



# Amperometric quantification of the pesticide ziram at boron doped diamond electrodes using flow injection analysis



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## ABSTRACT

In this paper sensitive and selective quantification of the pesticide ziram exploiting its oxidation at a boron doped diamond (BDD) electrode is evaluated. The voltammetric behavior of the pesticide shows in acidic media three well-defined oxidation peaks. For quantification an analytical procedure based on flow injection analysis has been developed. Under optimized experimental conditions a linear dynamic range from 10 to 1000 nM was obtained. The limit of detection (LOD) was estimated to be 2.7 nM. After evaluation of effects from possible interferences, the proposed procedure was successfully applied to real samples.

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## 1. Introduction

Ziram, zinc dimethyl-dithiocarbamate, is a pesticide which belongs to the dithiocarbamate group of widely used agricultural fungicides [1,2]. Cuman L is a commercially available product which contains 27% ziram in the form of micronized particles for greater effectiveness against blast and other fungal diseases. This compound also found uses in rubber industry as vulcanization accelerator. It shows low phytotoxicity and therefore it is nowadays widely used as a pesticide [1,3–5]. Up to date in the literature several analytical approaches are described dominantly based on chemiluminescence [6], chromatography [7,8] and spectrophotometry [9,10]. To the best of our knowledge, only one electroanalytical procedure is presented in the literature for the determination of ziram [2]. The method, like most procedures for the determination of pesticides with similar structure [11,12], is based on the determination of the metal components in these compounds predominantly with mercury electrodes. Due to the toxicity of mercury and a global mercuriphobia these electrodes are becoming eventually obsolete nowadays.

The aim of this work was to develop an analytical procedure for the sensitive and selective determination of ziram, based on its oxidation using a BDD electrode. For this purpose flow injection analysis was used. The electrochemical behavior of ziram was

studied by cyclic voltammetry and experimental parameters were investigated.

## 2. Experimental

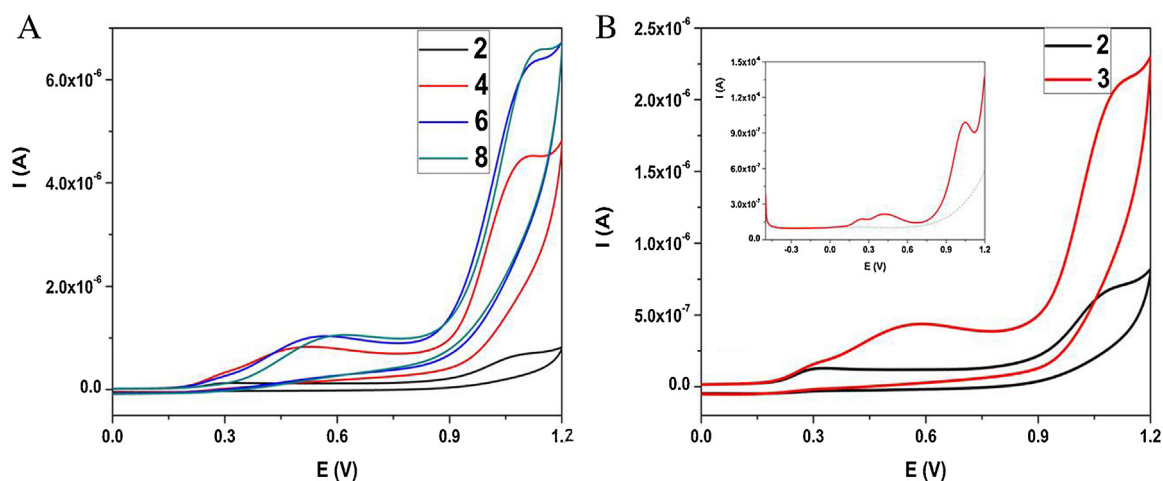
### 2.1. Apparatus and reagents

All reagents used in this study were of analytical grade. Ziram, boric acid, sodium hydroxide, acetic acid and phosphoric acid were purchased from Sigma Aldrich. A stock solution ( $10^{-4}$  M) of the pesticide was prepared in acetonitrile. Britton-Robinson buffer solution was used as the supporting electrolyte and was prepared by mixing aqueous solutions of boric, phosphoric and acetic acid (each 0.04 M), respectively. The pH value was adjusted with sodium hydroxide (0.2 M).

Voltammetric measurements were performed using a potentiostat/galvanostat (AUTOLAB PGSTAT 302N, Metrohm Autolab B.V., The Netherlands). The electrochemical cell (total volume 20 mL) was equipped with a boron-doped diamond working electrode embedded in a polyether ether ketone (PEEK) body with an inner diameter of 3 mm, a resistivity of  $0.075 \Omega \text{ cm}$  and a boron doping level of 1000 ppm (as indicated by the supplier, Windsor Scientific Ltd, Slough, Berkshire, UK), an Ag/AgCl (3 M KCl) as a reference electrode, and a Pt wire as a counter electrode. The system for flow injection analysis was set up from a peristaltic pump (model P-1, Pharmacia, Ealing, London), an injection block (Rheodyne 5020, Cotati, CA, USA) with a  $100 \mu\text{L}$  loop and an electrochemical thin layer flow cell (spacer thickness 0.19 mm, CC5, BAS, West Lafayette, Indiana, USA) in combination with a potentiostat (100B, BAS)

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**Fig. 1.** Cyclic voltammograms of 0.01 mM of ziram at BDD electrode in various pH (A, B; numbers indicate pH) the scan rate of 100 mV/s. Inset of figure B presents differential pulse voltammograms in presence and absence of 0.01 mM of ziram (pH 4.0); working electrode—BDD, supporting electrolyte BRBS—0.04 M, scan rate—100 mV/s.

operated with the corresponding software (100W, version 2). The thin layer cell was equipped with the working electrode (BDD) and an Ag/AgCl reference electrode (3 M KCl, BAS-RE-4) stored in 3 M KCl when not in use. The counter electrode was the steel plate of the electrochemical cell. The current flow was monitored in dependence of time.

All potentials reported in this paper are referred against the above mentioned reference electrode. The measurements were done at an ambient temperature. pH values were measured with a pH meter (model Orion 1230) equipped with a combined glass electrode (model Orion 9165BNWP). Prior to the start of the first measurement, the BDD electrode was rinsed with deionized water and gently rubbed with a piece of damp silk cloth until a mirror-like appearance of the surface was obtained (with minimal probability of mechanical damage of surface). Subsequently, it was anodically pretreated by setting +2.0V for 180 s in 1 M H<sub>2</sub>SO<sub>4</sub> in order to clean the electrode surface followed by a cathodic pretreatment at -2.0V during 180 s to renew the hydrogen terminated surface of the working electrode [13].

### 2.1.1. Sample analysis

Samples of river water (W1 and W2) were collected from the river Mur, Graz, Austria, at two different places and stored at 4 °C before use. Before use the samples were filtered through 0.45 μm filters and spiked with certain amounts of standard ziram solution followed by 10 times dilution with the supporting electrolyte.

## 3. Results and discussion

### 3.1. Electrochemical behavior of ziram at BDD electrode, influence of pH of supporting electrolyte

The electrochemical behavior of 0.01 mM of ziram using the BDD electrode in BRBS at various pH was evaluated using CV at scan rate of 50 mV/s. In the positive potential range oxidation of the dithiocarbamate ligand from ziram occurs. In strongly acidic media at pH 2, ziram provides two oxidation peaks (I and III). With increasing of pH, the cyclic voltammograms indicate a three-step oxidation of ziram (I, II and III, see Fig. 1A). In the reverse scan no reduction peaks were observed. Increase of the scan rate is followed with an increase of the oxidation currents of the second and third peak. At pH higher than 5, the first and second peak are overlapping and in this media the oxidation of ziram appears as a two-step process (Fig. 1B). The three-step oxidation of ziram was confirmed with the peaks with better resolution using differential pulse voltammetry

(inset of Fig. 1B). The dependence of anodic peak potentials (II and III) on the pH of supporting electrolyte was also studied. It was shown that increase of pH is accompanied with slight changes of peak potential of the second peak (II) whereas the peak potential from third peak remained practically constant. According to the literature dealing with structurally similar compounds, the first step is probably a one electron oxidation of the dithiocarbamate anion with the formation of a radical followed by a chemical reaction and dimerization. The second oxidation peak current increases rapidly with pH and this reaction can be explained similar the first peak, while the third peak can be attributed to the formation of disulfide species [14,15].

According to these measurements a pH of the supporting electrolyte of 4.0 and a working potential for the amperometric detection of +0.55 V were selected. At the chosen pH numerous organic compounds which could interfere (some phenols, and some tested structurally similar compound) require higher positive potentials to be oxidized than the operating potential used here, and, therefore, do not deteriorate the determination of ziram.

### 3.2. Flow injection analysis measurements

For FIA measurements the operating potential was set to +0.55 V, and the flow rate was optimized. It is important that the contact between electrode surface and the analyte lasts sufficiently long to obtain optimum signals. It was observed that with increasing the flow rate from 0.2 to 0.4 mL/min the peak current linearly increased as expected (data not shown) because a longer residence time in the capillary provokes a higher dispersion (and consequently a lower concentration) of the analyte in the carrier and a thinner diffusion layer. Further increase of the flow rate was accompanied with a decrease of the oxidation peak current due to diffusion effects; thus, a value of 0.4 mL/min was selected as optimum and used for all further experiments.

Calibration curves were constructed by plotting the oxidation peak currents obtained with FIA measurements versus the concentration of ziram (Fig. 2A and B). Under optimized experimental conditions the BDD electrode showed a linear working range from 10 to 1000 nM. The corresponding linear equation can be expressed as  $I(\mu\text{A}) = 15.66 + 0.31 c (\text{nM})$  with a regression coefficient of 0.9938. The limit of detection (LOD =  $3 \times \sigma_{\text{intercept}}/\text{slope}$ ) for the proposed method was calculated to be 2.7 nM. The relative standard deviations of five sequential injections of two different concentrations of 20 and 200 nM during one FIA run were 2.9 and 2.4%, respectively.

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