



# Sensitive voltammetric method for rapid determination of pyridine herbicide triclopyr on bare boron-doped diamond electrode



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## ABSTRACT

Voltammetric method for the determination of a pyridine herbicide triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid) is presented for the first time using bare boron-doped diamond electrode. Triclopyr provides one well-developed, pH-independent oxidation signal at ca. +1.9 V (vs. Ag|AgCl|KCl (sat.)) contrary to structurally related clopyralid, which is not oxidizable at the working electrode. Britton–Robinson buffer (pH 2.0) was chosen as optimal electrolyte for determination of triclopyr using square wave and differential pulse voltammetry. The latter method provided slightly better detection limit of 0.82  $\mu\text{mol L}^{-1}$  and linearity in the concentration range 1.0–108.8  $\mu\text{mol L}^{-1}$ . Applicability of the proposed method was verified by analysis of pesticide preparation, spiked water and urine with excellent results.

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## 1. Introduction

Triclopyr (TCP, 3,5,6-trichloro-2-pyridyloxyacetic acid) is a selective, systemic, pyridine herbicide, which is mostly employed for a control of woody and herbaceous broadleaf plants along right-of-ways, in forests, and in parks. It has little or none effect on grasses. It acts as a synthetic growth hormone, which causes uncontrolled plant growth in the susceptible plants [1,2]. TCP is water soluble and non-persistent in surface waters due to the sunlight degradation. It has limited mobility and moderate capability of the accumulation in soils and constitutes a slight risk of a groundwater contamination. The average half-life of TCP in soils is about 30 days [1–3]. Generally, TCP has low toxicity to mammals and other wildlife but its derivatives or metabolites are moderately toxic to aquatic fauna [2,3].

Various analytical methods have been developed for sensitive and precise determination of TCP. The most commonly used one is gas chromatography (GC) with an electron capture [4] and mass spectrometric [5–7] detector. High performance liquid chromatography (HPLC) with various preconcentration techniques in combination with UV detector was also applied for determination

of TCP [8,9]. Recently, derivative spectrophotometric method was utilized as a tool for determination of TCP and other member of pyridine herbicide family (picloram) in a mixture [10]. Possibilities of TCP analysis using immunoassay methods were investigated as well [11,12].

The electrochemical methods have many advantages, especially the low costs of equipment, undemanding samples treatment, and particularly fast and sensitive performance of analysis and thus they can be found as a suitable alternative option to the above mentioned analytical techniques [13]. On the basis of the literature survey, any described electrochemical method was not found for detection of TCP but electrochemical reduction of structurally related compounds to TCP like picolinic acid [14], 6-chloropicolinic acid [15], clopyralid [16,17], 3,5,6-trichloro-4-methyl-pyridine-2-carboxylic acid [18], and picloram, e.g. in [17,19,20], has been widely investigated using working electrodes made of liquid mercury in various construction [14–17,19,20] or glassy carbon electrode [18].

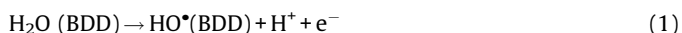
Boron-doped diamond (BDD) is one of the relatively novel and perspective electrode materials, which has been firstly described in the eighties [21] and has been widely investigated in electroanalysis in the last twenty years for its superior electrochemical properties such as a low and stable background over the wide potential range, high thermal conductivity, and chemical stability [22–24]. Application of this electrode material in

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electroanalysis of organic compounds has been reviewed e.g. in [22–27]. The newer and perspective trends include miniaturization of BDD sensors for their utilization in *in vivo/in vitro* analysis or for detection in capillary electrophoresis or micro total analytical systems [24,28,29], utilization of adsorptive techniques in the presence of surfactant interacting with organic analytes, which increases the selectivity and sensitivity of proposed methods [30,31], or modification of BDD surfaces and their utilizations in construction of BDD-based sensors (for details, see [32,33]). Promising strategies include e.g. amination or carboxylation of BDD surface to bond various receptor biomolecules [26,33,34], or covering of BDD thin films by molecularly imprinted conducting polymers such as polypyrrole [35,36].

At bare BDD electrodes, advantageous are primarily methods based on electrochemical oxidation due to extended potential window in aqueous or mixed aqueous-acetonitrile media. This is given by the high overpotential of oxygen evolution reaction, initiated by the one electron transfer from water under formation of hydroxyl radicals generated in the region of water decomposition as the first and rate determining step [22,26] (Eq. (1)):



Pesticides and their metabolites represent one group of compounds studied by means of bare BDD electrodes as demonstrated for carbamate pesticides [37,38], chloromethylphenoxy herbicides [39], fungicides kresoxim-methyl [40] and dimethomorph [41], triazine herbicide atrazine [42], insecticide methyl parathion and its degradation product 4-nitrophenol [43–47], insecticide mancozeb [48], and herbicide paraquat [49]. Our research group investigated the voltammetric behavior of pyridine herbicide picloram (PCR) on two types of BDD electrode – commercial [50–52] and self-assembled sensor [51,53]. The proposed reliable and sensitive methods were applied for analysis of model and spiked samples of natural and biological materials [50–53].

On the basis of the literature survey, any paper dealing with electrochemical determination of TCP using reductive processes or studies on its electrooxidation was not found. Thus, for the first time in this paper an electroanalytical approach using oxidation at bare BDD electrode, as a green and sensitive sensor is presented. The mechanism of electrooxidation has been proposed based on cyclic voltammetric experiments. Further, the used media and working parameters of pulse voltammetric techniques (differential pulse voltammetry (DPV) and square wave voltammetry (SWV)) have been optimized. Applicability of proposed methods was verified by analysis of spiked samples of complicated matrices (river water, urine) and pesticide preparation containing TCP salt. Further, the influence of potential interfering agents including selected heavy metals, pesticides and biomolecules possibly occurring in tested matrices was investigated.

## 2. Experimental

### 2.1. Reagents and materials

All used chemicals were of p.a. purity. Triclopyr of 99.9% purity declared by producer (Sigma–Aldrich, Germany) was used as received without any further purification. The standard solution of 0.01 mol L<sup>-1</sup> TCP was prepared by dissolution of an appropriate amount of TCP powder in 50% acetonitrile (Lach-ner, Neratovice, Czech Republic). The solution was stored in the dark in a refrigerator. Working solutions of TCP were prepared fresh daily by diluting of the standard solution in the supporting electrolyte.

Sulphuric, hydrochloric, and nitric acid and Britton–Robinson buffer solution (BRBS), consisting of 0.2 mol L<sup>-1</sup> NaOH and the same concentration (0.04 mol L<sup>-1</sup>) of orthophosphoric, boric and

acetic acid (all these chemicals Lachema, Brno, Czech Republic), were tested as supporting electrolytes. All solutions were prepared in distilled water.

Standard solutions of potential interfering agents, which could be present in the biological samples, such as ascorbic acid (AA), barbituric acid (BA), glucose (G), creatinine (C), sucrose (S), and urea (U) (all Sigma–Aldrich, Czech Republic), were prepared in distilled water. Solutions of folic acid (FA, Sigma–Aldrich, Czech Republic) and uric acid (UA) were, due to the better solubility in the alkaline media, dissolved in 0.01 mol L<sup>-1</sup> NaOH. The solutions of the heavy metal ions (Tl<sup>+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>) were also prepared by dissolving of the appropriate amount of their salts (Zn (NO<sub>3</sub>)<sub>2</sub> × 2H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub> × 2H<sub>2</sub>O, and Cd(NO<sub>3</sub>)<sub>2</sub> × 4H<sub>2</sub>O (all Lachema, Brno, Czech Republic)) in the distilled water or by dilution of the calibration standard solution (TlNO<sub>3</sub> (Analytika, Prague, Czech Republic)). The stock solutions of herbicides (all Sigma–Aldrich, Czech Republic; clopyralid (CLP), picloram (PCR), triasulfuron (TS) and linuron (LIN)) were prepared by dissolving of the calculated amount of the herbicide in 50% acetonitrile (Lach-ner, Neratovice Czech Republic); glyphosate (GLY; Sigma–Aldrich, Czech Republic) was dissolved in the distilled water.

### 2.2. Instrumentation

All measurements were carried out in three electrodes set up, where Ag|AgCl|KCl (sat.) served as a reference and platinum wire as a counter electrode (both Monokrystal, Turnov, Czech Republic). BDD electrode inserted in polyether ether ketone body with inner diameter of 3 mm, resistivity of 0.075 Ω cm and B/C ratio during deposition step of 1000 ppm (declared by Windsor Scientific, Slough Berkshire, United Kingdom as a producer) was used as a working electrode in all experiments. The voltammetric measurements were performed by AUTOLAB PGSTAT 12 (Metrohm Autolab, The Netherlands) potentiostat/galvanostat controlled by NOVA 1.10 software. All measurements were carried out at laboratory temperature (23 ± 2 °C). The pH values were measured by pH-meter Hanna 221 (Hanna Instruments, USA).

### 2.3. Procedures

#### 2.3.1. Voltammetric measurements

In the first set of experiments – effect of supporting electrolyte and scan rate – cyclic voltammetry (CV) scans were measured between –1.0 V and +2.2 V at scan rate ( $\nu$ ) of 100 mV s<sup>-1</sup> and linear sweep voltammetry (LSV) measurements were carried out with initial potential ( $E_{in}$ ) 0 V, final potential ( $E_{fin}$ ) +2.4 V and  $\nu = 10 - 1000$  mV s<sup>-1</sup>. DPV was used with the following working parameters (if not stated otherwise):  $E_{in} = +0.6$  V,  $E_{fin} = +2.2$  V, step potential of 0.01 V,  $\nu = 20$  mV s<sup>-1</sup>, modulation amplitude of 0.075 V and modulation time of 0.025 s. SWV was applied with the subsequent working parameters (if not stated otherwise):  $E_{in} = +1.0$  V,  $E_{fin} = +2.3$  V, step potential of 0.05 V, amplitude 0.04 V and frequency 50 Hz. All DP and SW voltammetric measurements were carried out in BRBS pH 2.0.

At the beginning of every work day, the surface of BDD electrode was rinsed with deionized water and anodically pretreated by applying +2.0 V during 60 s in 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution followed by –2.0 V for 60 s. Finally, 20 cyclic voltammograms from –1.0 V to +2.0 V in 1 mol L<sup>-1</sup> HNO<sub>3</sub> were measured to obtain stable response. Between individual measurements, the solution was stirred for 5 s.

The linear least-square regression in OriginPro 9 (OriginLab Corporation, USA) was used for the evaluation of calibration curve and the relevant results (slope and intercept) were reported with confidence interval for 95% probability. The limit of detection (LOD) and quantification (LOQ), respectively, was calculated as three times (LOD) and ten times (LOQ), the standard deviation of

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