



Voltammetric analysis of mancozeb and its degradation product ethylenethiourea



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ABSTRACT

The purpose of this work was to develop a reliable alternative method for the determination of the dithiocarbamate pesticide mancozeb (MCZ) in formulations. Furthermore, a method for the analysis of MCZ's major degradation product, ethylenethiourea (ETU), was also proposed. Cyclic voltammetry was used to characterize the electrochemical behavior of MCZ and ETU, and square-wave adsorptive stripping voltammetry (SWAdSV) was employed for MCZ quantification in commercial formulations.

It was found that both MCZ and ETU are irreversibly reduced (-0.6 V and -0.5 V vs Ag/AgCl, respectively) at the surface of a glassy carbon electrode in a mainly diffusion-controlled process, presenting maximum peak current intensities at pH 7.0 (in phosphate buffered saline electrolyte).

Several parameters of the SWAdSV technique were optimized and linear relationships between concentration and peak current intensity were established between 10 – 90 $\mu\text{mol L}^{-1}$ and 10 – 110 $\mu\text{mol L}^{-1}$ for MCZ and ETU, respectively. The limits of detection were 7.0 $\mu\text{mol L}^{-1}$ for MCZ and 7.8 $\mu\text{mol L}^{-1}$ for ETU. The optimized method for MCZ was successfully applied to the quantification of this pesticide in two commercial formulations. The developed procedures provided accurate and precise results and could be interesting alternatives to the established methods for quality control of the studied products, as well as for analysis of MCZ and ETU in environmental samples.

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1. Introduction

Dithiocarbamates (DTCs) are important organosulfur compounds discovered in the 1930s, usually used as pesticides to treat a wide variety of fungal diseases in plants [1,2]. Due to their high activity and low production costs, they have been applied on a large scale throughout the world on several types of crops. Furthermore, due to the possibility of their combination with new generation systemic fungicides these compounds are quite successful for the management of disease resistance, especially in horticultural crops [3,4]. Based on their carbon skeleton, DTCs can be categorized into three subclasses: dimethyldithiocarbamates (DMDs), ethylenebis(dithiocarbamates) (EBDCs), and propylenebis(dithiocarbamates) (PBDs). They are mainly complexed with transition metals (e.g., manganese or zinc) [5]. DTCs are medium to highly toxic substances, depending on their structure [6].

Mancozeb (MCZ; manganese ethylenebis(dithiocarbamate) (polymeric) complex with zinc salt), a broad spectrum fungicide with multi-site contact activity, is one of the most widely used protective fungicides in the world and constitutes 50% of the market share of the

EBDC fungicides [5,7]. MCZ is used to protect fruits and vegetables from foliar diseases and is also employed in the protection of such products during their storage and transportation. MCZ strongly adsorbs to soil particles and usually does not move below the upper layer of the soil [6]. MCZ is easily degraded to ethylenethiourea (ETU) in the presence of moisture or oxygen and biological systems [8,9]. This degradation product is more toxic than the parent compound. ETU is suspected to cause thyroid and neurotoxic effects and induces carcinogenesis, mutagenesis, and teratogenesis [10,11].

The analysis of DTCs is complex because of their insolubility in most solvents, their ability to form stable complexes with a variety of metal ions and their instability, which is promoted by oxygen, moisture, pH, temperature, and especially plant components [8,9].

There are several analytical methods available for DTC determination based on the use of spectrophotometry [12], capillary electrophoresis [8,13], gas chromatography [4,14], high-performance liquid chromatography [10,14,15], DART-TOF mass spectrometry [16], (adsorptive-stripping) voltammetry [2,17], batch injection analysis with amperometric detection [18], enzyme-linked immunosorbent assay [19], and flow injection-Fourier transform infrared spectrometry [20]. Many of these methods are based on the acid hydrolysis of DTCs in the presence of tin(II) chloride and the subsequent analysis of CS₂,

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H₂S, or amines [8]. However, these methods present some disadvantages because they are time consuming, expensive and environmentally unfriendly. Although electrochemical determinations of DTC have been described [2,17], they are based on the use of mercury electrodes. Mercury is toxic and has negative effects on the environment and human health. Therefore, its use constitutes a major drawback.

The aim of this work was to develop a simple, fast and cost-effective electrochemical method for MCZ and ETU detection and quantification in real samples. This proposed voltammetric method is environmentally friendly and is based on the study of the electrochemical reduction of MCZ and ETU on a glassy carbon electrode (GCE) surface. Performance characteristics such as linearity, limits of detection and quantification, precision, and accuracy were evaluated. This alternative methodology was applied to the analysis of MCZ in two commercial fungicide formulations available in Portugal and Spain (Micene WP® (Sipcam) and Mancozan® (Bayer CropScience)).

2. Experimental part

2.1. Reagents and solutions

Mancozeb (96.8%), ethylenethiourea (99.9%) and potassium hexacyanoferrate(III) (99%) were purchased from Sigma-Aldrich (Germany). Ethylenediaminetetraacetic acid disodium salt 2-hydrate (EDTA, ≥99%) was obtained from Panreac (Spain) and used to dissolve MCZ. For the voltammetric analyses phosphate buffered saline (PBS) solutions (pH 5.0–9.0) were used. These buffers were prepared using potassium dihydrogenphosphate (99%, Riedel-de Haën, Germany), sodium chloride (99.5%, Panreac, Spain), potassium chloride (99.5%, Riedel-de Haën, Germany), and di-sodium hydrogenphosphate 7-hydrate (Riedel-de Haën, Germany). Hydrochloric acid (37%, Scharlau, Spain) and sodium hydroxide (Pronalab, Portugal) solutions (both at 0.1 mol L⁻¹) were used to adjust the pH of the solutions. The fungicide formulations Micene WP® (Sipcam, Spain) and Mancozan® (Bayer CropScience, Portugal), both containing 80% (w/w) of MCZ, were used to evaluate the accuracy of the voltammetric method.

Because of the very low solubility of MCZ and ETU in water, EDTA was used to aid dissolution. Stock solutions of MCZ (1000 μmol L⁻¹) and ETU (1000 μmol L⁻¹) were prepared daily by dissolving an accurately weighed amount of the compound in an EDTA solution (3%) and ultrapure water, respectively. These solutions were stored in the dark at 4 °C until use.

Solutions of the commercial products Micene WP® and Mancozan® were also prepared by dissolving an accurately weighed amount in a 3% EDTA solution.

All solutions were prepared using ultra-pure water (resistivity = 18.2 MΩ cm) obtained from a Simplicity 185 water purification system (Millipore, France).

2.2. Equipment

All voltammetric measurements were performed using a computer-controlled Autolab PGSTAT12 potentiostat/galvanostat (Metrohm-Autolab, The Netherlands) and a Metrohm 663 VA Stand, containing a three-electrode cell composed of a glassy carbon electrode (GCE; working electrode), an Ag/AgCl (KCl 3 mol L⁻¹) reference electrode and a glassy carbon auxiliary electrode (Metrohm, Switzerland). The system was controlled by means of the General Purpose Electrochemical System (GPES) software package (v. 4.9, Metrohm-Autolab, The Netherlands). The GCE was manually cleaned before each measurement by polishing its surface with Micropolish Alumina (0.05 μm, Buehler, Germany) until a shining surface was obtained. The electrode was then rinsed with ultra-pure water before analysis. pH measurements were made with a Crison GLP-22 pH-meter and a combined glass electrode.

2.3. Voltammetric analysis

The voltammetric studies were conducted in PBS buffers (pH 5.0–9.0) using either cyclic voltammetry (CV) or SWAdSV. In these assays the GCE was immersed in a low-volume cell containing 1.0 × 10⁻³ L of PBS buffer. This cell was then inserted in a larger cell containing the reference and auxiliary electrodes and 40.0 × 10⁻³ L of the PBS buffer. Prior to the analysis, electrolytes were purged with nitrogen for 10 min to ensure complete oxygen removal. In the CV and SWAdSV assays, the potential was scanned between -0.20 and -1.0 V for MCZ, and between 0.20 and -1.2 V for ETU. In all the SWAdSV assays a step potential (ΔE_s) of 0.0051 V and a pulse amplitude (ΔE_p) of 0.01995 V were used. For the optimization of the SWAdSV procedure, the following parameters were studied: electrolyte pH, accumulation potential (E_{acc}), accumulation time (t_{acc}) and square-wave frequency (f). In Table 1 the used conditions in the optimization studies are shown. In the optimized SWAdSV procedure accumulation potentials of -0.50 V for MCZ and -0.10 V for ETU, a t_{acc} of 20 s, and an f of 100 Hz were used.

3. Results and discussion

3.1. Cyclic voltammetric studies

Cyclic voltammograms of 200 μmol L⁻¹ MCZ and ETU solutions in PBS buffer (pH 7.0) at different scan rates (ν) showed a single irreversible reduction process for both compounds at -0.6 V for MCZ and -0.5 V for ETU (Fig. 1). The peak potentials were found to be pH-independent (data not shown).

The influence of ν on the peak current intensity (i_p) was studied from 0.010 to 0.500 V s⁻¹ (Fig. 1). Within this interval, linear relationships between i_p and ν^{1/2} were established for MCZ: -i_p (μA) = 0.169 × ν^{1/2} (mV s⁻¹)^{1/2} + 0.742 (R = 0.973) and for ETU: -i_p (μA) = 0.163 × ν^{1/2} (mV s⁻¹)^{1/2} + 0.566 (R = 0.994). These equations indicate that the reduction processes of both compounds at the surface of the GCE are mainly controlled by diffusion [21].

3.2. Square-wave adsorptive stripping voltammetric studies

After the characterization of the electrochemical reduction behavior of MCZ and ETU, a more sensitive technique, SWAdSV, was used to develop an alternative procedure for their detection and quantification. For this purpose, the influence of several analytical features such as electrolyte pH, square-wave frequency (f), E_{acc} and t_{acc} on i_p and the peak width and shape was evaluated and optimized (Table 1). Fig. 2 shows the effects of these variables (univariable study) on the i_p values of 50 μmol L⁻¹ MCZ and ETU solutions.

For the optimization of the pH of the electrolyte (PBS buffer), several MCZ and ETU solutions with pH values ranging between 5.0 and 9.0 were analyzed (Fig. 2). It was found that the reduction peak potential was independent of pH and that the highest i_p values were obtained at pH 7.0. Therefore, this pH was selected for subsequent experiments.

The influence of f on i_p and peak width and shape was evaluated from 10 to 150 Hz. The i_p increased with frequency up to 100 Hz for MCZ and up to 150 Hz for ETU (Fig. 2). However for ETU the peak

Table 1
Parameters used in the optimization of the SWAdSV procedure.

Magnitude optimized	MCZ			ETU		
	E _{acc} (V)	t _{acc} (s)	f (Hz)	E _{acc} (V)	t _{acc} (s)	f (Hz)
E _{acc}	^a	5	10	^a	5	10
t _{acc}	-0.5	^a	10	-0.1	^a	10
f	-0.5	20	^a	-0.1	20	^a
pH	-0.5	20	100	-0.1	20	100

^a Varied.

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