



Sensitive voltammetric responses and mechanistic insights into the determination of residue levels of endosulfan in fresh foodstuffs and raw natural waters

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ABSTRACT

This paper describes the electroanalytical study of the organochlorine pesticide endosulfan (EDS) using square-wave voltammetry. The electrochemical behaviour showed a quasi-reversible process on a hanging mercury drop electrode (HMDE) in acid medium attributed to reduction of the carbon–chlorine bond. The constant of charge transfer obtained for this process was 354 s^{-1} . The redox mechanism was confirmed by quantum-chemical (Density Functional Theory, DFT) studies. The optimised experimental and voltammetric parameters were 0.04 mol L^{-1} Britton–Robinson buffer (pH 4.0), the pulse potential frequency of 200 s^{-1} , the amplitude of the pulse of 20 mV, and the height of the potential step of 4 mV. Analytical parameters such as linearity range, equation of the analytical curves, correlation coefficients, detection and quantification limits, recovery values, precision, and accuracy were obtained. The procedure was applied to the analysis of pesticide in complex samples: sugar cane, tomato, and raw natural waters. The recovery values demonstrated that the proposed methodology is suitable for determining EDS in such samples. The results indicated that the proposed procedure is stable and sensitive, with good reproducibility, and no complex procedure was necessary for sample preparation. The development of this electroanalytical procedure is therefore appropriate, as it provides adequate sensitivity and reliable methodology.

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1. Introduction

World pesticide amount used have been increasing dramatically around 93% with increased human population and crop production. Since 2008, Brazil has been considered the largest consumer of this type of chemical in agriculture. According to Agência Nacional de Vigilância Sanitária (ANVISA – National Health Surveillance Agency) it was found that Brazilian pesticide consumption has grown up 190%. Currently, Brazil is responsible for around 20% of world pesticide use [1].

As a result of pesticides in combat-specific activities, contaminating pesticide residues unfortunately end up in food, water, soil and the atmosphere [2,3]. Intake of pesticides can cause adverse effects on the nervous and immune systems, birth defects, and cancer, etc. [4], with the seriousness of the damage to human health dependent on the toxicity and amount of the consumed contaminant. The risks are various and many studies have shown that different classes of pesticides, such as organochlorine, may act as potential endocrine disruptors. These can either bind to the hormone's receptor or mimic the hormone itself, or

even block the action of the hormone. Secondly, they can stimulate or inhibit the enzyme responsible for the synthesis or clearance of a hormone and thereby give rise to increased or decreased action of the hormone [5]. The principal example of an organochlorine pesticide is DDT, for which studies have proved its endocrine action [4]. Another suspected endocrine-disrupting organochlorine pesticide is 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide, known as endosulfan (EDS), represented in Fig. 1.

EDS is a broad-spectrum insecticide and acaricide applied in different areas, such as a number of crop types including cotton, cereals, and fruit trees, and plantation crops such as tea, coffee and sugar cane [6,7]. EDS has been in use for about five decades; it is effective against a broad range of insect pests and mites, and fulfils all of the hazard criteria for classification as a Persistent Organic Pollutants (POP) under the UNECE Protocol on POPs and the UNEP Stockholm Convention [7]. Oestrogen is the hormone system affected by EDS, under the oestrogen-receptor agonist mechanism.

Due to harmful effects caused by EDS, ANVISA declared the ban of its application in Brazil. Its use will be gradually discontinued up to 2013, at which time it will be permanently banned [8–10]. Due to these effects, mainly in the contamination of foods and the environment from pesticides, the development of analytical methods for its identification and quantification has increased.

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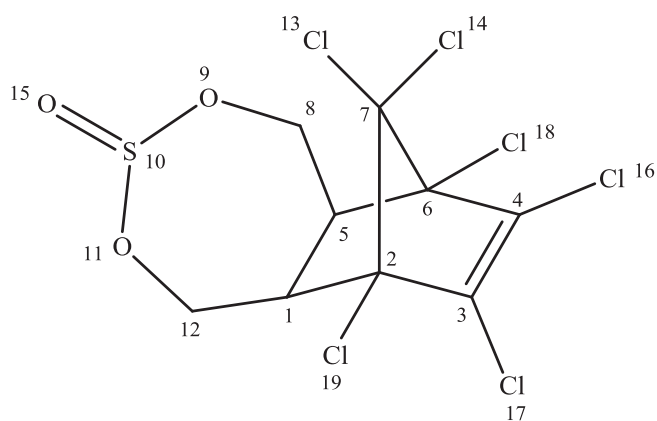


Fig. 1. Molecular structure of endosulfan.

In practice, several techniques have been employed to determine this pesticide, such as chromatography coupled with electron capture detector [11–15], UV-Visible [16] and mass spectrometric [17–19], spectrophotometry [20], and immunoassay [21]. However, although these techniques operate quite well, there are still several disadvantages, such as time delays, high costs, and laborious steps of sample pre-treatments and extraction in routine analyses. During the past decade, research projects dedicated to the implementation of suitable electrochemical devices for the detection of pesticides have gained much attention, which can be highlighted by the extensive number of articles involving electrochemical sensors. The main proposal of these is the development of sensitivity, accuracy, precision, and selectivity, as well as short analytical times and low-cost methodologies for rapid monitoring of pesticides.

Among these, several electroanalytical methods have been shown to be powerful tools for the analysis of pesticides, especially those using square-wave voltammetry (SWV) [22–24]. In addition to the advantages of these methods, kinetics and redox mechanism information can be obtained easily. This is due to the fact that the redox reactions occurring in the environment can be compared with redox reactions occurring at the electrified interface when electroanalytical techniques are employed [25].

According to the literature there are several combinations of techniques and electrode surfaces, such as conventional polarography [26], glassy carbon electrode [27], hanging mercury drop electrode (HMDE) allied with differential pulse voltammetry [28], glassy carbon electrode using wall-jet configuration [29], glassy carbon electrode coated with polypyrrole [30], glassy carbon modified with sodium montmorillonite clay [31], C18-modified carbon-paste electrode [32], electrochemical immunosensor [33], and biosensor based in acetylcholinesterase on iron oxide nanoparticle-decorated carboxylated multiwalled carbon nanotubes electrodeposited onto indium tin oxide-coated glass plate [34] for electroanalytical studies of EDS. However, the voltammetric data have not been well explored regarding kinetics and mechanistic aspects. HMDE is feasible for use in EDS pesticide determination allied to SWV because the controlled formation of the electrode surface offers highly reproducible, readily renewable, stable and smooth surfaces, which are important properties of this substrate. The use of modern voltammetric techniques promotes a substitution of traditional polarographic techniques, reducing mercury residues and decreasing the delay time for each analysis [35].

In order to obtain information about the redox mechanism, quantum-chemical methods were used allied to the experimental results [36–38]. Therefore, the aim of this study was to develop a detailed investigation employing SWV and quantum-chemical studies for the determination of EDS residues on HMDE in trace concentrations present in foodstuffs such as sugar cane and tomato samples, and in raw natural waters.

2. Experimental procedure

2.1. Equipment and reagents

A potentiostat/galvanostat, AUTOLAB model PGSTAT 30 (Metrohm-Eco Chemie, Netherlands), controlled by a personal computer using Model GPES version 4.9 software (General Purpose Electrochemical System, Metrohm-Eco Chemie), was used for all electrochemical measurements. A conventional cell with a three-electrode system was employed, consisting of an HMDE with a surface area of 0.52 mm² as working electrode, an Ag/AgCl/KCl_(sat'd) system as reference electrode, and glassy carbon as auxiliary electrode.

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 solutions were prepared with water purified by a Milli-Q system (Millipore Corp.). Stock solutions of 1.0 × 10⁻³ mol L⁻¹ and 1.0 × 10⁻⁴ mol L⁻¹ of EDS from Sigma-Aldrich (99.9% purity and proportion α:β of the 1:3) were prepared daily by dissolving a suitable quantity in pure ACN, which was then stored in a dark flask and kept in a refrigerator to prevent degradation (Caution: EDS is toxic and it should be handled with extreme caution to avoid accidental exposure). 0.04 mol L⁻¹ of Britton–Robinson (BR) buffer was used as supporting electrolyte and the pH was adjusted to the desired value by adding suitable amounts of 1.0 mol L⁻¹ NaOH stock solution. All reagents were of analytical grade and were used directly without further purification. All measurements were performed in triplicate.

2.2. Optimisation procedure for voltammetric determination

For this experimental sequence, the working electrode was placed in a measuring cell filled with 20 mL of BR buffer solution containing a known concentration of EDS. Before each experiment, a stream of purified N₂ (White Martins, Brazil) was passed through the solution for 10 min. All measurements were performed at 26 ± 1 °C. The electrochemical behaviour of EDS was investigated in BR buffer (pH 2.0–11.0) following optimisation of the SWV parameters: the pulse potential frequency (*f*) related to total pulse duration, the amplitude of the pulse (*a*), and the height of the potential step (ΔE_s). All parameters were optimised in relation to the maximum value of the peak current and the maximum selectivity (half-peak width). Analytical curves were obtained in electrolyte solutions by the standard addition method. The detection and quantification limits (DL and QL, respectively) were calculated based on the International Union of Pure and Applied Chemistry (IUPAC) guidelines [39,40].

These experiments were carried out by adding a known amount of EDS to the supporting electrolytes followed by standard additions from the EDS stock solutions and plotting the resulting analytical curves. The recovery values were calculated considering the ratio between the value of the concentration obtained by extrapolating the analytical curves of the corresponding spiked samples and the concentration previously added. The precision of the proposed procedure was evaluated based on reproducibility experiments realised with different standard solutions of EDS on different days (interday). The accuracy was evaluated from repeatability experiments obtained in 10 replicated determinations with the same EDS solution in the same day (intraday). The relative standard deviation values (RSD) were calculated for reproducibility and repeatability measurements using the relationships between the standard deviation and the mean of the peak current values obtained.

2.3. Application of methodology

The efficiency of the methodology for EDS quantification was examined for application in complex samples. For this evaluation, recovery experiments were carried out in three different samples: sugar cane, tomato, and raw natural waters.

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