oxidase
Putrescine
Cadaverine
Screen-printed electrodes
Enzymatic amperometric biosensor

ABSTRACT

The selective and simultaneous amperometric determination of putrescine (Put) and cadaverine (Cad) has been carried out using a novel design of screen-printed carbon electrode (SPCE) with two working electrodes connected in array mode. A mixture of 3% of tetrathiafulvalene (TTF), as mediator, and carbon ink was used for the construction of the screen-printed working electrode. The employment of different amounts of monoamine oxidase (MAO) enzyme on these modified TTF/SPCEs and the use of gold nanoparticles (AuNPs) allowed performing the simultaneous determination of both analytes. The amperometric detection has been performed by measuring the oxidation current of the mediator at a potential of +250 mV vs. screen-printed Ag/AgCl reference electrode. A linear response in the Cad concentration range from 19.6 till 107.1 μM and from 9.9 till 74.1 μM for Put was obtained at the MAO/AuNPs/TTF/SPCE biosensor. This device showed a capability of detection of 9.9 and 19.9 ± 0.9 μM ($n=4$ $\alpha=\beta=0.05$) and a precision of 4.9% and 10.3% in terms of relative standard deviation for Put and Cad, respectively. The developed biosensor was successfully applied to the simultaneous determination of Put and Cad in octopus samples.

1. Introduction

Biogenic amines (BAs) are organic bases with aliphatic (putrescina (Put), cadaverine (Cad), spermine (Spm) and spermidine (Spd)); aromatic (tyramine (Tyr) and phenylethylamine (Pea)) or heterocyclic (histamine (His) and tryptamine (Tryp)) structures [1]. These natural contaminants are synthesized and degraded during normal metabolism of animals, plants and microorganisms [2].

High amounts of certain amines may be present in a wide range of food products including fish, meat, wine, beer, vegetables, fruits, nuts and chocolate [2], as a consequence of microbial contamination and inappropriate conditions during processing and storage. Therefore, the content of BAs, especially Put, Cad, His and Tyr can be considered as freshness markers and could be used as indicator of microbial spoilage [3]. Ingestion of food contaminated with BAs, can lead to several health problems, such as headache, blushing, itching, skin irritation, impaired breathing, tachycardia, hypertension, hypotension and vomit [4]. Moreover, it has been reported that certain types of cancer produce an increase of Put and Cad concentration in some human tissues. In this way, Put is often accumulated in blood, serum and mucous of cancer patients. Thus, Put and Cad are listed as tumor markers and their determination in clinical samples can be important for diagnosis of malignancy and, even for monitoring the efficiency of treatments, such radio or chemotherapy [5]. For these reasons, monitoring of BAs amount present in food and beverages is becoming increasingly demanded by regulatory commissions as the Commission Regulation (EC 2073/2005) [6].

Since BAs is usually present at low levels in complex matrices, the determination of these compounds requires the use of sensitive and selective analytical methods. Traditionally, BAs are determined using chromatographic methods [7,8], which are time-consuming and require special instrumentation. Contrary to the above mentioned methods, biosensors offer simple, rapid and cost-effective solution for the determination of BAs [9]. Amperometric enzymatic sensors hold a leading position among the presently available biosensor systems. These devices combine the selectivity of the enzyme for the recognition of a given target analyte with the direct transduction of the rate of the biocatalytic reaction into a current signal, allowing a rapid, simple and direct determination of numerous compounds [10]. Among the different transducers used, screen-printed electrodes offer additional advantages related to their disposable character and great versatility. This versatility lies in the wide range of possible methods of modification of this kind of electrodes, since the composition of the printing inks may be altered by the addition of different

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http://dx.doi.org/10.1016/j.talanta.2013.09.043

Table 1
Biosensors for the detection of biogenic amines.

Enzyme	Working electrode	Immobilization	Potential (mV)	pH	Capability of detection	Biosensor selectivity	Sample	References
DAO	Graphite	Crosslinking (PEGDGE)	−50	7.0	5 μM His	867% Cad, 809% Pea, 686% Put, 215% Spd, 100 His, 40% Tryp, 43% Tyr	Pork, Fish	[3]
MAO			−50	8.0	2 μM Tyr	100% Tyr, 90% Pea, 72% Tryp, 1.8 His, 1.2 Spd		
PUO-HRP			+50	8.0	5 μM Put	100% Put, 11% Cad, 5% Spd, 2% Tyr		
PAO	C-SPE	Crosslinking (GA-BSA)	+260	6.65	2 μM Tyr	100% Cad, 87% Put, 84% Tyr, 74% His, 55% Spm, 36% Spd, 31% Tryp	Cheese	[35]
PUO-HRP	Graphite	Crosslinking (PEGDGE)	+50	8.0	5 μM	100% Put, 10.7% Cad, 5.2% Tryp, 5% Spd, 2% Tyr, 1.7% *His*	Beer	[9]
PSAO	Carbon paste electrodos	membrane NAFION	+400	7.5	10 μg/L Cad 8 μg/L Put	*Put+Cad*	Fish	[12]
DAO	C-SPE	Entrapping polymer	–	–	0.65ppm His	–	Tiger Prawn	[13]
DAO	Pt	Crosslinking (GA-BSA)	−600	7.4	0.01 mg/L	100% His, 39.7% Put, 18.5%	Sausages	[14]
DAO	Nano-Fe_3O_4	Covalent	+400	7.2	0.65 nM	–	–	[15]
DAO	Pt-SPCE Au-SPCE	Crosslinking (BSA-PAP)	+600	7.4	0.2 mg/L	Total BAs	Wine, Beer	[6]
MAO-HRP DAO-HRP	C-SPE	Covalent	+250	9.3	0.18 μM His 0.40 μM His	100% Put, 95% Cad, 80% His, 73% Tyr, Spm, Spd, 23% Tryp	Anchovy	[16]
DAO	C-SPE	Crosslinking (GA-BSA)	−50	7.4	0.1 μM Put	100% Put, 90% Cad, 72% Spd, 70% Spm, 92% His, 85% Pea	Human Saliva	[17]
PSAO	Oxygen sensor	Dissolution	−800	7.0	10 μM (His, Cad, Put)	Total BAs	–	[50]
GPAO-HRP	Graphite	Crosslinking (membrane polymeric)	−50	7.2	500 μM (His, Cad, Put, Spd, Tyr)	Separation in chromatographic column	Cod	[2]
DAO	C-SPE	Photopolymerization (Hydrogel)	+350	7.4	*His* 70 μM	100% His, 5.7% Put and Cad	Tiger prawn	[18]
DAO	Pt	Crosslinking (GA+Gel)	+700	7.0	125 μM His, 250 μM Put, 500 μM Cad	–	Cheese, Anchovy	[19]
HRP	Graphite	Crosslinking (membrane polymeric)	−50	7.0	17 ng/mL	Total BAs	Plasma of rat blood	[20]
PUO	GC (MWCNTS/ APTES)	Mixture MWCNTS-PODA-APTES	−450	7.0	5 μM	100% Put, Spd, Spm and Cad < 6.8%	Mamalian plasma	[21]
PUO	GC (MWCNTS/ APTES)	Crosslinking (GA-BSA)	−250	8.4	0.5 μM Put	100% Put, 35.5 % Spd, 32.8 % Cad, 2.7% Spm	–	[22]
PUO-HRP	GC	Crosslinking (GA-BSA)	+50	8	5 μM Put	100% Put, 123% Spd, 98% Cad, 2% Spm	Fish	[23]
SPP-AO SSP-GOx SSP-ALCOx	Graphite	Hydrogel (PEGDGE)	−50	7.0	100 μM Put 2 mM Ethanol	–	–	[24]
PUO	Pt – (film photolithography)	Crosslinking (membrane+GA)	+600	8.5	0.5 μM Put	–	Human blood and plasma	[5]
PAO TAO DAO	Pt-SPE	Crosslinking (GA-transglutaminase)	+700	7.5	100 mg/kg His 5 mg/kg Put	100% Tyr, < 1% Put-Cad-His-Spd-Spm-Agm 100 % His, 90 % Tyr, 13% Spd, < 5 % Put-Cad-Spm, < 1% Agm 100% Put, 50% Spd, 8% Spm, 2% His-Cad, < 1% Agm	Salmon, Beer, Cheese, sauerkraut, Wine.	[25]
DAO	GC-Pt GC-Rh/Ru	Crosslinking (membrane+GA) and Electropolymerization	+200	8.0	DAO-GC-Rh/Ru (1 μM Put, Cad, Pea; 10 μM Tryp, 5 μM His and Tyr) DAO-GC-Pt (0.5 μM Put, His, Tyr, Pea; 1 μM Cad, 2 μM Tryp)	Total BAs	Cheese	[26]
PUO	Chitosan porous beads	GA	+500	7.8	0.1 mM Put	Total diamines	Chicken	[27]
AO	Graphite	Crosslinking	+200	7.0	2.2 μM His	Cys>His>Tyr>Agm>Spd>Put>Cad.	–	[28]