

# Square-wave voltammetric determination of fungicide fenfuram in real samples on bare boron-doped diamond electrode, and its corrosion properties on stainless steels used to produce agricultural tools



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## ABSTRACT

A simple, selective, and sensitive electroanalytical method for the determination of a novel fungicide, fenfuram (*Fnf*), on a bare boron-doped diamond electrode (BDDE) using square-wave voltammetry (SWV) was developed. For the first time, the electrochemical oxidation of *Fnf* at BDDE at about 1.5 V vs. Ag/AgCl reference electrode in 0.35 mol L<sup>-1</sup> sulfuric acid was investigated. To select the optimum experimental conditions, the effects of the supporting electrolyte, pH, frequency, amplitude, and step potential were studied. The developed method allowed the determination of *Fnf* in the concentration range of  $2.4 \times 10^{-5}$  to  $2.6 \times 10^{-4}$  mol L<sup>-1</sup> ( $LOD = 6.3 \times 10^{-6}$  mol L<sup>-1</sup>,  $LOQ = 2.1 \times 10^{-5}$  mol L<sup>-1</sup>). The validation of the method was carried out. The proposed procedure was successfully applied to determine *Fnf* in the spiked natural water samples collected from Polish rivers and in the spiked triticale seed samples by the standard addition method. To understand the *Fnf* electrode mechanism, the cyclic voltammetry (CV) technique was applied. The oxidation mechanism was also confirmed using mass spectrometry with the electrospray ionization (ESI-MS) technique. Using electrochemical techniques, the effect of *Fnf* on the corrosion properties of stainless steel which is used to produce agricultural tools was studied.

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## 1. Introduction

Fenfuram (*Fnf*, 2-methylfuran-3-carboxanilide, CAS Reg. No. 24691-80-3, Fig. 1) is a new-generation systemic fungicide containing anilide group bonded to a furan ring, which is used in cereal seed treatments. *Fnf* is highly active as a seed dressing against the smuts and bunts of temperate cereals. It controls *Tilletia* and *Ustilago* spp. including *Ustilago nuda*. *Fnf* was discovered by Shell Research Ltd. and developed by Aventis CropScience in 1974 [1,2].

Although *Fnf* is a compound of biological interest [3–5], the published data regarding the analytical studies are very limited. To the best of our knowledge, only several multiresidue pesticide analytical methods have been developed and reported [6–8]. Moreover, no information about the electrochemical behavior of *Fnf* has been so far reported in the scientific literature. Therefore,

for the first time, this paper describes an electrochemical study of *Fnf* on a bare boron-doped diamond electrode (BDDE) and methods for its square-wave voltammetric (SWV) determination in spiked natural river waters and triticale samples. Also, using electrochemical techniques, this paper is the first to report the effect of *Fnf* on the corrosion properties of stainless steel which is used to produce agricultural tools.

Nowadays, pesticides are important in the protection of agricultural production. Although using pesticides solves the problem of unwanted pests and weeds, unfortunately it also constitutes a risk of environmental pollution. Generally, pesticides are toxic for living organisms, and they are usually persistent in the environment and can be accumulated in the human body through the food chain [9].

The study of the effect of *Fnf* on the corrosion properties of metal substrates is equally important since many commercial chemicals used in farming, including pesticides, may be significantly corrosive. The elements most exposed to the corrosive effects of pesticides are the metal parts of agricultural tools and equipment [10]. The literature sources report the corrosivity of some pesticides when in contact with aluminum, brass, steel [10],

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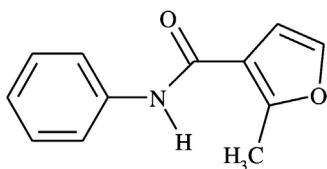


Fig. 1. Chemical structure of *Fnf*.

and copper [11]. The resistance against uniform and pitting corrosion may be determined under laboratory conditions. Typical corrosion tests are performed using electrochemical methods such as polarization resistance (linear polarization) and potentiodynamic anodic polarization [12,13].

There exist many papers that deal with the analytical determination of pesticides. Chromatographic methods are by far the most frequently used methods for the detection of pesticide residues. Nevertheless, these methods are relatively expensive, instrumentally demanding, and time consuming. Electrochemical methods represent an appropriate alternative to the aforementioned analytical methods, particularly because of their operation simplicity, satisfactory sensitivity, wide linear concentration range, low cost of instrumentation, possibility of miniaturization, and suitability for real-time detection [14]. Thus, they are suitable for large-scale monitoring of different electrochemically active environmental pollutants [15,16].

Nowadays, there is an increasing demand for sensors which not only are able to give a stable response, in short time, but also are sensitive, selective, with high precision, and inexpensive. Development of new electrode materials is one of the current trends of electrochemistry. Boron-doped diamond electrode (BDDE) is one such relatively new-generation environmentally friendly electrode. Since the first report on its analytical applications in 1993 [17], BDDE became a popular electrode material for electroanalysis because of its commercial availability and advantageous electrochemical properties, such as very low and stable background current, wide working potential window, and high current density [18,19]. It also exhibits excellent physical and chemical robustness [20]. Furthermore, high hardness, high thermal conductivity, and chemical inertness of the electrode [21] offer quick and reliable analysis. BDDE has been successfully applied in the voltammetric analysis of biologically active compounds [9,14,19,22–33].

The aim of this work was to develop the procedure to determine *Fnf* on a bare BDDE and methods for its SWV determination in spiked natural river waters and triticale samples. Moreover, to understand the process of *Fnf* electrode mechanism, the cyclic voltammetry (CV) was also applied. To confirm the *Fnf* oxidation mechanism, mass spectrometry with the electrospray ionization (ESI-MS) technique was used. Furthermore, the effect of *Fnf* on the corrosion properties of stainless steel which is used to produce agricultural tools was studied using several electrochemical methods (linear polarization close to  $E_{cor}$  for corrosion rate determination, and potentiodynamic anodic polarization to characterize the resistance to pitting corrosion).

## 2. Experimental

### 2.1. Instrumentation

SWV and CV were carried out using an Autolab PGSTAT 128N potentiostat–galvanostat (Metrohm Autolab B.V., Utrecht, the Netherlands) controlled by GPES software and an M164 electrode stand (MTM Anko Instruments, Cracow, Poland). The cell stand included a three-electrode system with a silver/silver chloride electrode/potassium chloride ( $\text{Ag}/\text{AgCl}$ ,  $3.00 \text{ mol L}^{-1}$  KCl) as a

reference electrode; a platinum wire as a counter electrode; BDDE inserted in polyether ether ketone body with inner diameter of 3 mm, electrical resistivity of  $0.075 \Omega \text{ cm}$  and B/C ratio during deposition step of 1000 ppm (declared by Windsor Scientific Ltd. United Kingdom as a producer) as a working electrode.

The pH measurements were made on an Orion Star pH meter (Model A111, Thermo Scientific, the Netherlands) with a pH electrode (type Polilyte Lab Hamilton, Switzerland).

ESI-MS measurements were performed on a Varian 500-MS LC ion-trap mass spectrometer (Varian, Palo Alto, CA, USA).

Corrosion tests were carried out using an Autolab PGSTAT 30 potentiostat–galvanostat (EcoChemie Autolab B.V., Utrecht, the Netherlands) controlled by GPES, version 4.9 software. Corrosion measurements were performed in a three-electrode electrolytic cell consisting of an AISI Type 316L stainless steel (Medgal, Poland) as a working electrode with an exposed area of  $0.64 \text{ cm}^2$ , a saturated calomel electrode ( $E = 0.236 \text{ V}$  vs. standard hydrogen electrode) as a reference electrode, and a platinum foil as a counter electrode. The corrosion damage was characterized using an optical microscope MMT 800BT (mikroLAB, Lublin, Poland).

The topography of BDDE surface was characterized by an atomic force microscope Dimension Icon (Bruker, Santa Barbara, CA, USA). The atomic force microscopy (AFM) measurements were performed in tapping mode using silicon probe with nominal spring constant of  $42 \text{ N} \cdot \text{m}^{-1}$  and resonance frequency of 320 kHz.

### 2.2. Reagents and Solutions

All chemicals used were of analytical reagent grade (POCH SA Gliwice, Poland; Sigma-Aldrich, Poland). The analytical standard of *Fnf* (CAS No. 24691–80–3) was purchased from Sigma-Aldrich, Poland. The *Fnf* stock solution ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ) was prepared in a glass flask by dissolving exact weight of the reagent in water–acetone mixture (1:1, v/v). All chemicals for the preparation of Britton–Robinson (B–R) buffer ( $0.04 \text{ mol L}^{-1}$ , pH 2.1–10.2) and sulfuric acid ( $0.05$ – $0.5 \text{ mol L}^{-1}$ ) as supporting electrolytes were of analytical reagent grade (POCH, Merck or Sigma-Aldrich). All solutions were prepared in triply distilled water. All electrochemical measurements were carried out at the laboratory temperature. Argon (5N, Linde gas, Poland) in electrochemical measurements was used without further purification. All solutions were stored at  $4.0^\circ \text{C}$  in a refrigerator. Sodium chloride of analytical reagent grade (POCH SA Gliwice, Poland) was used as the corroding medium. Corrosion tests were performed in a 3.5% solution of NaCl prepared in water–acetone mixture (1:1, v/v) both with and without the addition of *Fnf* ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ). The solutions were used in corrosion tests without further deoxygenation. Methanol (Baker HPLC Analyzed, HPLC Gradient Grade) was used as a solvent in ESI-MS measurements, and helium (5N, Linde gas, Poland) was used as the nebulizing gas.

### 2.3. Measurements Procedure

#### 2.3.1. Voltammetric procedures

The surface of the BDDE was polished using  $0.3 \mu\text{m}$  alumina slurry on a polishing pad with subsequent washing with water. Prior to each measurement, the electrodes were immersed into a methanol and sonicated for 5 min.

The general procedure used to obtain the SW voltammogram was as follows: A volume of 10 mL of the supporting electrolyte ( $0.35 \text{ mol L}^{-1}$  sulfuric acid) was transferred to the voltammetric cell. When an initial blank was recorded, the required volumes of *Fnf* solutions were added using a micropipette. SWV scanning was performed in the range 0–1.8 V, for which frequency, amplitude, and step potential were 120 Hz, 60 mV, and 10 mV, respectively.

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