



Green electrochemical sensor for environmental monitoring of pesticides: Determination of atrazine in river waters using a boron-doped diamond electrode

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ABSTRACT

A novel, simple and sensitive electrochemical method for the determination of atrazine using a square-wave voltammetry on boron-doped diamond electrode was developed. Atrazine provided a single well-defined reduction peak at -1.1 V vs. Ag/AgCl electrode in Britton–Robinson buffer solution at pH 3. The effect of supporting electrolyte, pH and scan rate on the current response of atrazine was studied to select the optimum experimental conditions. The linear concentration range from 0.05 to 40 μM ($R^2 = 0.999$, $n = 6$), the good repeatability (relative standard deviation of 2.9% at 10 μM for $n = 6$) and the detection limit of 10 nM were achieved at optimized square-wave voltammetric parameters (step potential of 5 mV, frequency of 60 Hz and amplitude of 80 mV). The influence of possible interfering agents appeared to be minor which evidently proved the good selectivity of method. The proposed method was successfully applied for the determination of atrazine in spiked river water samples with satisfactory recoveries (92 to 100%) and the good agreement to results obtained by reference high performance liquid chromatography method at confidence interval for 95% probability. In this way, boron-doped diamond could represent an environmentally acceptable (green) alternative to highly toxic mercury electrodes for monitoring of pesticides.

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1. Introduction

Nowadays, the large amounts of various harmful chemicals are used in agriculture. These substances (usually organic compounds such as herbicides, insecticides and fungicides) are very persistent in the environment and their prolonged use involves the hazards of retention in soils. Subsequently they could pass into surface and ground waters due to washing and leaching processes. From these reasons, an enhancing attention is given to the increase of health risks associated with exposure of human population to harmful substances occurring in the environment. Their monitoring is one of the most important tasks of modern analytical chemistry [1].

Atrazine (IUPAC name: 6-chloro-*N*-ethyl-*N'*-isopropyl-1,3,5-triazine-2,4-diamine; ATZ) is the most known triazine herbicide with toxic effects on aquatic organisms. It has been used in the annual control of some grasses and broadleaf weeds in corn, sugar cane, pineapple, pinus and other cultures. Due to its low reactivity, water solubility and slow degradation, ATZ is reasonably stable, mobile and persistent in the environment for a longer period (half life varying among 20 and 100 days) [2,3]. In very small quantities, it may act as a carcinogen of type C and an endocrine disruptor

of the hormonal system [4]. ATZ is classified as a priority pollutant which use in agriculture is currently prohibited according to the EC legislation (Commission Decision 2004/248/EC) [5] as well as to the Slovak legislation (Parliamentary Act No. 364/2004 Coll., Government Ordinance No. 296/2005 Coll.). This herbicide belongs to the list of dangerous substances in Slovak Republic, whereby it has been considered within the document for lowering of water pollution especially by toxic and harmful compounds [6]. Because of these objectives, there is a still growing need for the development of sensitive and selective analytical methods for environmental monitoring of residual amounts of (prohibited) pesticides.

A literature research shows many reports describing various analytical methods for the determination of ATZ and other triazine herbicides in recent years. These particularly involve spectrophotometric [7] and especially chromatographic methods such as high performance liquid chromatography (HPLC) [8–11] and gas chromatography (GC) [12–14] which have become the most widely used analytical methods for determination of trace amounts of triazine herbicides because of their absolute best sensitivity and selectivity. However, these techniques require the complicated sample preparation usually involving the pre-concentration step prior to the analysis. In addition, they are expensive, time-consuming, solvent waste-producing as well as the demands for highly skilled personnel often restrict their use in routine analytical practice.

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The electrochemical methods are especially suitable for the environmental monitoring of heavy metals and electroactive organic pollutants. They are simple, inexpensive, sufficiently sensitive as well as they can represent an independent alternative to so far dominant spectrophotometric and chromatographic techniques [1]. Regarding the determination of ATZ, the enzyme biosensors and immunosensors are used [15,16] or processes occurring on mercury electrodes, such as hanging mercury drop electrode (HMDE) [17–19], static mercury drop electrode (SMDE) [20–22] and mercury film electrode (MFE) [23] are mostly exploited. These methods belong to the most sensitive ones thanks to the excellent electrochemical properties of mercury. On the other hand, the highly toxic nature of mercury insists on the necessary search for the alternative electrode materials. Therefore, the novel, simple and environmentally acceptable electrochemical tool for the sensitive environmental monitoring of pesticide residues is great of importance. The several solid electrode surfaces have been proposed for the determination of pesticides with the main target of avoiding the use of mercury. In this context, the solid amalgam electrodes are used due to the mechanic stability, easy preparation and nontoxicity. They also have solid and homogeneous surfaces that allow easy renewal by mechanical polishing and minimize the environmental mercury contamination since the amount of mercury discarded in analysis is minimal [24]. Bismuth film [25] and carbon paste electrodes either bare or modified [26,27] have also been designed in order to produce electroactivity for the detection and quantification of pesticides.

Generally, an irreversible adsorption of products of electrode reaction resulting in the passivation layer usually occurs in the electrochemical measurements. By the end of 20th century, a boron-doped diamond (BDD) as the new perspective carbon-based electrode material was discovered [28,29]. This electrode has the minimal noise due to the low residual current, good mechanical robustness, stability in both alkaline and acidic media, biocompatibility, the widest usable potential range from all electrode materials (up to 3 V) and minimal problems with passivation pertinent to sp³ character of diamond carbon [30]. The development of new electrochemical methods using BDD electrode can provide the invaluable services in the monitoring of compounds important in terms of protection of human health, environment and food chemistry. The recent reports of our working group have shown that several important biomolecules are able to be satisfactorily determined using BDD electrode [31–34].

In this paper, the voltammetric determination of ATZ using square-wave voltammetry on BDD electrode is described. Generally, to the best of our knowledge, the detection and determination of ATZ on this perspective and environmentally acceptable electrode material has not been previously investigated in literature with the exception of oxidation on BDD electrode for the mineralization of triazines including ATZ [35]. The practical applicability of proposed method is demonstrated in the determination of ATZ in spiked river water samples. The developed procedure could also find an application in environmental monitoring of other harmful organic compounds thanks to rapidity, simplicity and sensitivity.

2. Experimental

2.1. Chemicals

ATZ standard (CAS No. 1912-24-9, purity of 99%) was obtained from Sigma–Aldrich (Slovak Republic) and used as received without any further purification. The studied supporting electrolytes were hydrochloric acid, acetic acid, acetate buffer, phosphate buffer and Britton–Robinson buffer solution (Lachema Brno, Czech Republic). Britton–Robinson buffer solution was prepared from a mixture of

phosphoric acid (pK_a 2.14, 7.20 and 12.15), acetic acid (pK_a 4.75) and boric acid (pK_a 9.24, 12.74 and 13.80), with all components at concentration of 40 mM and adjusting to the required pH value with sodium hydroxide (0.2 M). All other chemicals were of analytical grade purity. Stock solution of ATZ (1 mM) was prepared by dissolution of solid standard in 5 mL of methanol and then diluted with double-distilled deionized water with resistivity above 18 MΩ cm. Working and calibration solutions of lower concentrations of ATZ were freshly prepared by diluting with supporting electrolyte. Acetonitrile (Merck, Czech Republic) was used as organic component in mobile phase for the purposes of HPLC analysis.

2.2. Apparatus

The voltammetric measurements were performed with an AUTOLAB PGSTAT 302 N (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat controlled by NOVA 1.9 electrochemical software. The three electrode system consisted of Ag/AgCl/3 M KCl and platinum wire as reference and counter electrode, respectively. BDD electrode inserted in polyether ether ketone (PEEK) body with disk inner diameter of 3 mm, resistivity of 0.075 Ωcm and boron doping level of 1000 ppm (declared by Windsor Scientific Ltd, United Kingdom as manufacturer) was used as working electrode. The glassy carbon (GC) with disk diameter of 2 mm was used as comparative working electrode (Metrohm, Slovak Republic). All the pH values of solutions were measured using pH meter Model 215 (Denver Instrument, USA) with combined electrode (glass-reference electrode), which was daily calibrated with standard buffer solutions. All the potentials reported in this paper were given against Ag/AgCl/3 M KCl reference electrode at a laboratory temperature of 25 ± 1 °C.

The determination of ATZ by HPLC as a reference (comparative) method was carried out using a Young Lin 9100 system, with Photodiode Array (PDA) detector set at 220 nm. A GraceSmart RP-18 (6.0 mm × 150 mm, 5 μm) chromatographic column was used. The mobile phase was mixture of acetonitrile–water (30:70, v/v) at flow rate of 1.0 mL min⁻¹, while the injection volume was 10 μL.

2.3. Measurement procedures

A particular volume of standard solution of ATZ was pipetted into a 20 mL volumetric flask, then filled up with the supporting electrolyte and transferred quantitatively into voltammetric cell. Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were employed for optimization study and quantification of ATZ, respectively. Ultrapure N₂ (O₂ < 2 ppm) was used to remove dissolved O₂ from each solutions and to provide an inert atmosphere inside the voltammetric cell. Five CV voltammograms were obtained for each measurement, and the last scan was always considered for evaluation and making the figures reported in this paper. SW voltammograms were recorded after optimization of instrumental parameters (step potential, frequency and amplitude). The peak currents (*I_p*) recorded using CV and SWV were evaluated from the straight lines connecting the minima before and after the peak maximum without background correction. In order to clean BDD electrode surface prior to start the first voltammetric measurement, CV measurements were performed from –2 to +2 V vs. Ag/AgCl electrode for 10 min in 1 M HNO₃. After this procedure, BDD electrode was rinsed with deionized water and polished with a piece of damp silk cloth until a mirror-like character of surface was attained. Calibration curve was constructed from the average of six replicate measurements for each calibration solution of ATZ and analyzed by linear least-square regression in OriginPro 8.0 (OriginLab Corporation, USA) with the relevant results (slope and intercept) reported with confidence interval for 95% probability. The detection limit was calculated as three times the standard deviation for the blank

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