



Parameters affecting the determination of paraquat at silver rotating electrodes using differential pulse voltammetry



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ABSTRACT

The electrochemical determination of aqueous paraquat PQ(II) by differential pulse voltammetry at a solid rotating silver electrode (RSE) is described. The aim of this work is to optimize all factors that can influence this determination. Potential wave forms, potential scan parameters and deposition time were examined for their effect on the paraquat peak shape and intensity. The best responses were obtained with differential pulse voltammetry in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ as supporting electrolyte using amplitude 50 mV, scan increment 5 mV, deposition time 120 s, frequency 50 s^{-1} and step amplitude 0.05 V. Electrochemical and mechanical surface cleaning, aimed at removing the amount of paraquat deposited onto the silver surface, were necessary for obtaining a good performance of the electrode. Response linearity, repeatability, accuracy and detection limit were also evaluated. The obtained detection limits were $7.1 \times 10^{-9} \text{ mol L}^{-1}$ and $2.8 \times 10^{-9} \text{ mol L}^{-1}$ for peak 1 and peak 2 respectively. The relative standard deviation (RSD) was found to be 1.19% in $1.0 \times 10^{-4} \text{ mol L}^{-1}$ paraquat. The applicability of the RSE for PQ(II) determination in milk samples, without any sample pretreatment, was successfully demonstrated.

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1. Introduction

Paraquat (PQ) was invented in England in 1956 and has been continuously used for agriculture all over the world for its splendid herbicidal. It is used to control weeds and grasses in many agricultural and other areas. Paraquat products have been classified as restricted pesticides and even banned in some countries [1]. Moreover, the occurrence of agrochemical residues in foodstuffs, crops, vegetables and milk products have been reported by different authors [2–8]. On several occasions, incidents of poisoning after consuming these plants and animal products have been reported [9]. These incidents were attributed to grower's misuse of the pesticides or to negligence in observing a safety interval after harvest. The paraquat residue levels, in some vegetables and fruits, was commonly used in order to assess the possible predisposition of human to this herbicide and its associated health risks such as Parkinson's disease, Alzheimer's disease and Amyotrophic lateral sclerosis [10].

Due to high toxicity of the paraquat has made it necessary to develop a sensitive and rapid method for the determination of this herbicide. Numerous methods were reported in the literature, for the determination of paraquat [11,12], including a biological dosage [13,14], spectrophotometry [15], immunoassay [20,21], potentiometry [22,23], gas and high performance liquid chromatography (CPG/HPLC) using UV [16–19].

These techniques, commonly used for trace measurements of paraquat in the laboratory, are not suitable for in situ testing and monitoring. Electrochemical methods are among the most favorable techniques for determination of paraquat ions because of its high sensitivity easy operation and its ability to carry out speciation analysis.

The reversible redox property of paraquat facilitated its determination using voltammetry techniques [25–28,29]. Several solid electrodes, such as carbon paste electrode modified with fluoroapatite [26], natural phosphate [25] and kaolin [27] have been employed in electrochemical determination of paraquat. The selectivity and sensitivity of the voltammetric determination of paraquat can be improved by using electrodes chemically modified with Amberlite XAD-2 by cathodic stripping voltammetry [30]. However, the detection limit (0.10 mg mL^{-1}) achieved by this method was not very satisfactory. Moreover, surfactants interfere

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strongly with this method. Recently, clay-modified paste and glassy carbon electrodes were shown to be very promising for determining paraquat with a good detection limit [25].

Electrochemically, paraquat has been analyzed on different electrode surfaces, i.e., noble metals [31,32], mercury [24] and chemically modified electrodes [33], which makes the electrochemically behavior of this molecule a well-known one.

In this paper, we present results of detecting paraquat at silver rotating electrode (SRE) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution. This method features fast experimentation time, good suitability for field trace paraquat analysis and an acceptable electrode lifetime. Analytical performances of the method and the silver interaction were investigated using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Instrument and reagent

All chemicals used were of analytical grade or of the highest purity available. Sodium sulfate and sodium hydroxide, chloridric acid, were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies and were used as received.

Paraquat ions (Sigma, St. Louis, MO, USA) were dissolved in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ to prepare stock solutions of $1.0 \times 10^{-3} \text{ mol L}^{-1}$. Then the working standard solutions were prepared by successive dilution of the stock solutions by sodium sulfate.

The working electrodes were constructed from 5 mm diameter silver wire, which was inserted into glass tubing of approximately 10 mm internal diameter, and insulated with Epoxy resin. After the drying of the resin the electrodes were polished with a mechanical polisher and glass paper of different sizes and then cleaned with distilled water.

Cyclic voltammetry and differential pulse voltammetry were carried out with a voltalab (model PST 050, Radiometer Analytical Inc.) driven by the general purpose electrochemical systems data processing software (voltalab master 4software). The electrochemical cell was configured to work with three electrodes; using silver rotating electrode (RSE) as the working, platinum plate for counter and a system Ag/AgCl ($3.00 \text{ mol L}^{-1} \text{ KCl}$) as reference electrodes. Electrochemical impedance spectroscopy analyses were performed with a PGZ 100 potentiostat (Radiometer Inc.). The pH-meter (Radiometer, SENSION™, PH31, Spain) was used for adjusting pH values.

2.2. Procedure

Fourteen-millilitre test solutions of supporting electrolyte were delivered into the voltammetric cell. No electrochemical activation procedure and no deaeration before voltammetric determination were needed. After recording the differential pulse voltammogram of the blank, aliquots of PQ(II) were added and the corresponding signals were recorded. A cell containing $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of PQ(II) was utilized to investigate the effects of the different parameters on the signal of paraquat. After 120 s of deposition a voltammetric scan was performed. Initially, the scan parameters were modulation amplitude 0.2 V, scan increment 5 mV and frequency 50 s^{-1} . The detection limit was estimated as seven times the standard deviation of the blank signal. All experiments were performed in triplicate. Bulk stripping voltammetric signals (without blank subtraction) were used for peak current measurement.

The method described above was also applied to commercial milk samples. A 20 mL sample of milk was placed in a 50 mL Erlenmeyer flask containing $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ and spiked by adding an appropriate amount of paraquat. The contents of the flask were

then mixed and, after homogenization, 40 mL was transferred to an electrochemical cell for analysis. PQ(II) quantification in the milk samples was performed by external calibration and standard addition method.

3. Result and discussion

3.1. Preliminary voltammetric characterization

According to previous work [25–27], the differential pulse voltammograms obtained for paraquat herbicide present two voltammetric peaks towards the negative sweep direction, the first one around -0.7 V and the second at approximately -1.0 V (Fig. 1). The PQ dication may be reduced reversibly to the cation radical in dilute solution. The cation radical can then be further reduced to neutral moiety. The half-wave potential ($E_{1/2}$) for both reduction peaks remains approximately constant, with almost no shift from this value as the scan rates increased, behavior characteristic of a typical reversible process. The influence of the scan rate was studied with RSE in $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of paraquat. The peaks currents exhibit a linear dependence on the root of potential scan rate in the range from 1 to 150 mV s^{-1} indicating that the paraquat reaction at RSE involves adsorption as the rate-determining step.

3.2. Optimization of experimental conditions

Analysis with the rotating silver electrode was performed using differential pulse voltammetry (DPV) to achieve peak responses which are relatively simple to evaluate in a relatively short time. The conditions which most affect the measurement process were optimized to determine paraquat like frequency of the pulse potential (v), scan increment (ΔE_s) and amplitude of the pulse (a). The rotation speed of the rotating electrode and the proton concentration in the support electrolyte was also initially evaluated. All these parameters exert an intense effect on the peak current or peak potential.

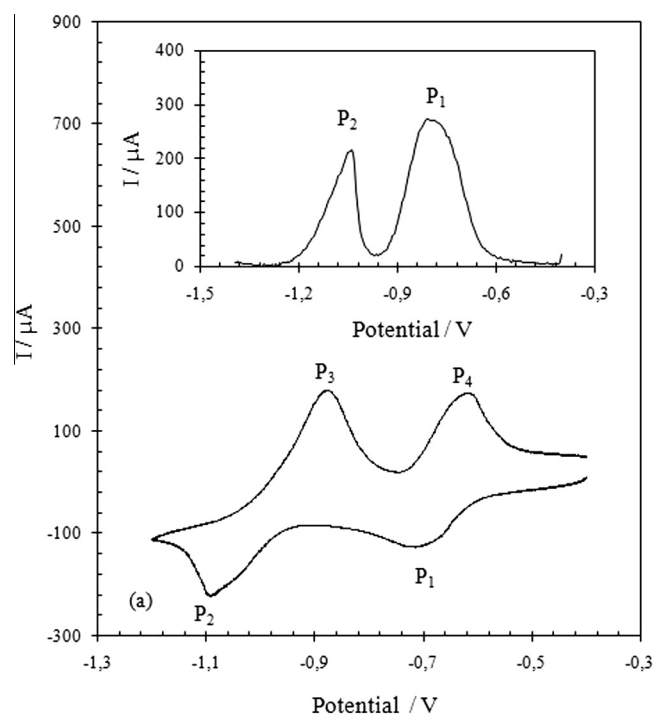


Fig. 1. Voltammograms CV and DPV of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ paraquat in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at rotating silver electrode (RSE).

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