International Journal for Research in Engineering Application & Management (IJREAM)
ISSN : 2454-9150 Vol-12, Issue-01, Apr 2020

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 mol L_1 Na2SO4 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 _ 10_9 mol L_1 and 2.8 _ 10_9 mol L_1 for peak 1 and peak 2 respectively.

The relative standard deviation (RSD) was found to be 1.19% in 1.0 _ 10_4 mol L_1 paraquat. The applicability of the RSE for PQ(II) determination in milk samples, without any sample pretreatment, was successfully demonstrated.

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]. More- over, 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 Amyotropic 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 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 electro- chemically behavior of this molecule a well-known one.

 DOI : 10.35291/2454-9150.2026.0021

In this paper, we present results of detecting paraquat at silver rotating electrode (SRE) in 0.1 mol L^{-1} Na_2SO_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

a. *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 mol L^{-1} Na_2SO_4 to prepare stock solutions of 1.0×10^{-3} 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 pro- cessing 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 mol L^{-1} 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.

Procedure

Fourteen-millilitre test solutions of supporting electrolyte were delivered into the voltammetric cell. No electrochemical activation procedure and no deaireation 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 1.0×10^{-4} 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 Erlen- meyer flask containing 0.1 mol L Na_2SO_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.

Result and discussion

Preliminary voltammetric characterization

According to previous work [25–27], the differential pulse vol- tammograms obtained for paraquat herbicide present two voltam- metric 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 the further reduced to neutral moiety. The half-wave potential (E1/2) for both reduc- tion 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 1.0×10^{-4} 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.

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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 (t), scan increment (D*E*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.

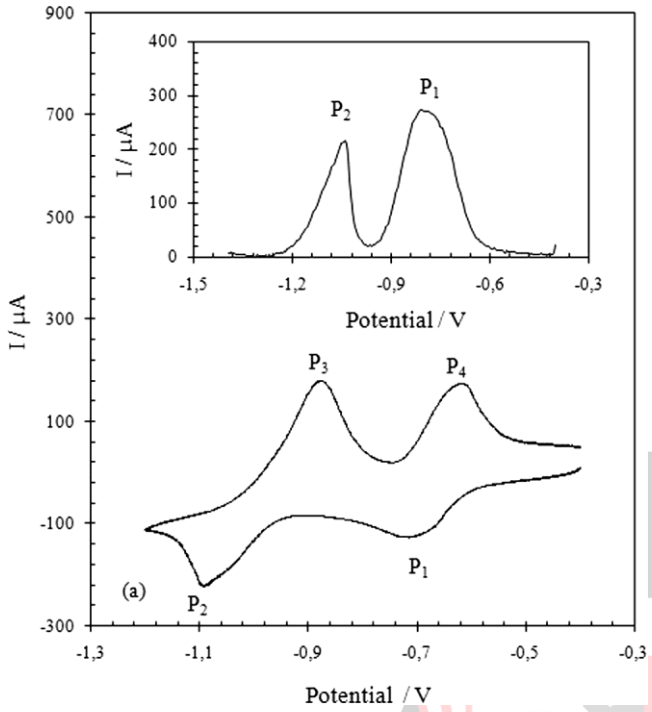

Fig. 1. Voltammograms CV and DPV of 1.0 × 10^{-4} mol L^{-1} paraquat in 0.1 mol L^{-1} Na_2SO_4 at rotating silver electrode (RSE).

The relationship between peak current and frequency for 1.0 ×10^{-4} mol L^{-1} PQ was also studied using rotating silver elec- trode (Fig. 2). The variations in the t values showed that an increase promoted a proportional increase of the peak currents of both peaks without any loss of quality in the electrochemical signal. Moreover, the peak potentials of peak 2 show a shift towards more negative values while that of peak 1 remains practically constant. The peak current was directly proportional to the frequency (t), indicating that this redox process is a reaction that involves adsorption as the rate-determining step [34]. This behavior is typical of the responses obtained at electrodes, where the electroactive species interact with working electrode, in the adsorption process, before the redox reaction occurs. Besides, it was observed that the peak currents of peak 2, increased linearly with square root of frequency (t) below 100 s^{-1}, without signal distortion. The low values of t used are probably associated with the slow diffusion of paraquat to or from the electrode surface, typical of the employment of rotating silver electrodes. Thus, in further experiments a value of 50 s^{-1}, corresponds to 0.02 s of duration for each step, was employed to ensure the maximum diffusion of the electroactive species.

Also, the peak potentials of peak 2 varies linearly with the logarithmic value of the frequency according to the expression [34]: D*E*p = —(2.3RT/bnF) Dlog(t)$^{1/2}$, where R is the gas constant, T the temperature, b the electron transfer coefficient, n the number of electrons, and F is the Faraday constant. It is apparent from this equation that a plot of D*E*p against Dlog (t)$^{1/2}$ will be a straight line. The slope of this plot, determined experimentally, was 0.15. Considering b = 0.5, and substituting the known values of R, F, and T, room temperature, into the right-hand side of the equation, and the known value of the slope, n was found to be equal to ≈1.

In order to get more information about the reaction behavior of silver with paraquat compound, electrochemical impedance spectroscopy (EIS) measurements have been carried out at 298 K. Preconcentration of paraquat species in the silver surfaces under open circuit potential was usually performed by dipping carefully the RSE into 5.0 × 10^{-4} mol L^{-1} paraquat solution for 30 min. The obtained surface was rinsed thoroughly with distilled water and electrochemical determination of the paraquat content was carried out in a paraquat-free fresh

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supporting electrolyte.

The charge-transfer resistance (Rt) values are calculated from the difference in impedance at lower and higher frequencies [35]. The double layer capacitance (C_{dl}) and the frequency (t) at which the imaginary component of the impedance is maximal (-Zmax) are found as represented in equation: $C_{dl} = (Rt)/(2p\ t_{max})$. The impedance parameters derived from these investigations are mentioned in Table 1. The reactivity efficiency got from the charge-transfer resistance is calculated by: $E(\%) = [(1\text{-}Rt\ (PQ))/Rt\ (blanc))] \times 100$. Rt (PQ) and Rt (blanc) are the charge-transfer resistance values with and without paraquat, respectively.

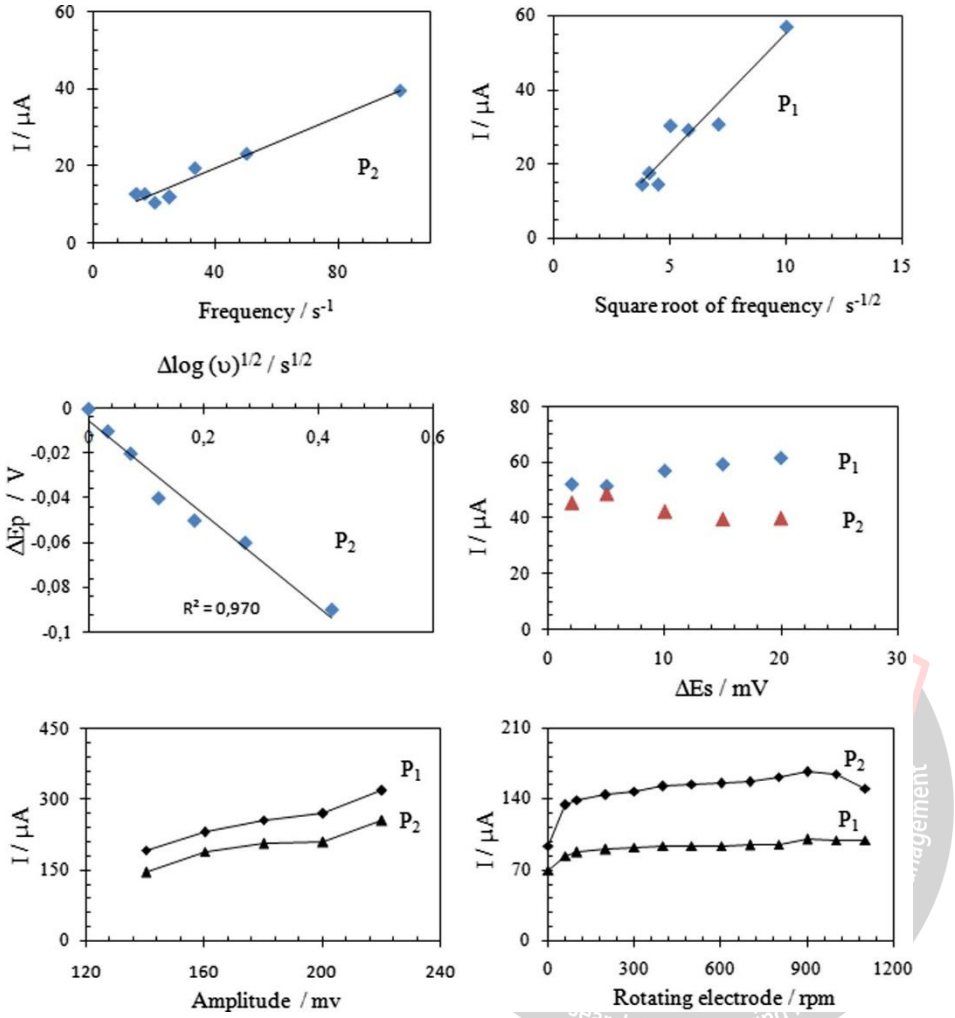

Fig. 2. Influence of the experimental variables (scan increment, modulation amplitude, frequency, deposition potential and rotation speed of the rotating electrode) involved in the differential pulse voltammetry. Response to 1.0×10^{-4} mol L^{-1} PQ(II) in 0.1 mol L^{-1} Na_2SO_4 using a solid rotating silver electrode (RSE).

Table 1

Electrical parameters calculated from the impedance spectra in 0.1 mol L^{-1} Na_2SO_4 for the (RSE) and 1.0×10^{-4} mol L^{-1} PQ(II)/(RSE) solution interfaces.

	R_1 (Kohm cm^2)	R_2 (Kohm cm^2)	C (lF/cm^2)	Diameter of cerecle
Na_2SO_4/ (RSME)	0.03366	12.64	15.85	14.12
PQ(II)/(RSME)	0.05489	1.21	20.85	1.361

As I notice, Fig. 3, the impedance diagrams show perfect semi-circles indicating a charge-transfer process mainly controlling the reaction of paraquat with sliver surface. Table 1 gives the values of the charge-transfer resistance, *R*t, double-layer capacitance and (C_{dl}) derived from Nyquist plots. From the impedance data, we conclude that the *R*t values decrease with the presence of accumulated paraquat. The values of double-layer capacitance are also brought down to the minimum extent in the presence of paraquat and the increase in the values of (C_{dl}). The increase in (C_{dl}) is due to the accumulation of paraquat on the silver surface. In fact, the

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presence of paraquat enhances the value of the conductivity of silver electrode in aqueous solution. EIS study shows that the paraquat is an efficient adsorbate at silver surfaces with 90.5% of adsorption efficiency.

An increase of the amplitude of the pulse caused an increase ofthe signal intensities, probably due to the larger difference between the currents before and after the application of the pulse. As expected from square wave theory [34,36], the values of ip show a linear variation with the pulse amplitude for values from 5 to 50 mV, while in practice, there Ep shows no variation as a function of amplitude (a). Both behaviors, however, point to a reversible redox process. For analytical applications, a value of 50 mV was chosen for amplitude (*a*).

The scan increment D*E*s was also evaluated for the reduction of paraquat. Results obtained demonstrated that an increase in scan increment results in a decrease in intensity (ip) of peak 2, which indicate an adsorption process as the rate-determining step. This behavior is confirmed by previous results obtained in the study of the relation between frequency of pulse potential and ip. In subsequent experiments, a value of D*E*s = 5 mV was adopted.

The amount of paraquat deposited onto a RSE surface should be carefully controlled to avoid saturation and to maintain linearity with increased loading. The greater adsorption of paraquat in silver compared to other metals could result in non-linear performance. Therefore, we investigated the effect of the deposition time on the peak currents. As expected, the height of paraquat peak increased with increasing deposition time (Fig. 4). However, with deposition times longer than 300 s the electrochemical cleaning procedure was not sufficient to remove all deposited paraquat, causing a worsening in the repeatability of the subsequent analyses. Taking into account the results obtained, a deposition time of 120 s were adopted.

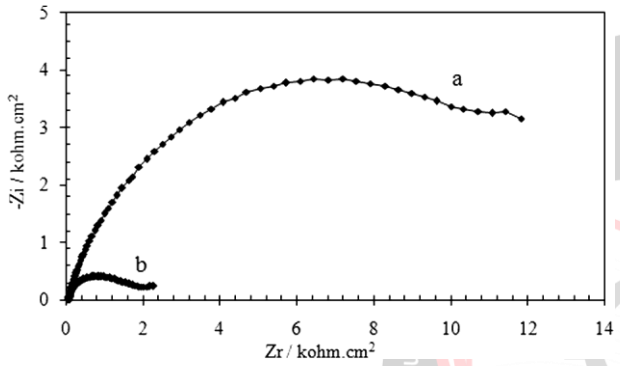

Fig. 3. Impedance spectra at 0 V (a) 0.1 mol L^{-1} Na_2SO_4 for the (RSE) and (b) 1.0×10^{-4} mol L^{-1} PQ(II)/(RSE), pH = 7.30.

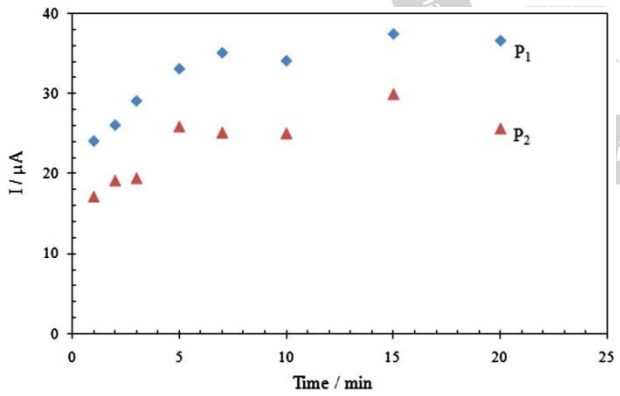

Fig. 4. Effect of deposition time on the reduction peaks intensity of 1.0×10^{-4} - mol L^{-1} paraquat in 0.1 mol L^{-1} Na_2SO_4, pH = 7.5, at a solid rotating silver electrode (RSE).

From the optimization experiments described above, the conditions selected for subsequent studies, with both pieces of equipment, were: deposition time 120 s, frequency 50 s^{-1}, amplitude 0.2 V, and step amplitude 0.05 V.

The pH effect of the supporting electrolyte on the voltammetric behaviour of the rotating silver electrode versus paraquat species was also investigated under these selected conditions at constant paraquat concentration (1.0×10^{-4} mol L^{-1}). It clearly appears from these results that pH of supporting electrolyte plays an important role in the voltammetric response of the paraquat. Between pH 2.5 and 11.30, the peak of reduction increased and reached a maximum value around pH 7.6; above pH 8.8 the peak height rapidly

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decreased, probably due to formation of the film of paraquat onto silver surfaces. The peak potentials do not, how- ever, seem to be affected by the concentration of H^+, suggesting the absence of any protonation step in the reduction mechanism, which is in close agreement with published works [24–27,33]. Consequently, pH 7.6 was selected to carry out the determination. The effect of rotation speed of the rotating electrode on the differential pulse voltammetric response of the RSE was studied. Consecutive measurements at different stirring speeds in the range from 0 to 1100 r.p.m. were carried out on the silver electrode on a 0.1 mol L^{-1} Na_2SO_4 electrolyte containing 1.0×10^{-4} mol L^{-1} of PQ(II). Voltammetric signal stability was found to be strongly dependent on stirring speed variable (Fig. 2). Significant differences in terms of peak height were observed at different stirring speed values following Levich equation [37]: $ip = 0.62\ n\ F\ A\ D^{2/3} C \nu^{-1/6}\ x^{1/2}$, where ip is the limiting current in amperes, n the number of electrons transferred per mole of analyte, F the Faraday's constant in coulombs mol^{-1}, A the area of the electrode in cm^2, D the diffusion coefficient in $cm^2\ s^{-1}$, C the analyte concentration in mol L^{-1}, ν the kinematic viscosity of the solution in $cm^2\ s^{-1}$ and x the angular velocity of the electrode in rad s^{-1}. The working electrode showed a stable behaviour for the determination of paraquat up 900 r.p.m. with a relative standard deviation of 1.19%. No hydrodynamic accumulation of the analyte was applied in further experiments. Efficient analyte deposition in absence of stirring is a typical advantage of the silver electrodes in stripping analysis, probably due to enhanced mass transfer to the silver electrode by diffusion [10]. This can be viewed as an analytical advantage due to the simplification of the equipment.

1.1. Analytical curves

Under these selected conditions, the peak current increased linearly with the paraquat concentration in solution. The linear dynamic range was comprised between 1.0×10^{-8} and 1.0×10^{-3} mol L^{-1} in terms of the relationship between paraquat concentration and the reduction peak current (Fig. 5). The relationship can be described in the following linear regression equation in the mentioned concentration range: $Ip_1 = 0.502\ [PQ] + 31.981$ ($r^2 = 0.981$) and $Ip_2 = 1.076\ [PQ] + 39.2$ ($r^2 = 0.992$) of peaks P_1 and P_2 respectively. The standard deviation of the mean current (r) measured at reduction potential of paraquat for seven voltammograms of the blank solution in pure electrolytes was calculated.

The calculated standard deviation was used in the determination of the detection limit (DL, 3r) and the quantification limit (QL, 10r). From these values, the detection and quantification limits were 7.1×10^{-9} mol L^{-1} and 23.9×10^{-9} mol L^{-1} for peak 1 respectively and for peak 2 were found to be 2.8×10^{-9} mol L^{-1} and 9.2×10^{-9} mol L^{-1} respectively (Table 2). The precision of this methodology for the determination of paraquat was evaluated for eight successive measurements of the same samples containing 1.0×10^{-4} mol L^{-1} paraquat. The repeatability obtained (RSD 1.19%) attests to the good performance of rotating silver electrode for paraquat analysis. The good performance of the rotating silver electrode has advantages such as low cost, ease of handling and absence of toxic waste; the last is a problem with mercury-drop electrodes and mercury-film electrode.

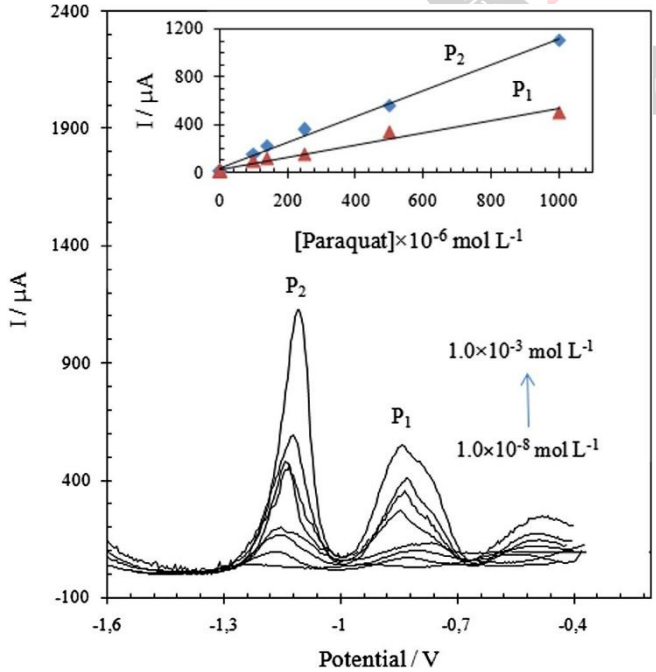

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Fig. 5. Calibration curve and respective stripping voltammograms for increasing concentrations of PQ(II) from 1.0×10^{-8} to 1.0×10^{-3} mol L^{-1} in Na_2SO_4 0.1 mol L^{-1} by using the DPV optimized method at the RSE.

Table 2

Results obtained from the linear regression curves (Fig. 5) for the determination of paraquat at RSE in pure waters.

Parameters	Peak 1	Peak 2
R^2	0.901	0.972
Slop (A mol L^{-1})	0.105	0.327
Deviation standard ($\times 10^{-10}$ A)	2.49	0.972
Detection limit ($\times 10^{-9}$ mol L^{-1})	7.1	2.8
Quantification limit ($\times 10^{-9}$ mol L^{-1})	23.9	9.2
Relative standard deviation (%)	2.82	3.87

1.2. Application to milk samples

The pesticide paraquat is widely used to control ticks in cows. It can therefore be a potential source of contamination of cows' milk. To determine the possibility of such contamination, cows' milk samples prepared as described above (Application of the method) were tested for paraquat.

The proposed method was applied to determine paraquat in milk under the optimized condition described above. The support electrolytes were prepared by addition of 0.1 mol L^{-1} of Na_2SO_4 to a fresh milk samples. The electroanalytical curves were obtained by using DPV in the range from 1.0×10^{-7} to 5.0×10^{-4} mol L^{-1} of paraquat, it was observed that the peak currents increased linearly versus paraquat added into milk sample solution, hence the proposed methodology is suitable for the determination of paraquat in the milk samples.

The statistical calculations for the assay results showed suitable precision of the proposed method (Table 3). It observed, however, the decrease of the sensitivity of RSE for the determination of paraquat in milk due probably to the presence of fat mater, which can inhibit the adsorption process of paraquat onto silver surface. Results obtained for RSD and percentage recovery were, respectively 2.82 and 89.07%. Notwithstanding, they can be regarded as satisfactory, considering that neither extraction nor preparation of the samples is necessary in the proposed method. The proposed method is therefore proven to be suitable for appli- cation to complex samples.

The interference effect was carried out, under the optimized conditions, in 5.0×10^{-5} mol L^{-1} of paraquat solution containing Ca^{2+}, Mg^{2+}, K^+, vitamins D_3, B_2 and B_{12} (all at 5.0×10^{-5} mol L^{-1}). The addition of this species did not cause any remarquable changes

Table 3 Results obtained from the linear regression curves for the determination of PQ(II) in cows' milk at RSE.

Paraquat added	Paraquat found	Recovery
(mol L^{-1}) $\times 10^{-6}$	(mol L^{-1}) $\times 10^{-6}$	(%)
4.0	3.15 ± 0.37	78.75
6.0	5.31 ± 0.23	88.50
8.0	7.08 ± 0.28	88.50
10.0	8.11 ± 0.34	81.10
14.0	12.74 ± 0.51	89.07
16.0	13.45 ± 0.62	84.06

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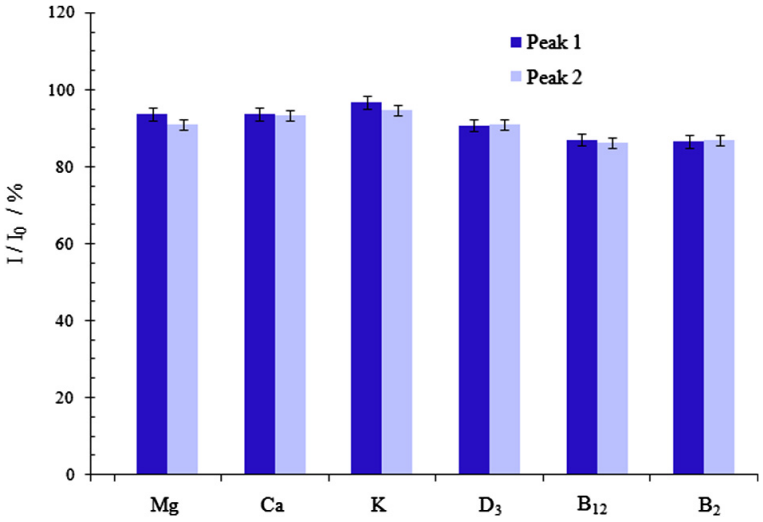

All samples were analyzed using standard addition method ($n = 4$). Mean value {±} ecart-type ($n = 4$).

Fig. 6. Paraquat responses at RSE in presence of Ca^{2+}, Mg^{2+}, K^{+}, vitamins D_3, B_2 and B_{12} (all at 5.0×10^{-5} mol L^{-1}). in paraquat response, showing that the present method is efficiency to study the speciation of parquat in real sample, especially the milk samples (Fig. 6). The presence of most vitamin D_3, B_2 and B_{12} gives rise to a small decreasing of the intensity of paraquat peak; it is due probably to the immobilization of such compounds on silver surfaces.

1. Conclusion

It can be concluded that the previously used electrode, which has an advantage of easy utilization and fast response can also be used for the determination of paraqaut ions. The results obtained showed the efficiency of the rotating silver electrode for the determination of low concentrations of PQ(II) by differential pulse voltammetry.

I also demonstrated that the determination of PQ(II) at a rotating silver electrode is negatively affected by the incomplete removal of previously deposited paraquat. To eliminate this draw-back, an electrochemical and a mechanical cleaning procedure are essential.

The reproducibility, sensitivity and accuracy are good, provided the proper instrumental parameters and supporting electrolyte are used. The use of the rotating silver electrode makes the direct analysis of the milk samples possible without any necessity of pre-treatments or chemical preparation stages, the observed recovery percentage values were in a range (2.82–62.34%), which is considered very satisfactory for analytic applications.

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 DOI : 10.35291/2454-9150.2026.0021