Original Article

Electrochemical determination of paraquat in citric fruit based on electrodeposition of silver particles onto carbon paste electrode

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Carbon paste electrodes (CPEs) modified with silver particles present an interesting tool in the determination of paraquat (PQ) using square wave voltammetry. Metallic silver particle deposits have been obtained via electrochemical deposition in acidic media using cyclic voltammetry. Scanning electron microscopy and X-ray diffraction measurements show that the silver particles are deposited onto carbon surfaces in aggregate form. The response of PQ with modified electrode (Ag-CPE) related to Ag/CP loading, preconcentration time, and measuring solution pH was investigated. The result shows that the increase in the two cathodic peak currents (Peak 1 and Peak 2), under optimized conditions, was linear with the increase in PQ concentration in the range 1.0 \times 10^{-7} \text{ mol/L} to 1.0 \times 10^{-3} \text{ mol/L}. The detection limit and quantification limit were 2.01 \times 10^{-8} \text{ mol/L} and 6.073 \times 10^{-8} \text{ mol/L}, respectively for Peak 1. The precision expressed as relative standard deviation for the concentration level 1.0 \times 10^{-5} \text{ mol/L} (n = 8) was found to be 1.45%. The methodology was satisfactorily applied for the determination of PQ in citric fruit cultures.

1. Introduction

Paraquat (1,1-dimethyl-4,4-bipiridyl) is a biquaternary ammonium compound that is normally synthesized as the dichloride salt. It was introduced in the 1960s, and today it is used in > 100 countries in plantations of tobacco, apples, and other crops [1]. Paraquat (PQ) is very toxic to all living organisms, and many cases of acute poisoning and death have been reported over the past decade. Numerous studies suggest a

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link between exposure to PQ and an increased risk for developing Parkinson’s disease (PD) [2]. This herbicide is structurally similar to MPP+ (1-methyl-4-phenylpyridinium), the active metabolite of MPTP (1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine), which is known to produce parkinsonian symptoms in drug users [3] and PD pathologies in animals [4]. In addition, a recent epidemiologic study shows the possible correlation between exposure to PQ and PD development in humans [5].

The main suggested potential mechanism for PQ toxicity is the production of superoxide radicals from the metabolism of PQ by microsomal enzyme systems, and by inducing mitochondrial toxicity [6]. Since July 2007, the use of this pesticide in the European Union (EU) has been banned; however, this does not preclude farmers outside the EU from continuing to use PQ and export their products to the EU. Therefore, PQ is included in the EU database between the compounds that should be monitored in food samples, and maximum residue limits have been established for different commodities [7]. Thus, for the case of citric fruit cultures, the maximum residue limit is 20 mg/kg [8]. The detection of PQ and herbicide residues in food samples is hampered owing to their particular physicochemical features and because this process requires the application of specific extraction and analytical procedures. The latter can be limited by interferences from food caused by a species with a similar structure (diquat), even at concentrations of the same order as PQ [9]. Currently, there is an urgent and specific increasing requirement for a more accurate and reliable detection method to cope with the more subtle adulterations in food. Several voltammetric methods have been developed to study the electrochemical behavior of PQ using dental amalgam and mercury [10], bismuth film [11], gold electrode [12,13], pyrolitic graphite [13], chemically modified carbon paste electrode (CPE) [14], and modified film electrodes [15–18]. The use of voltammetric methods has a considerable drawback that is related to the adsorption process of the analyte and/or the resulting products of the electrochemical reactions on the electrode surface. Indeed, low analytical sensitivities and reproducibility of the electroanalytical response were also observed [19,20]. The substantial versatility of carbon electrodes resides in their wide range of possible modifications. In fact, the electrode composition can be modified via the addition of different substances, such as metals, polymers, and enzymes [21–24]. The design of new nanoscale materials has acquired ever-greater importance in recent years owing to their various applications. Among these materials, metallic particles are of great interest because of their numerous properties [25,26]. Numerous methods describing the synthesis of metallic silver particles in solution as well as by deposition on solid surfaces have been presented. These include chemical synthesis by means of reduction with different reagents [27], UV light or electron beam irradiation [28], and electrochemical methods [29–32]. The latter provides an easy and rapid alternative for the preparation of metallic particle electrodes.

Recently, in our laboratory silver was used as a modifier of carbon paste, and we characterized these modified electrodes as sensing probes of PQ [33]. The used electrode was prepared by solid reaction between silver nitrates and carbon powder. However, the obtained silver was found to be supported heterogeneously as agglomerates onto the carbon paste. In this work, in order to overcome this problem, modified electrodes have been employed using the electrochemical deposition of silver from electrolytic solution. This methodology has been successfully applied to determine PQ in food samples, without any prepurification or preparation step of the sample. The modified electrode is compared with other related reports in the literature and is also independently tested with high-performance liquid chromatography (HPLC) toward the sensing of PQ in citric fruit cultures where good agreement is found.

2. Methods

2.1. Reagents

All chemicals were of analytical grade or of the highest purity available. Sodium sulfate, sodium hydroxide, silver nitrate, acetic acid, and chloridric acid were obtained from Merck (Darmstadt, Germany), Fluka (St. Gallen, Switzerland), and Riedel de Haen (Seelze, Germany) Chemical Companies and were used as received. PQ ions (Sigma Aldrich, St. Louis, MO, USA) were dissolved in 0.1 mol/L Na2SO4 to prepare stock solutions of 1.0 × 10−3 mol/L. The working standard solutions were prepared by successive dilution of the stock solutions by sodium sulfate. Carbon paste was supplied from Carbone Lorraine (Lorraine, France; ref 9900). All other reagents used were of analytical grade. Distilled water was used throughout the preparation of the solutions.

2.2. Instruments

Cyclic and square wave voltammetry (SWV) were carried out with a voltalab potentiotstat (model PGZ 100; Radiometer Analytical Inc., Hegnau, Switzerland) driven by the general-purpose electrochemical systems data processing software (voltalabmaster 4 software). The electrochemical cell was configured to work with three electrodes, using silver-modified carbon paste as the working platinum plate for counter and a system Ag/AgCl (3.00 mol/L) as reference electrodes. The pH meter (Radiometer, SENSION; PH3, Leganés, Spain) was used for adjusting pH values. X-ray diffraction studies of prepared powder Ag/CP were carried out using a diffractometer (XRD: Cu Ka radiation, XPERT-PRO). CuKα radiation (λ = 1.5406 nm) produced at 30 kV and 25 mA scanned the diffraction angles (2θ) between 10° and 80° with a step size of 0.02° 2θ per second. Scanning electron microscopy (SEM) measurements were performed on an FEI Nova SEM (Philips) instrument with an AMETEK energy dispersive X-ray system (Nova 200) operated at an accelerating voltage of 30 kV. Imaging of solids deposited on the 3-mm GC electrodes was performed with the aid of a custom-built electrode holder. Prior to SEM imaging, samples were thoroughly rinsed with acetone and Milli-Q water and dried under a flow of nitrogen.

2.3. Procedure

We describe an easy procedure to obtain silver particle-modified CPE. The method is based on the electrochemical deposition of silver on CPE surface from Britton–Robinson...
electrolyte (pH 2) containing silver nitrates. The silver deposition on CPE was performed using cyclic voltammetry. Initially, the electrochemical response of PQ at Ag-CPE is measured. A standard solution of PQ was added into the electrochemical cell containing 40 mL of supporting electrolyte (0.1 mol/L Na₂SO₄). The mixture solution was kept quiet for 20 seconds at open circuit for each electrochemical measurement. SWV was recorded in the range from −0.3 V to −1.4 V, for which the scan rate is 1 mV/s, the pulse is 50 mV, amplitude is 1 mV, and duration is 1 second. The optimal conditions were established by measuring the current peaks depending on all parameters. The suitability of the electroanalytical method in the determination of PQ in orange juice and orange juice samples was tested under optimal conditions. All experiments were carried out at room temperature and performed in triplicate.

3. Results and discussion

3.1. Preparation of silver particle-modified carbon electrodes

Previous experiments [34] showed that very acidic pH values are required to electrodeposit silver on CPEs. For this reason, pH 2 Britton–Robinson solution was used for modified electrode preparation. Silver electrodeposition was performed with cyclic voltammetry between different potential ranges for 1.5 cycles in a solution containing 1.0 × 10⁻³ mol/L AgNO₃ and Britton–Robinson buffer (pH 2.0). A carbon electrode was used for the deposition of silver. Fig. 1 shows the SEM image of Ag/CP pastes prepared in a sweeping potential range of −1.4 V to 0.0 V. The SEM images show the formation of silver particles on the carbon surface, indicating that they are deposited in aggregated form. The X-ray diffraction analysis of carbon paste after electrochemical deposition of silver on the working-electrode surface shows the formation of silver particles on the carbon surface. However, the presence of three peaks of metallic silver at 2θ of 38.18, 46.62, and 66.42 affirms the metallic state of the coated silver as seen in Fig. 1 according to the literature [35].

The voltammograms of PQ obtained at unmodified and modified CPE are shown in Fig. 2 as curve 1 and curve 3, respectively. At the CPE, in the potential range scanned from −0.3 to −1.3 V, a fairly small peak current due to reduction of PQ was observed. On the other side, the electrochemical response of PQ that occurred at the silver-modified CPE is much more distinguishable. The result indicates that silver can considerably promote the preconcentration of PQ at the CPE and significantly increase the sensitivity of the determination of PQ. The performance of the newly developed silver-modified CPE is based on the accumulation of PQ from

Fig. 1 – X-ray diffraction (XRD) patterns and imagery by scanning electron microscopy of CP and Ag/CP after electrodeposition step.
the aqueous solution onto the surface of the modified electrode.

3.2. Optimization of experimental conditions

3.2.1. Effect of silver electrodeposition conditions on PQ responses

The influence of the experimental variables of electrodeposition (scan rate, sweeping potential range, cycle number, concentration of silver in electrolytic solution) involved in the SWV determination of PQ was investigated.

The effect of the scan rate of electrodeposition of silver particles on the SWV response of PQ was studied in a solution containing 1.0 × 10⁻⁴ mol/L of PQ in the range 1.0–10 mV/s (Fig. 2). The voltammogram of silver deposition was recorded by making a scan cyclic from −1.4 V to 0.0 V with a cycle number of 1.5 in Britton–Robinson buffer at pH 2.0. The highest response obtained was achieved at a scan rate of 3 mV/s. Fig. 2 shows the square wave voltammogram of PQ on the different electrodes, in a solution consisting of 1.0 × 10⁻⁴ mol/L and 0.1 mol/L Na₂SO₄ with pH 7.0. Curve 2 is the square wave voltammogram of PQ on a Ag-CPE electrode prepared in a sweeping potential range of −1.4 V to −0.6 V, in which the peak of the intensity is 43.62 μA. Curve 3 is the cyclic voltammogram of PQ on a Ag-CPE electrode prepared in a sweeping potential range of −1.4 V to 0.0 V, in which the peak of the intensity is 86.31 μA, which is much higher than that in curve 2. Curve 4 is square wave voltammogram of PQ on Ag-CPE electrode prepared in a sweeping potential range of −1.4 V to 0.3 V, in which the peak of the intensity is 79.45 μA. Curve 5 is the square wave voltammogram of PQ on Ag-CPE electrode prepared in a sweeping potential range of −1.4 V to 0.6 V, in which the peak of the intensity is 61.56 μA. This result demonstrates that the Ag-CPE electrode prepared in a sweeping potential range of −1.4 V to 0.0 V can be efficient for the detection of PQ. The oxidative removal of silver from electrode surfaces may be complicated because of the formation of some surface oxides on silver during the oxidation scan. This may account for the lack of full chemical reversibility [36].

The highest peak intensity was reached for the total cyclic potential of 1.5 cycles. It has been observed that a poor response for PQ is obtained when the number of cycles exceeds 1.5 cycles, and as expected, electrodeposition of silver on electrode paste carbon did not occur further and the paste of carbon was dispersed in the solution. Hence, for all subsequent measurements, a scan rate of 3 mV/s with a cycle number of 1.5 in the sweeping potential range −1.4 V to 0.0 V was used to prepare silver particles on CPE.

The concentration of silver was optimized with addition of different volumes of 5.0 × 10⁻² mol/L AgNO₃ into 40 mL cells containing Britton–Robinson buffer under the following conditions: pH, 2; scan rate, 3 mV/s; number of cycles, 1.5. As shown in Fig. 2, the highest peak intensity was reached for 0.4 mmol AgNO₃. It has been observed that a poor response for PQ is obtained for high concentrations of AgNO₃. This behavior was attributed to the formation of a partial silver film on CPE [34].

Fig. 2 — Influence of the experimental variables of the electrodeposition (scan rate, sweeping potential range, cycle number, concentration of silver in electrolytic solution) and of measurement conditions on square wave responses of paraquat (PQ), [PQ] = 1.0 × 10⁻⁴ mol/L Ag-CPE, pH 2.
The results indicate that increase in the variable levels provides an increase in the electrical response of PQ. However, although the mass of silver makes it possible to increase the sensitivity of the electrode, 0.4 mmol was fixed in order to avoid overweight of silver and the formation of the silver film onto electrode surface. This was expected as the increase in concentration of silver and sweeping potential range would entail a deposition of the silver onto the electrode, which enhanced the sensitivity of the electrode. Concerning the scan rate, the effect of the electrodeposition of the silver onto the CPE is very important. The interaction between sweeping potential, preconcentration time, and effect of pH is not significant. This was verified experimentally (Table 1).

The model has been validated using analysis of the report (F_{ratio} = mean squares regression/mean squares residues) and the correlation coefficient \( R^2 = \) (are square regression/are total sum of squares)\( R^2 \) = 0.9061. The value found in the report \( F_{(PQ)} \) was higher than the critical value of Fischer. The regression coefficient is considered significant with a risk of 5%. According to the obtained value of the regression coefficient, we can deduce that the electrode response is strongly dependent on the concentration of silver.

### 3.4. Calibration graph

Under the optimized conditions, the square wave as a function of PQ concentration was linear between 1.0 \( \times \) 10^{-7} mol/L and 1.0 \( \times \) 10^{-3} mol/L (Fig. 3). The linear correlation coefficients are 0.9872 and 0.9751 of P1 and P2, respectively. The detection limit (DL) and quantification limit (QL) were 2.01 \( \times \) 10^{-8} mol/L and 6.073 \( \times \) 10^{-8} mol/L for P1 and 7.9 \( \times \) 10^{-8} mol/L and 26.5 \( \times \) 10^{-8} mol/L for P2, respectively. The precision of this methodology for the determination of PQ was evaluated for eight successive measurements of the same samples containing 1.0 \( \times \) 10^{-5} mol/L PQ. The deviation coefficients were 1.45% and 1.36% for Peaks 1 and 2, respectively. The sensitivity is obviously higher than that of other methods such as spectrophotometry (8.56 \( \times \) 10^{-8} mol/L) [9], gas chromatography–mass spectrometry (1.94 \( \times \) 10^{-7} mol/L) [38], differential pulse voltammetry (9.3 \( \times \) 10^{-8} mol/L) [11], pthalocyanine-based pyrolytic graphite electrode (1.0 \( \times \) 10^{-7} mol/L) [17], and gold electrodes (3.9 \( \times \) 10^{-8} mol/L) [12]. However, it was comparable to the result obtained with HPLC (1.94 \( \times \) 10^{-6} mol/L [39] and square wave voltammetry (1.0 \( \times \) 10^{-8} mol/L) [40].

### 3.5. Interference

The effect of foreign species was also studied in the range of 5.0 \( \times \) 10^{-5} mol/L to 1.0 \( \times \) 10^{-3} mol/L in the presence of 5.0 \( \times \) 10^{-5} mol/L PQ in order to evaluate the effect of interferences (Table 2). This was considered when the analytical signal varied > 5% in the presence of foreign species. Table 2 shows that the addition of glyphosate herbicide did not cause changes in the peak PQ; however, it interfered when its concentration is in a 20 \( \times \) excess. The presence of most citric and ascorbic acids gives rise to a small decrease in the intensity of PQ peak. The obtained results also demonstrated that the second reduction peak of PQ is more likely distorted owing to the presence of these contaminants. The fact that their peaks occur at approximately 1.20 V indicates the

### Table 1 – Estimated values of coefficients for response yield.

| Coefficient | Standard error | t. exp. | Significance (%) |
|-------------|----------------|---------|------------------|
| b0          | 31.236         | 0.730   | 42.77            | <0.01 *** |
| b1          | -1.863         | 0.730   | -2.55            | 2.05 *    |
| b2          | 1.507          | 0.730   | 2.06             | 5.3       |
| b3          | 7.949          | 0.730   | 10.88            | <0.01 *** |
| b4          | 0.182          | 0.730   | 0.25             | 80.1      |
| b5          | 1.396          | 0.730   | 1.91             | 7.1       |
| b12         | 0.240          | 0.730   | 0.33             | 74.4      |
| b13         | -2.209         | 0.730   | -3.02            | 0.788 **  |
| b23         | 1.620          | 0.730   | 2.22             | 3.95 *    |
| b34         | -0.549         | 0.730   | -0.75            | 46.9      |
| b44         | -1.084         | 0.730   | -1.48            | 15.4      |
| b14         | -1.124         | 0.730   | -1.54            | 14.0      |
| b15         | -0.841         | 0.730   | -1.15            | 26.6      |
| b25         | -0.370         | 0.730   | -0.51            | 62.4      |
| b35         | 0.622          | 0.730   | 0.85             | 41.2      |
| b45         | -0.058         | 0.730   | -0.08            | 93.6      |

*Statistically non-significant at the 99% level (p > 0.01).
**Statistically significant at the 99% level (p = 0.01).
***Statistically very significant at the 99% level (p < 0.01).

b = scan rate; b = sweeping potential range; b = concentration of silver; b4 = pH; b5 = preconcentration time.
presence of a significant interference in the second peak. The presence of most ions (Ca\(^{2+}\), Mg\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), and Cu\(^{2+}\)) gives rise to a small decrease in the intensity of PQ peak, because of their precipitation with the SO\(_4^{2-}\) generated from electrolytes. KCN should be added in the electrolytic solution to inhibit the interference effects of these ions. We also noticed that NO\(_3^-\) stirs competition with PQ, leading to an interaction of NO\(_3^-\) with silver-modified CPE and then to a decrease in peak currents of PQ.

### 3.6. Practical application

#### 3.6.1. Orange samples

The methodology developed in the preceding sections was applied to determine PQ in the orange samples obtained from an agricultural area in the Souss Massa Draa region, Agadir, Morocco. First, 20 g of orange free from pesticides was transferred into an electrochemical cell, then mixed and homogenized and spiked with appropriate amounts of PQ, and then adjusted to pH value of 7.5. The samples were used as received in preparing the supporting electrolyte (adding 0.1 mol/L Na\(_2\)SO\(_4\)), and the analytical curves were again obtained using SWV experiments. The analytical sensitivities, defined by the slope of the analytical curves, were compared with those obtained with purified water, where it is possible to observe that the peak current values for the PQ reduction process displayed some influence from the components of the samples used, characterized by a decrease in the slope of the curves obtained. It was found that peak currents P\(_1\) and P\(_2\) versus PQ added into orange samples increased linearly in the range of 1.0 × 10\(^{-6}\) mol/L to 6.0 × 10\(^{-4}\) mol/L of PQ (Fig. 4). These results indicate that the proposed methodology is suitable for the determination of PQ in samples of commercial orange juice (Table 3). The statistical calculations for the assay results showed the suitable precision of the proposed method. Recovery experiments were also carried out in order to evaluate the interference of matrix effects of the orange samples on the detection of PQ on Ag-CPE. Results obtained for RSD and percentage recovery for the samples spiked with 5.0 × 10\(^{-5}\) mol/L PQ were 2.35% and 90.0%, respectively. The results presented satisfactory values for the proposed electroanalytical methods, thus indicating the suitability of the proposed method for use in orange samples.

#### 3.6.2. Commercial orange juice

SWV was also used to evaluate the performance of the analytical method to determine PQ in orange juice free from pesticides. The support electrolytes were prepared by addition of 0.1 mol/L of Na\(_2\)SO\(_4\) to orange juice and were adjusted to a pH value of 7.5. The linear calibration curve was obtained in the concentration range of 5.0 × 10\(^{-6}\) mol/L to 6.0 × 10\(^{-4}\) mol/L for PQ (Fig. 4). The correlation coefficient of the curve was 0.983. The DL and QL were 5.58 × 10\(^{-7}\) mol/L and 18.58 × 10\(^{-8}\) mol/L, respectively (Table 3). These results indicate that the proposed method is suitable for the determination of PQ in commercial orange juice samples (Table 3).

When the method was applied to orange samples and commercial orange juice, the concentration of the residues of PQ was found to be lower than the DL. A comparison of the analytical sensibility of the methodology obtained for orange samples and commercial orange juice was investigated. The results showed that the slope of the calibration curve of the commercial orange juice has not changed much; it decreased

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**Table 2** Effect of foreign species on parquat (PQ) analysis.

| Added species | Concentration (mol/L) × 10\(^{-5}\) | Signal variation (%) |
|---------------|------------------------------------|----------------------|
|               |                                    | Peak 1   | Peak 2   |
| Ca\(^{2+}\)   | 5.0                                | −2.59    | −2.17    |
| Mg\(^{2+}\)   | 5.0                                | −2.73    | −2.05    |
| Fe\(^{3+}\)   | 5.0                                | −2.66    | −2.61    |
| Cd\(^{2+}\)   | 5.0                                | −2.83    | −2.92    |
| Cu\(^{2+}\)   | 5.0                                | −2.65    | −2.51    |
| Pb\(^{2+}\)   | 5.0                                | −3.22    | −2.56    |
| NO\(_3^-\)    | 10.0                               | −3.56    | −2.69    |
| Fe\(^{2+}\)   | 10.0                               | −2.75    | −2.63    |
| Glyphosate     | 100.0                              | +4.43    | +4.04    |
| Citric acid    | 100.0                              | −3.34    | −5.44    |
| Ascorbic acid  | 100.0                              | −3.45    | −5.66    |

* The PQ concentration was fixed at 5.0 × 10\(^{-5}\) mol/L, and the concentration of the foreign species was varied from 5.0 × 10\(^{-5}\) mol/L to 1.0 × 10\(^{-3}\) mol/L.

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**Fig. 3** Square-wave voltammograms in 0.1 mol/L Na\(_2\)SO\(_4\), pH 7.5, t\(_p\) = 10 minutes, at Ag-CPE of different concentrations of PQ: (a) 12.0 × 10\(^{-4}\), (b) 8.0 × 10\(^{-4}\), (c) 7.0 × 10\(^{-4}\), (d) 4.0 × 10\(^{-4}\), (e) 2.0 × 10\(^{-4}\), (f) 1.5 × 10\(^{-4}\), (g) 1.0 × 10\(^{-4}\), (h) 1.0 × 10\(^{-5}\), (i) 1.0 × 10\(^{-6}\), and (j) 1.0 × 10\(^{-7}\). CPE = carbon paste electrode.
by 2% relative to the slope of the orange. This can be attributed to the adsorption of the acids present at a slightly higher proportion. HPLC [41] was used to perform the comparison with the results obtained using the proposed voltammetric method. The results presented in Table 4 using the proposed method and the comparative HPLC method are in good agreement at a confidence level of 95% (F test and paired t test) and in agreement with the Environmental Protection Agency [42] and Health Canadian Agency [43]. Using SWV, the background currents in lemon and orange were intense and not flat. This behavior is attributable to the presence of other matrix electroactive components, which—in the case of citrus fruits—are basically ascorbic acid (vitamin C) and citric acid, which can inhibit the detection process of PQ at silver surfaces.

### 4. Conclusion

The silver particles were deposed electrochemically on CPE using cyclic voltammetry. The obtained electrode was used to determine PQ in juice orange samples without any pretreatment or extraction procedure. The results obtained showed the efficiency of the silver-modified carbon electrode for the determination of low concentrations of PQ(II) by SWV. The repeatability, sensitivity, and accuracy rates are good,

### Table 3 – Results obtained from linear regression curves for the determination of PQ at Ag-CPE in orange juice samples and commercial orange juice.

|          | Orange  | Commercial orange juice |
|----------|---------|-------------------------|
|          | P₁      | P₂                      | P₁     | P₂     |
| R²       | 0.987   | 0.993                   | 0.983  | 0.992  |
| Slope A (mol⁻¹ L⁻¹) | 1.082   | 0.541                   | 1.049  | 0.500  |
| DL (mol/L) × 10⁻⁷ | 2.58    | 4.58                    | 5.58   | 7.22   |
| QL (mol/L) × 10⁻⁷ | 6.60    | 15.20                   | 18.58  | 24.04  |
| RSD (%)   | 2.35    | 2.13                    | 2.25   | 2.18   |

Ag = silver; CPE = carbon paste electrode; DL = detection limit; PQ = paraquat; QL = quantification limit; RSD = relative standard deviation.

### Table 4 – Paraquat (PQ) determination in spiked samples.*

| Samples                  | Ag-CPE | HPLC                  |
|--------------------------|--------|-----------------------|
|                          | Added  | PQ(II) found          | Recovery (%) | PQ(II) found | Recovery (%) |
|                          | (mol/L) × 10⁻⁵ | (mol/L) × 10⁻⁵          |              | (mol/L) × 10⁻⁵ |              |
| Orange                   | 4      | 3.53                  | 88.25 ± 18.43 | 3.68        | 92.00        |
| Orange                   | 6      | 5.34                  | 89.00 ± 17.88 | 5.76        | 96.00        |
| Commercial orange juice  | 4      | 3.36                  | 84.00 ± 20.97 | 3.64        | 91.00        |
| Commercial orange juice  | 6      | 4.98                  | 83.00 ± 21.67 | 5.68        | 94.66        |
| Commercial orange juice  | 8      | 6.66                  | 83.25 ± 21.44 | 7.28        | 91.00        |

CPE = carbon paste electrode; HPLC = high-performance liquid chromatography.

* Recovery (R) = √(R₀(1−R₀)/n) (n = 3), where R₀ is the percentage recovery and t is the distribution value chosen for the desired confidence level. Theoretical values at 95% confidence limits: t = 2.45.
provided that the proper instrumental parameters are used. The analytical results show that the proposed modified electrode was able to detect $2.01 \times 10^{-8}$ mol/L of PQ with good sensitivity and repeatability.

**Conflicts of interest**

The authors declare that they have no conflicts of interest.

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**REFERENCES**

[1] Almeida GL, Schmitt GC, Bairros AV, Emanuelli T, Garcia SC. Os riscos e danos nas intoxicações por paratext em animais domésticos. Ciência Rural 2007;37:1506–12.

[2] Dinis-Oliveira RJ, Remiao F, Carmo H, Duarte JA, Navarro AS, Bastos ML, Carvalho F. Paratext exposure as an etiological factor of Parkinson's disease. Neurotoxicology 2006;27:1110–22.

[3] Langston JW, Forno LS, Tetrud J, Reeves AG, Kaplan JA, Karluk D. Evidence of active nerve cell degeneration in the substantia nigra of humans years after 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine exposure. Ann Neurol 1999;46:598–605.

[4] Burns RS, Chiueh CC, Markey SP, Ebert MH, Jacobowitz DM, Kopin JJ. A primate model of parkinsonism: selective destruction of dopaminergic neurons in the pars compacta of the substantia nigra by N-methyl-4-phenyl-1,2,3,6-tetrahydropyridine. Proc Natl Acad Sci USA 1983;80:4546–50.

[5] Costello S, Cockburn M, Bronstein J, Zhang X, Ritz B. Parkinson's disease and residential exposure to maneb and paraquat from agricultural applications in the central valley of California. Am J Epidemiol 2009;169:919–26.

[6] Mohammadi-Bardboria A, Ghazi-Khansarib M. Alternative electron acceptors: proposed mechanism of paraquat mitochondrial toxicity. Environ Toxicol Pharmacol 2008;26:1–5.

[7] Commission Regulation (EC) No 149/2008 of 29 January 2008 amending Regulation (EC) No 396/2005.

[8] Commission Regulation (EU) No 520/2009 of 6 May 2011.

[9] Infante CMC, Morales-Rubio A, Guardia MDI, Rocha FRP. A new osmium-polymer modified electrode for determination of paraquat using a DNA-modified carbon nanotube composite electrodes. Electrochim Acta 2010;55:7892–6.

[10] Lopes IC, De Souza D, Machado SAS, Tanaka AA. Voltammetric determination of paraquat pesticide on a phthalocyanine-based pyrolic graphite electrode. Anal Bioanal Chem 2007;388:1307–14.

[11] De Oliveira UMF, Lichtig J, Masini JC. Evaluation of a Nafon coated glassy carbon electrode for determination of paraquat by differential pulse voltammetry. J Braz Chem Soc 2004;15:735–41.

[12] Ruhling I, Schafer H, Ternes W. HPLC online reductive scanning voltammetric detection of diquat, paraquat and difenzoquat with mercury electrodes. Fresenius J Anal Chem 1999;364:565–9.

[13] Metters JP, Kadara RO, Banks CE. New directions in screen printed electroanalytical sensors: an overview of recent developments. Analyst 2011;136:1067–76.

[14] Laschi S, Bulukin E, Palchetti I, Cristea C, Mascini M. Disposable electrodes modified with multi-wall carbon nanotubes for biosensor applications. IJBM-SBM 2008;29:202–7.

[15] Antiochia R, Gorton L. A new osmium-polymer modified screen-printed graphepl electrode for fructose detection. Sensor Actuators B Chem 2014;195:287–93.

[16] De Lacey AL, Bes MT, Gómez-Moreno C, Fernández VM. Amperometric enzyme electrode for NADP+ based on a ferrodoxin-NADP+ reductase and viologen-modified glassy carbon electrode. J Electroanal Chem 1995;390:69–76.

[17] Ramdane-Terbouche CA, Terbouche A, Djebbar S, Hauchard D. Electrochemical sensors using modified electrodes based on copper complexes formed with Algerian humic acid modified with ethylenediamine or triethylentetramine for determination of nitrite in water. Talanta 2014;119:214–25.

[18] Starowicz M, Stypula B, Banasz J. Electrochemical synthesis of silver nanoparticles. Electrochem Commun 2006;8:227–30.

[19] Welch CM, Compton RG. The use of nanoparticles in electroanalysis: a review. Anal Bioanal Chem 2006;384:601–19.

[20] Sun L, Zhang Z, Mater HD. A novel method for preparation of silver nanoparticles. Mater Lett 2003;57:3874–9.

[21] Fukushima M, Yanagi H, Hayashi S, Suganuma N, Taniguchi Y. Fabrication of gold nanoparticles and their influence on optical properties of dye-doped sol–gel films. Thin Solid Films 2003;438–439:39–43.

[22] Dai X, Nekrassova O, Hyde ME, Compton RG. Anodic stripping voltammetry of arsenic(III) using gold nanoparticle-modified electrodes. Anal Chem 2004;76:5924–59.

[23] El-Deab MS, Okajima T, Ohaka T. Electrochemical reduction of oxygen on gold nanoparticle-electrodeposited glasy carbon electrodes. J Electrochem Soc 2003;150:A851–7.
[31] Welch CM, Banks CE, Simm AO, Compton RG. Silver nanoparticle assemblies supported on glassy-carbon electrodes for the electroanalytical detection of hydrogen peroxide. Anal Bioanal Chem 2005;382:12–21.

[32] Yin B, Ma H, Wang S, Chen S. Electrochemical synthesis of silver nanoparticles under protection of poly(N-vinylpyrrolidone). J Phys Chem B 2003;107:8898–904.

[33] Farahi A, Achak M, El Gaini L, El Mhammedi MA, Bakasse M. Silver particles-modified carbon paste electrodes for differential pulse voltammetric determination of paraquat in ambient water samples http://dx.doi.org/10.1016/j.ijaubas. 2014.06.011.

[34] Encarnación BCM, Olga DR, Julia AMM. Determination of lamotrigine by adsorptive stripping voltammetry using silver nanoparticle-modified carbon screen-printed electrodes. Talanta 2007;74:59–64.

[35] Rameshbabu N, Sampath Kumar TS, Prabhakar TG, Sastry VS, Murty KVGK, Prasad Rao1 K. Antibacterial nanosized silver substituted hydroxyapatite: Synthesis and characterization. J Biomed Mater Res Part A 2007;80:581–91.

[36] Basile A, Bhatt AI, O’Mullane AP, Bhargava SK. An investigation of silver electrodeposition from ionic liquids: Influence of atmospheric water uptake on the silver electrodeposition mechanism and film morphology. Electrochim Acta 2011;56:2895–905.

[37] El Harmoudi H, Achak M, Farahi A, Lahrich S, El Gaini L, Abdennouri M, Bouzidi A, Bakasse M, El Mhammedi MA. Sensitive determination of paraquat by square wave anodic stripping voltammetry with chitin modified carbon paste electrode. Talanta 2013;115:172–7.

[38] Almeida RMD, Yonamine M. Gas chromatographic-mass spectrometric method for the determination of the herbicides paraquat and diquat in plasma and urine samples. J Chromatogr A 2007;1133:260–4.

[39] Brunetto MR, Morales AR, Gallignani M, Burguera J, Burguera M. Determination of paraquat in human blood plasma using reversed-phase ion-pair high performance liquid chromatography with direct sample injection. Talanta 2003;59:913–21.

[40] Livia LCG, Luiz CSF, Geiser GO, Orlando F, Craig EB. Square-wave voltammetric determination of paraquat using a glassy carbon electrode modified with multiwalled carbon nanotubes within adiheaxadecyl hydrogen phosphate (DHP) film. Sens Actuators B 2013;181:306–11.

[41] Hodgeson JW, Bashe WJ, Eichelberger JW. Method 549.1, Revision 1. 0, Environmental Monitoring Systems Laboratory, Office of research and development. U.S. EPA; 1992.

[42] EPA, http://www.epa.gov/pesticides/reregistration/REDs/factsheets/0262fact.pdf.

[43] Health Canadian Agency, http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/water-eau/paraquat/paraquat-eng.pdf.