



Carbon-fibre microelectrodes coupled with square-wave voltammetry for the direct analysis of dimethomorph fungicide in natural waters

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ABSTRACT

This paper describes the development and electrochemical behaviour of a quick, easy, cheap and eco-friendly electroanalytical procedure for the direct analysis of dimethomorph fungicide (DIM) in natural water samples using a carbon-fibre microelectrode (CFM) coupled with square-wave voltammetry (SWV). The optimized experimental and voltammetric parameters employed were a 0.04 mol L⁻¹ Britton–Robinson buffer (pH 3.0), a pulse potential frequency of 70 s⁻¹, a pulse amplitude of 30 mV and a scan increment of 2 mV. It was possible to observe a well-shaped oxidation peak at +1.25 V (vs. Ag/AgCl/saturated Cl⁻), which was related to a two-electron transfer in the quasi-reversible redox process affected by a strong adsorption of reactants and products on the electrode surface. Analytical parameters such as linearity range, correlation coefficients, detection and quantification limits were evaluated and compared to similar results obtained using gas chromatography coupled with mass spectrometry. However, by using SWV, no clean-up, extraction or pre-concentration procedures were necessary, making the electroanalytical procedure more feasible for analytical routine analysis.

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1. Introduction

In recent years, the requirement for the production of high-yield and high-quality crops has increased the variety and quantity of pesticides employed in production, transport and particularly in the storage of agricultural products. Around 800 types of pesticides are widely used today in agricultural practices, and their intensive and abusive use has led to an increase in the levels of residues present in soils, waters and foods [1].

One particular kind of chemical pesticide associated with the protection and conservation of agricultural compounds is the morpholine class; these are used as systemic fungicides with protective and curative properties to control powdery mildew and to prevent Peronosporales germ disease in vegetables and fruits [2]. Additionally, some morpholines have been listed as potential endocrine disruptors, due to being potent inhibitors of the human sterol isomerase enzyme, which is part of the cholesterol biosynthesis pathway [3].

Among these compounds, dimethomorph {(E,Z)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloyl]morpholine} (DIM), is also suspected to be an endocrine disruptor, interfering in the functioning of the hormonal system in humans and animals [4]. Despite its beneficial effects for agricultural practices, DIM shows marked toxicity

for both humans and other living organisms, including soil and water microflora, by modifying DNA profiles, causing undesirable genetical changes. After its application, DIM can accumulate in the environment, such as in surface and ground waters, waste water, sludge, soils, food and other food products. Furthermore, it can concentrate in living organisms, changing important biological functions, even at very low concentrations [5].

As a consequence of the environmental and health problems surrounding the use of DIM, several precise and sensitive analytical procedures have been developed all around the world for DIM quantification in a variety of food samples. All previously published studies have described the simultaneous analysis of a large number of agrochemical compounds, including DIM, employing liquid [6–9] or gas [10,11] chromatography in tandem with mass spectrometry. In these studies, the procedures required a previous step of extraction and clean-up of the samples.

In spite of the fact that DIM presents significant solubility in water, and thus can be released in the environment, no methodology for its detection in natural water samples can be found in the available literature. Furthermore, to the best of our knowledge, no study using electroanalytical procedures to determine DIM, in any type of matrix, has been previously reported. For this reason, the aim of this study was the development of a quick, easy, cheap and eco-friendly electroanalytical procedure for the direct analysis of DIM in natural water samples using a carbon-fibre microelectrode (CFM) in combination with square-wave voltammetry (SWV).

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Several electroanalytical methods using microelectrodes, including CFM, have been used in a variety of applications due to their advantages over conventional electrodes [12]. The high current densities measured (due to spherical diffusion), the minimized ohmic drop and capacitive effects that make possible an increase in the signal-to-noise ratio, fast responses and the effects of insensitivity in the convection process, allow the working of the microelectrode in organic solvents of low dielectric constant in the study of fast electron transfer reactions, coupled reactions, in flow systems and in vivo analysis [13]. In particular, CFMs are constituted by carbon fibres with small diameters that range from several micrometres to several tens of micrometres, which offers some advantageous properties including a wide-ranging positive potential window, simplicity of construction and low cost. As a consequence of these properties, CFMs can be used in the analytical determination of various pesticides in different samples, without pre-treatment or clean-up steps, thus offering an excellent alternative to the use of chromatographic techniques [14].

Among the electroanalytical techniques currently available for use with CFM [15], SWV has proved to be extremely sensitive for the detection of several pesticides [16–18]. Their use, by the appropriate application of a well-developed theoretical model considering current and potential responses, allows valuable information concerning the kinetics and mechanisms of electron transfer to be obtained. This information is important to identify the intermediate reactive species, to elucidate the mechanism of action of pesticides and also to supply information about its redox properties in the environment. This is due to the fact that redox reactions that occur in the environment can be compared with redox reactions that occur at the electrified interface (electrode/solution) when electroanalytical techniques are employed [19].

2. Experimental section

2.1. Reagents and equipment

Electrochemical measurements were carried out using a potentiostat (Autolab PGSTAT 30, Metrohm-Eco Chemie) equipped with a low-current module (low-current measurements with resolutions down to 0.3 fA), controlled by a personal computer, using GPES version 4.9 software (General Purpose Electrochemical System, Metrohm-Eco Chemie). An Ag/AgCl/saturated Cl⁻ electrode was used as the reference electrode while the working electrode was a lab-made electrode constructed from carbon-fibre micro-wire.

A Micronal B474 pH meter equipped with a 3.0 mol L⁻¹ Ag/AgCl/KCl-glass combined electrode was used to adjust the pH values. All the solutions were prepared with water purified by a Milli-Q system (Millipore Corp.).

A stock solution of 1.0 × 10⁻³ mol L⁻¹ of DIM (CAS: 110488-70-5), kindly supplied by Bayer-Brazil, was prepared daily by dissolving an appropriate quantity in acetonitrile and stored in a dark flask. A 0.04 mol L⁻¹ of Britton–Robinson (BR) buffer, prepared as described in a previous paper [20], was used as the supporting electrolyte and the pH was adjusted to the desired value by adding appropriate amounts of 1.0 mol L⁻¹ NaOH stock solution.

A gas chromatography-mass spectrometer (GC-MS) system from Shimadzu, model GCMS-QP2010, equipped with a mass spectrophotometer detector, in conjunction with a 30 m DB1-MS J&W Scientific capillary column (100% methylpolysiloxane, 0.25 mm i.e., 1 mm film thickness) was employed in chromatography data acquisition. Instrument operation and data processing was carried out with Labsolution (GC-MSsolution, release 2.30) software.

2.2. Construction and characterization of the microelectrode

The CFM was constructed from a 7 μm diameter carbon-fibre wire produced by CTA-Brazil. The micro-wires were inserted into a 1.0 mL tip pipette and filled with epoxy resin. After this, the CFM was

polished using a mechanical polisher and glass paper of different granulations. Finally, the microelectrode was cleaned with water and a microdisk surface was obtained.

The voltammetric characterization was carried out by studying the electrochemical response of the potassium hexacyanoferrate (III) solutions in acid medium, due to its well-established behaviour, and the voltammograms exhibited sigmoid profiles, characteristic of the utilization of microelectrodes [13].

2.3. Electrochemical working procedure

All measurements were performed under ambient conditions. A two-electrode configuration was used with the reference electrode (Ag/AgCl/saturated Cl⁻) also acting as counter electrode, and CFM with 38.5 μm² of electroactive surface as working electrode. The appropriate solutions were transferred into the electrochemical cell and the optimization of the analytical procedure for SWV was carried out following a systematic study of the experimental parameters, such as pH of the medium, the pulse potential frequency (*f*), pulse amplitude (*a*) and the height of the potential step (ΔE_s) or scan increment, for a potential window ranging from 0 to +1.45 V.

All parameters were properly optimized since their values exert considerable influence on the sensitivity of voltammetric measurements [15,21]. The optimization was related to the maximum value of peak current and the maximum selectivity (half-peak width). Before each experiment, a stream of N₂ was passed through the solution for 2 min to renew the electrode surface by removal of adsorbed products.

To accomplish that which has been mentioned above, the working electrode was placed in a measuring cell filled with 10 mL of a supporting electrolyte solution, and before initiating the measurements, some cyclic voltammograms at fast scan rates, in the potential interval of the DIM oxidation process, were carried out for the best results of the CFM. A known concentration of DIM was added to the cell and the experimental and voltammetric parameters were studied. In all measurements, the electrochemical cell was placed in a Faraday cage in order to minimize background noise.

After the optimization of voltammetric parameters, analytical curves were obtained in pure electrolyte by the standard addition method. The standard deviation of the mean current measured at the oxidation potential of DIM for 10 voltammograms of the blank solution in purified electrolyte was used (*S_b*) [22,23] in the determination of the detection and quantification limits (DL and QL, respectively) together with the slope of the straight line of the analytical curves (*b*) as follows:

$$DL = \frac{3S_b}{b} \quad (1)$$

$$QL = \frac{10S_b}{b} \quad (2)$$

The recovery experiments were carried out by adding a known amount of DIM to the supporting electrolyte followed by standard additions from the DIM stock solution and plotting the resulting analytical curves. All measurements were performed in triplicate. The recovery efficiencies (%R) were calculated using Eq. (3). Here the value [DIM]_{found} refers to the concentration obtained by extrapolating the analytical curves of the corresponding spiked samples:

$$\%R = \frac{[DIM]_{found}}{[DIM]_{added}} 100 \quad (3)$$

The precision and accuracy of the methodologies were tested with different standard solutions of DIM and the relative standard deviations (RSD) were calculated as follows:

$$RSD = \frac{S}{\bar{x}} \quad (4)$$

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