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Sensitive determination of paraquat by square wave anodic stripping voltammetry with chitin modified carbon paste electrode



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ABSTRACT

A novel analytical approach has been developed and evaluated for the quantitative analysis of paraquat herbicides which can be found at trace levels in olive oil and olives. The aim of this work is to optimize all factors that can influence this determination by a carbon paste electrode modified with chitin (Chit-CPE). The best responses were obtained with square wave potential in diluted Na₂SO₄ as supporting electrolyte. The influence of various parameters on the Chit-CPE was investigated. Under the optimized working conditions, calibration graphs were linear in the concentration ranges of 5.0×10^{-9} – 1.0×10^{-5} mol L⁻¹. For 180 s preconcentration, detection limits of 2.67×10^{-10} mol L⁻¹ (peak 2) was obtained at the signal noise ratio (SNR) of 3. To evaluate the reproducibility of the newly developed electrode, the measurements of 1.0×10^{-5} mol L⁻¹ PQ were carried out for seven times at Chit-CPE and the relative standard deviation was 5.2%. The analytical methodology was successfully applied to monitor the paraquat content in olives and olive oil.

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1. Introduction

Paraquat (1,1-dimethyl-4,4-bipyridinium dichloride), a fast-acting non-selective contact herbicide, is widely used to control broad-leaved weeds in growing corn, fruit trees and vegetables. It is also used as a desiccant before harvesting and for destroying marijuana plants. Accidental and occupational exposures of agriculture workers are the primary hazards for human health. During the past few decades, paraquat (PQ) has proved to be a popular agent for intentional poisonings. Paraquat is extremely toxic to humans (LD50 35 mg/kg) and animals (rats: LD50 is 110–150 mg/kg), by all means of exposure. Since recently, the use of PQ has been restricted [1–4]. There is no specific treatment for PQ poisoning. Hence the management of poisonings is to relieve symptoms and treat complications [5]. Paraquat is an herbicide that is used in weeding many crops and there have been many authenticated cases of detection of its residues in water sources [6]. Its residues constitute a potential danger for health since it is a highly persistent molecule when present in the environment. This fact increases the contamination risk when paraquat is overused. Therefore, there is an urgent need to determine paraquat in the environment, air and food. PQ is polar, highly soluble in water and

has a low volatility. According to its properties, this compound is usually determined by ion-pair HPLC with UV detection [7], this latter being the method recommended by the Environmental Protection Agency (EPA) [8].

Standardized analytical methods for paraquat determination in environmental samples, mainly based on gas and liquid chromatography [9–11] or mass spectrometry (MS) [12–15], and more recently, on electrophoretic methods, with either UV detection [16] or mass spectrometry [17] have certain disadvantages because they require rather complicated and expensive instruments and time-consuming procedures, especially for in situ applications or in decentralized laboratories. Electroanalytical stripping techniques, however, prove to be the ideal alternative in such a case [18–20].

Literature has so far reported different electroanalytical approaches in order to determine paraquat [21,22]. They are mainly based on the stripping voltammetry technique [23–25]. An increase in the sensitivity of electroanalytical methods, using chemically modified electrodes (CMEs), can be achieved by its combination with an effective method of pre-concentration. The basic carbon electrode materials most frequently used for electrochemical measurements are glassy carbon and carbon paste electrode (CPE) [25–27].

The main objective of this work was to develop a procedure for the determination of paraquat by square wave anodic stripping voltammetry (SWASV) using a carbon paste electrode modified

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with commercial chitin particles (Chit-CPE). The advantages of using this electrode include the availability of a wide potential range of CPE for analysis, the easily renewable surface and the simplicity of fabrication. Among the different inorganic solids, chitin has advantages because it is biocompatible, biodegradable, antibacterium and almost non-toxic [28]. Its high hydrophilicity and its high chemical reactivity are attributed to a large number of functional groups [26].

All experimental variables involved in the stripping method were investigated in detail in order to identify the best working conditions. A fast, sensitive method for determining paraquat in oils (especially olive oil) is described. In principle, considering the extreme lipophobicity of the bipyridyl herbicides, it is quite unlikely to find such residues in olive oil. Nevertheless, they could appear at ppb levels. This is particularly critical in the case of organic oils which are, by definition, supposed not to contain pesticides. Therefore, we must ensure that such oils fulfill the legislation.

2. Experimental

2.1. Equipment and reagent

A stock solution of 10^{-3} mol L $^{-1}$ PQ was prepared by dissolving the corresponding amount of paraquat chloride in bidistilled water. A working solution of 10^{-4} mol L $^{-1}$ PQ was prepared daily from the stock solution, by dilution in bidistilled water. pH was adjusted by adding H $_2$ SO $_4$ or NaOH. All chemicals used in these experiments were extremely pure (used without further purification). They were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies.

Electrochemical measurements were carried out by using an eDAQ e-corder/potentiostat EA163 controlled by eDAQ EChem data acquisition software. A voltammetric cell with three electrodes was used: a carbon paste electrode modified with the chitin as the working electrode (WE), a platinum electrode as the auxiliary electrode (AE) and an Ag/AgCl/Cl $^{-}$ (3 M) as the reference electrode (RE). A pH-meter sensION $^{\text{TM}}$, (pH31) with the glass-Ag/AgCl/KCl (3.00 mol L $^{-1}$) combined electrode, was used for adjusting pH values.

2.2. Working procedure

The working electrode was constructed from 1 mm diameter bar of carbon which was partially inserted into PTFE cylindrical tubing of approximately 5 mm internal diameter, forming a cylindrical cavity. A chemically modified carbon paste electrode (Chit-CPE) was prepared by mixing amounts of chitin and carbon paste thoroughly until obtaining a uniformly wetted paste. Portions of the resulting composite material were then packed into a home built electrode assembly consisting of the cavity (geometric area 0.1256 cm 2) of PTFE tube electrode of a plastic pipette tip. Electrical contact was established with a bar of carbon.

The electrode, after having been washed with distilled water and heated at room temperature, was transferred into the sample cell (10 mL). Two-step procedures were followed for the analytical determination of the concentration of paraquat in aqueous samples. The working electrode was first immersed in a Na $_2$ SO $_4$ solution containing paraquat at open circuit. Where the accumulation of paraquat ions was achieved chemically, the electrochemical experiments were performed in 0.1 mol L $^{-1}$ Na $_2$ SO $_4$ electrolyte solutions at Chit-CPE.

Several supporting electrolytes namely (NaClO $_4$, Na $_2$ SO $_4$, CH $_3$ COOH, and HClO $_4$) were tested. Each of the four considered electrolytes was tested working in SWASV. After recording the

voltammogram of the blank, the test solutions were spiked with paraquat solution (10^{-4} mol L $^{-1}$). The best electrochemical response, measured in terms of the highest analytical signal and improved reproducibility, was obtained in Na $_2$ SO $_4$. This means that 0.10 mol L $^{-1}$ of Na $_2$ SO $_4$ was used throughout the experimental program as the supporting electrolyte.

The appropriate solutions of paraquat were transferred into the electrochemical cell and the optimization of the analytical procedure for SWASV was carried out following a systematic study of the experimental parameters that affect the SWASV responses; such as, the pH of the medium, frequency, amplitude, deposition potential and deposition time. After the optimization of the voltammetric conditions, analytical curves were obtained by the standard addition method. Recovery experiments were then performed by adding a known amount of PQ to the supporting electrolyte, followed by standard additions from the paraquat stock solution and by plotting the resulting analytical curve. All measurements were performed in triplicate under ambient conditions.

The analytical utility of this procedure was assessed by applying it to the determination of paraquat in realistic samples containing this herbicide. The experiments were carried out by adding a known amount of paraquat to the supporting electrolyte followed by standard additions from the diquat stock solution and by plotting the resulting analytical curve. The supporting electrolytes were prepared by addition of 0.1 mol L $^{-1}$ Na $_2$ SO $_4$ to fresh oil and olive samples.

3. Result and discussion

The voltammetric response of paraquat at the chitin modified carbon paste electrode Chit-CPE was investigated using cyclic voltammetry (Fig. 1). The results show two voltammetric peaks toward the negative and the positive sweep direction as indicated in the literature [20,26,29–31]. According to the experiment undertaken, the electrochemical process related to the experiment presents a totally reversible behavior indicated by the presence of direct and reverse currents with similar values of peak current. In addition, the difference between peak potential for forward and reverse scans, presented values about 58 mV. This indicates of the transfer of one electron during the redox process, a behavior similar to that published in previous literature reports [21,22,25]. The two peaks can hence be used, with great success, for the electroanalytical determinations of paraquat residues in different samples.

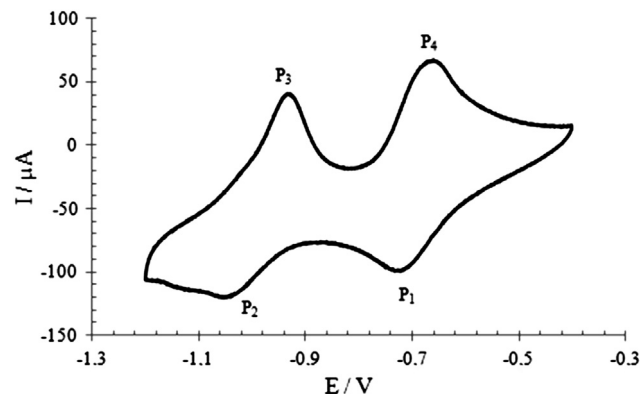


Fig. 1. Cyclic voltammogram for 5.0×10^{-4} mol L $^{-1}$ of paraquat in 0.10 mol L $^{-1}$ of Na $_2$ SO $_4$, pH 6.0, scan rate, 50 mV s $^{-1}$ on the Chit-CPE.

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