



Electrochemical behavior of methamphetamine and its voltammetric determination in biological samples using self-assembled boron-doped diamond electrode



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ABSTRACT

An electrochemical behavior of methamphetamine on a self-assembled boron-doped diamond electrode was studied by cyclic voltammetry. Methamphetamine yielded a single irreversible oxidation peak at a higher positive potential of +1.23 V (vs. Ag/AgCl/3 M KCl electrode) in Britton-Robinson buffer solution at pH 10. The nature of the electrode reaction was found to be diffusion controlled with minor contribution of adsorption. The differential pulse voltammetric methodology was proposed for the sensitive determination of methamphetamine in a linear concentration range from 0.07 to 80 μM with a detection limit of 0.05 μM ($7.46 \mu\text{g L}^{-1}$) and a good repeatability (relative standard deviation of 2.8% at 20 μM concentration level, $n = 6$). The effect of interfering agents (common urinary compounds) was appeared to be negligible confirming a favorable selectivity of method. The practical usefulness of method was demonstrated in the assessment of methamphetamine content in model human urine samples with good accuracy (recoveries varied from 93.4% to 97.6%). The proposed procedure could represent a suitable alternative to other analytical methods for the determination of low concentration levels of methamphetamine in biological samples. It may enable methamphetamine excreted in urine of drug addicted people to be assayed sensitively and selectively.

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1. Introduction

Currently, the drug abuse has widely spread on the global scale. It brings the great effects for human health and social behavior leading to increased rates of drug-related deaths, human immunodeficiency virus (HIV), hepatitis C and hepatitis B infection [1]. The list of abused drugs can vary depending on the context in which the samples are analyzed. Clinical and forensic toxicology, testing of driving under the influence of drugs, anti-doping analysis and various rehabilitation programs, all these attributes focus on different abused drugs: opiates, cocaine and amphetamines [2]. In this sense, the determination of particular drugs in biological fluids is of great importance in clinical and forensic toxicology.

Methamphetamine ((2S)-N-methyl-1-phenylpropan-2-amine, METH) has received much attention as an amphetamine-like stimulant drug that, even in small amounts, has strong effect on brain and nervous system causing mental alertness and increase of energy [3]. The usual way of intake is performed by mouth, snorting, injecting and smoking. METH is addictive narcotic which

can elevate body temperature to dangerous or lethal levels causing convulsions. Chronic users may also develop a violent behavior, anxiety, insomnia, paranoia, delusions and psychological dependency [4]. On the other hand, this drug is used by population of patients receiving chronic opioid therapy for pain [5]. METH is simple to produce and inexpensive to buy in public field as well as more potent abused drugs are still being produced. Hence, the analytical laboratories should take it into account in the development of rapid, simple and economical procedures for drugs determination exhibiting sufficient sensitivity and selectivity.

Recently, various analytical methods including high performance liquid chromatography coupled with mass spectrometry [6–9], gas chromatography coupled with mass spectrometry [10–12], capillary electrophoresis [13,14] and spectrometry [15,16] have been developed for the determination of METH and other amphetamine-like drugs. However, most of these methods suffer from problems such as time-consuming procedures, expensive apparatuses and tedious and complicated sample pretreatment. The development of rapid, simple and efficient analytical methods for detection and quantification of amphetamine-like drugs is still of great interest in public safety field.

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Electroanalytical techniques have proved to be excellent alternatives for the determination of various electroactive drugs. They are simple, low-cost and require relatively short analysis times without need for derivatization or time-consuming extraction steps [17]. In addition, they render information about kinetics and charge transfer mechanism of electrode reaction [18,19]. A literature survey revealed few reported studies concerning with electrochemical determination of METH. Regarding the conventional electrodes (glassy carbon, carbon paste and graphite) the difficulties usually consist in electrode surface fouling and highly positive oxidation potential of amphetamine-like drugs with interference of oxygen evolution current. Some electroanalytical procedures for the determination of METH have been reported, but most of them are based on principles of immunosensing and electrochemiluminescence. Yagiuda et al. proposed a simple conductometric immunosensor for the assessment of METH content in urine composing of an immobilization of anti-METH antibody on a surface of platinum electrodes followed by decrease of conductivity due to the reaction of METH with the antibody [20]. An amperometric immunosensor based on anti-METH antibody as a biorecognition element in urine with a detection limit of 1.3 μM for METH was developed by Luangaram and co-workers [21]. An organically modified silicates (ORMOSILs) film electrode was constructed and applied for the electrochemiluminescence determination of METH in scout cases with a wide linear range of 0.5–1000 μM and a detection limit of 0.2 μM [22]. Cai et al. prepared and used a Ru(bpy)₃²⁺-doped silica nanoparticles/Nafion modified glassy carbon electrode (GCE) and reached a very low detection limit of 0.026 μM for METH [23]. An electrochemical impedance spectroscopy (EIS) technique was used for the evaluation of aptamer interaction with METH for its fast and low-cost determination [24]. Watanabe and Okada developed a potentiometric method using a METH-sensitive membrane electrode with a detection limit of 10 μM [25]. Garrido et al. studied an electrochemical oxidation of amphetamine-like drugs on GCE with emphasis on the quantification of methylenedioxymethamphetamine in ecstasy tablets in Portugal [26]. In this study, METH provided a single anodic peak at potential of +0.92 V vs. Ag/AgCl electrode in phosphate buffer solution at pH 9, however, with necessity for electrochemical pretreatment and regeneration of GCE surface owing to the strong adsorption of oxidation products of electrode reaction.

A development of new electrode materials which could replace toxic liquid mercury is one of the current trends of electrochemistry [27–31]. Boron-doped diamond (BDD) electrodes offer the attractive advantages in electroanalysis of organic compounds such as high stability with respect to the adsorption of chemical species (the presence of *sp*³ hybridized diamond carbon atoms), the ability to work in the wide usable potential range and the easiness of cleansing of the surface when compared to GCE [32]. In addition, they possess the useful properties for determination of highly oxidizable analytes including low and stable background current (high *S/N* ratio) and mechanical robustness [33]. In this way, BDD electrodes represent the effective alternatives to conventional carbon-based electrodes and may be extensively used as a versatile electrochemical tool for various applications in analytical chemistry [34–36].

Taking our interest in electroanalysis of drugs using BDD electrodes in last reports [37–39] into account, herein, we demonstrate a novel method for the sensitive determination of METH as a simple, rapid and low-cost alternative to so far dominant separation methods. A study of electrochemical behavior of METH on self-assembled BDD electrode is also presented. It is important to point out the fact that according to literature survey no report dealing with the electrochemical determination of amphetamine-like drugs using BDD electrode has been published until now. The practical usefulness

of the proposed electrochemical methodology is demonstrated in the quantification of METH in model human urine samples.

2. Experimental

2.1. Reagents

(+)-Methamphetamine hydrochloride (CAS No. 51-57-0, purity $\geq 99\%$, METH) was purchased from Sigma–Aldrich (Austria) and used without any further purification. Britton–Robinson (BR) buffer solution was prepared in a usual way by mixing of phosphoric acid, acetic acid and boric acid, with all components at 40 mM concentration, and adjusting with sodium hydroxide (0.2 M) to the desired pH value. A stock standard solution of METH (1 mM) was prepared by dissolving 18.6 mg of its solid hydrochloride standard in 100 mL of deionized water and stored in refrigerator at 4–6 °C. The working solutions of lower concentrations were freshly prepared on the day of experiment by appropriate diluting the standard solution of METH with supporting electrolyte. All other chemicals were of analytical reagent grade. Deionized water with a resistivity not less than 18 M Ω cm (Millipore Milli-Q system) was used for preparation of all solutions.

2.2. Apparatus

The voltammetric measurements were performed with an AUTOLAB PGSTAT 302N (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat controlled by NOVA 1.10 electrochemical software. The three electrode system consisted of an Ag/AgCl/3 M KCl and a platinum wire as reference and counter electrode, respectively. A self-assembled BDD electrode was served as the working electrode. The pH of solutions was measured using a pH meter (model 1230, Orion, Austria) with a combined electrode (glass-reference electrode) with an accuracy of pH ± 0.05 , which was weekly calibrated with standard buffer solutions. The BDD electrode morphology and structure were characterized by scanning electron microscopy (SEM, JEOL JSM-7500F) and Raman spectroscopy (HORIBA JOBIN YVON LABRAM 300, He–Ne laser 632.8 nm). Each potential reported in this paper is given against the Ag/AgCl/3 M KCl reference electrode and all experiments were carried out at a laboratory temperature of 25 ± 1 °C.

2.3. Fabrication of BDD electrode

Polycrystalline (1.2 μm) thick heavily BDD films with resistance 20 k Ω (2-point measurement) were grown by double bias enhanced hot filament chemical vapor deposition (HF CVD) technique previously described [40]. As a substrate, highly conductive (0.008–0.024 Ω cm) N (100) type silicon substrate with 2 μm thick SiO₂ layer (CVD, Oxford PlasmaLab 80) was used. A deposition process was divided into three steps: (i) 25 min ultrasonic seeding of diamond nanoparticles (CAS No. 7782-40-3, Sigma Aldrich) diluted in deionized water, (ii) 2 h growth of the BDD thin film with 2% concentration of CH₄ in H₂ and trimethylboron (TMB) to obtain the 10,000 ppm boron to carbon ratio (B/C) within the gas mixture. The total pressure in the reactor was kept at 3 000 Pa and temperature was set up to 650 ± 20 °C, (iii) a hydrogen termination of the as grown BDD layer within the one vacuum cycle (10 min, H₂, 3000 Pa, 650 ± 20 °C). The working electrode active surface (0.43 mm²) was created in 400 nm SiO₂ (CVD, Oxford PlasmaLab 80) by using a standard optical lithography (SUSS, MA6) and wet etching in BOE solution (6:1 volume ratio of 40% NH₄F in water to 49% HF in water). Subsequently, the electrode chip (10 \times 3 mm²) was electrically connected by Ag polymer paste (CB115,

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