Investigation of Voltammetric Behavior of Herbicide N,N'-Ethylene-2,2'-Bipyridinium using the Copper Modified Carbon Paste Electrode

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The reactivity of Diquat ion at the carbon paste electrode (C.P.E) modified by the copper (C.P.E-Cu) has been reported. The working electrode was prepared by mixing the copper with the carbon powder. The optimal potential window has been selected in the range from -1 V to 1.5 V. The effect of parameters such as pH, scan rate, preconcentration time and concentration has been studied by cyclic voltammetry. The preconcentration time is 13 minutes. The reactivity of Diquat on the electrochemical detector has been characterized by the appearance of the cathodic peak at 0.6 V in a solution of sodium sulfate (pH 3). Catalytic influence has been examined by cyclic voltammetry and electronic impedance spectroscopy. The calculated limits of detection and quantification have been $9.48 \cdot 10^{-6}$ and $3.16 \cdot 10^{-6}$ mol L^{-1}, respectively. Then relative standard deviation (RSD) at $0.8 \cdot 10^{-4}$ mol L^{-1} of Diquat was 5.77% for nine repetitions. The analytical application was done in the determination of Diquat in real samples of apple juice with satisfying results.

Keywords: N,N'-ethylene-2,2'-bipyridinium, cyclic voltammetry, electronic impedance spectroscopy, apple juice, electroanalysis, mixing, copper

The N, N'-ethylene-2,2'-bipyridinium (Diquat) ion belongs to the herbicides family and plays the role of a plant development regulator, structurally similar to paraquat. The use of. in agriculture can cause renal and hepatic toxicity [1]. Quantitative analyses of this herbicide are of particular concern because of its acute toxicity to humans and mammals [2, 3]. Numerous analytical technics were cited in the bibliography for the analysis of Diquat, such as electrospray ionization mass spectrometry liquid chromatography [4], solid-phase extraction [5], raman spectrometry [6], HPLC [7, 8], EC [9], and kinetic spectrophotometric method [10]. However, most of these analytical techniques are not suitable for on-site analysis because of their size, price, and the time required to perform the analyzes. It requires a simple, sensitive, cheaper and reliable technique to on-site analysis of toxic products in several application sectors, such as biomedical, natural and industrial analyzes. A fast and reliable technique for on-site analysis of toxic products in several application sectors, such as biomedical, natural and industrial analyzes. A fast, repeatable and accurate analysis method for determination the Diquat is therefore important. In the last decades, the electrodes modified by inorganic and organic compounds are widely used in analytical determinations [11-13]. The reactivity of its chemically modified electrodes comes from its ability to act as redox intermediates by increasing the charge transfer between the electrodes surface and the redox species [14]. Electrochemical techniques use carbon-modified electrodes, such as carbon paste electrodes modified by aluminum [15], carbon paste electrode modified by heavy metals [16], carbon paste electrode modified by zinc [17] and natural phosphate modified carbon paste electrodes [18]. The electrochemical analysis techniques are less sensitive to interferences influences, characteristic of their success in the electrochemical analysis [19]. In this work, we report the electrochemical determination of Diquat at the C.P.E-Cu surface. The electrochemical characterization of Diquat adsorbed at this electrode surface was studied using cyclic voltammetry (CV) and electronic impedance spectroscopy (EIS) methods.

Experimental part

Apparatus and reagents

The cyclic voltammetry and electronic impedance spectroscopy methods were recorded by a voltalab potentiostat (model PGSTAT 100) driven by the electrochemical data processing software during analysis (voltalab master 4 software). The electrochemical compartment was operated with three electrodes: a C.P.E-Cu working electrode, a reference electrode (saturated Calomel electrode) and an auxiliary electrode (platinum electrode). The pH meter (Radiometer Copenhagen, PHM210, Tacussel

and French) was used to adapt the pH of the medium. Diquat, $CuSO_4$ and Na_2SO_4 were bought from Sigma-Aldrich. The pH was adjusted by sulfuric acid or potassium hydroxide. All solutions were prepared by distilled water. All experiments were realized at 25 °C.

Preparation of the C.P.E-Cu and procedure

The copper used in this work is obtained in the laboratory by electrochemical deposition on the surface of a metal electrode ($CuSO_4$ + H_2O) then recovered in powder form. The C.P.E-Cu was prepared by completely mixing the carbon and copper powder in the presence of a few drops of paraffin oil until a homogeneous paste was obtained. The body of this electrode was a cylinder tightly filled with paste. The surface of this working electrode is 0.1256 cm^2. Electrical contact was provided by a carbon rod.

Several supporting electrolytes were tested such as Na_2SO_4, K_2SO_4, H_2SO_4, NaOH, KCl, and NaCl. The excellent electroanalysis responses were obtained by Na_2SO_4 (0.1 M, pH 3). The working procedure consists in measuring the electrochemical responses at the C.P.E-Cu surface in the presence of Diquat concentration. An amount of Diquat was added to the electrochemical cell containing 20 mL of sodium sulfate as an electrolytic medium. The cyclic voltammetry method was recorded in the potential range between -1 V and 1.5 V. The excellent analysis conditions were determined by measuring the peak current reduction as a function of the parameters. Electrochemical determination was obtained at 25 °C.

Results and discussion

CV and EIS characterization

Fig. 1 shows the cyclic voltammetry obtained in the potential range between -1 V and 1.5 V on the surface of C.P.E and C.P.E-Cu at the scan rate of 100 mV s^{-1}. The cyclic voltammograms have different shapes, which indicates that the surface of the C.P.E has been well modified by copper. The electrochemical responses of the C.P.E and C.P.E-Cu toward Diquat reduction were studied by cyclic voltammetry in 0.1 M Na_2SO_4 (pH 3) containing $2.0 \cdot 10^{-5}$ mol L^{-1} of Diquat. No peak is recorded using C.P.E (Fig. 2a). Fig. 2b shows the cathodic peak at about Epc = 0.6 V. The C.P.E-Cu exhibited an excellent electrocatalytic reduction of Diquat compared to C.P.E.

The electronic impedance spectroscopy method confirmed the sensitivity of this electrode (Fig. 3). The electronic impedance spectroscopy shows another evidence of reactivity of Diquat on the C.P.E-Cu surface according to a process electrolytic reduction of Diquat on the C.P.E-Cu. The remarkable diminish of the charge transfer resistance means that the C.P.E-Cu is more conductive, which can be explained by the presence of Diquat on the C.P.E-Cu surface.

Influence of accumulation time and % Cu

In addition to its electrocatalytic properties, the C.P.E-Cu shows a big capacity for the detection of Diquat. This electroanalytical study was carried out by the cyclic voltammetry method. Firstly, all electroanalysis parameters were optimized in 0.1 M Na_2SO_4 (pH 3) containing $3.0 \cdot 10^{-5}$ mol L^{-1} of Diquat.

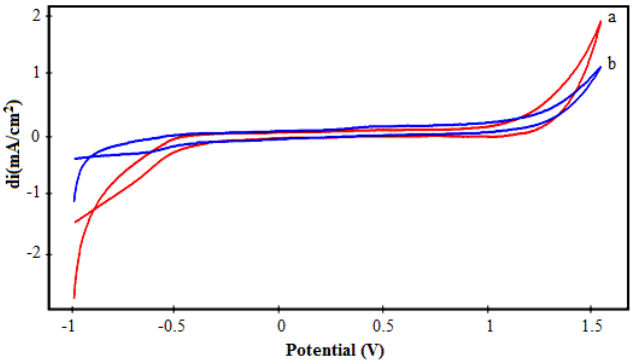

Fig. 1. CVs obtained for C.P.E (a) and C.P.E-Cu (b), in Na_2SO_4 (0.1 M, pH 3) at 100 mV s^{-1}.

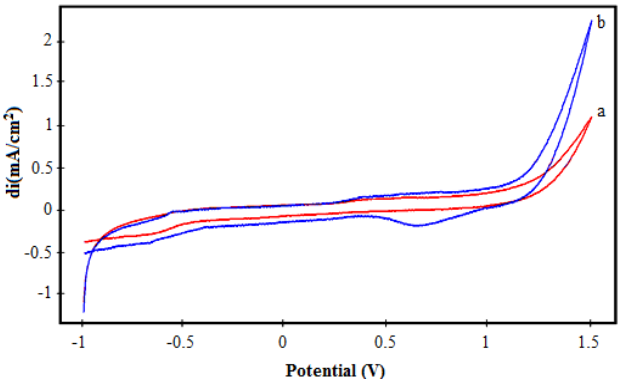

Fig. 2. CVs obtained for C.P.E (a) and C.P.E-Cu (b) in presence of $2 \cdot 10^{-5}$ mol L^{-1} Diquat, scan rate 100 mV s^{-1}, pt = 13 minutes.

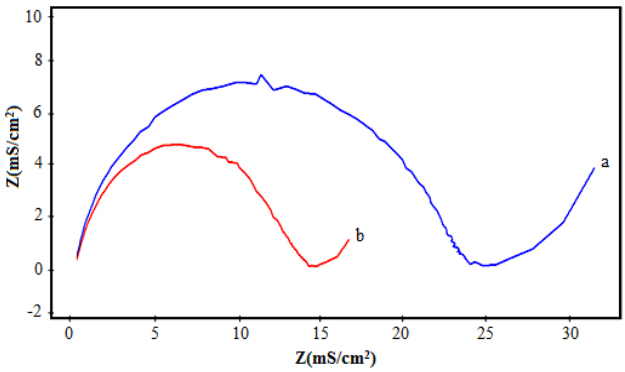

Fig. 3. EIS obtained for C.P.E (a) and C.P.E-Cu (b) in presence of $2 \cdot 10^{-5}$ mol L^{-1} Diquat, Na_2SO_4 (0.1 M, pH 3).

The increase of the modifier's loading (from 2 to 60 % by weight of carbon paste) affects the Diquat determination at the C.P.E-Cu surface represented in Fig. 4. The height of the reduction peak of Diquat increases with increasing copper percentage up to

16%. In the range of 16 to 25% Cu the maximum of the peak remains unchanged and after 25% Cu the height of the peak decreases. Therefore, 16% of the weight ratio was used in all experiments.

The effect of the accumulation time on the voltammetry responses was carried out. Fig. 5 shows an increase in current intensity as a function of preconcentration time during the first 13 minutes. Another increase in preconcentration time does not change the Diquat at the C.P.E-Cu surface, which produces stability in the peak current reduction. This phenomenon is attributed to the saturation of the C.P.E-Cu surface by adsorption of Diquat. Hence a 13 min was used in this work.

In another experimental investigation, the optimal electroanalysis parameters to perform the Diquat determination was found to be 20 mV s^{-1}, 140 ms, 160 mV, 200 ms for the step, pulse, width, and period, respectively.

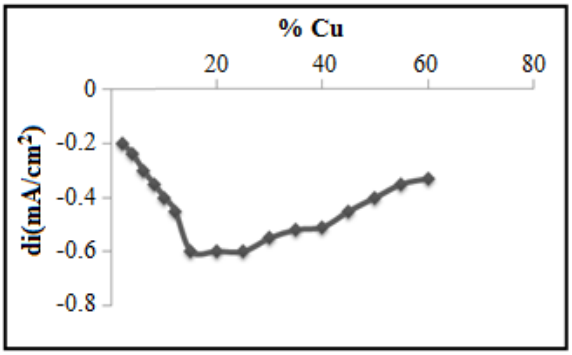

Fig. 4. Influence of % Cu in presence of 3 × 10^{-5} mol L^{-1} Diquat in 0.1 M Na_2SO_4 (pH 3) at the C.P.E-Cu.

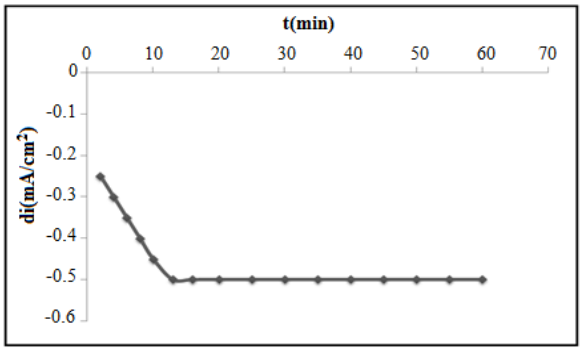

Fig. 5. Influence the accumulation time in presence of 3·10^{-5} mol L^{-1} Diquat at the C.P.E-Cu surface on the peak current reduction.

Effect of scan rate and pH

The effect of the scan rate and pH on the cathodic peak current of Diquat were investigated on the C.P.E-Cu surface under the concentration of 4·10^{-5} mol L^{-1} of Diquat in 0.1 M Na_2SO_4 (pH 3). The peak reduction current of Diquat increased with increasing scanning rate (Fig. 6). The cathode peak shifted to a negative potential with increasing scanning speed. The linearity of the cathode peak current with the square root of the slew rate was determined in Fig. 7. Since the current is proportional to $V^{1/2}$, the current is controlled by diffusion at the C.P.E-Cu surface. The effect of pH on cyclic voltammetry responses of the C.P.E-Cu was further studied in the pH range from 3 to 12 and well-defined cyclic voltammetry curves were observed (Fig. 8). With the increase of pH, the reduction peaks are currently decreasing. Therefore, pH 3 is the excellent electrocatalytic activity of the working electrode toward Diquat reduction (Fig. 9).

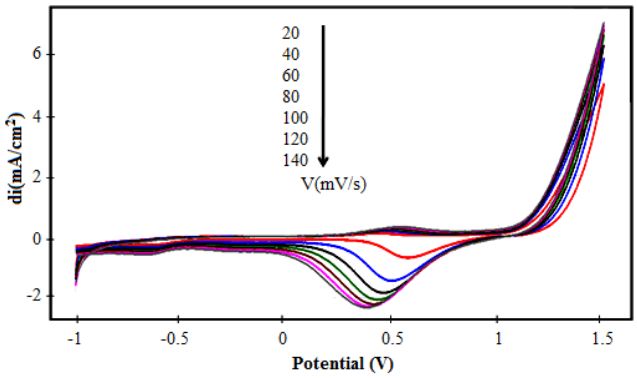

Fig. 6. CVs obtained on the C.P.E-Cu surface in the presence of 4·10^{-5} mol L^{-1} Diquat for different scanning rates.

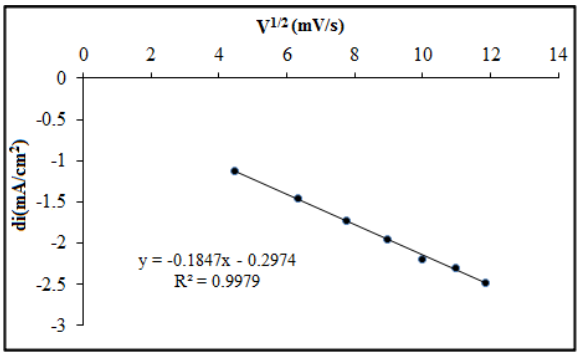

Fig. 7. The plot of the current density as a function to the scanning rate.

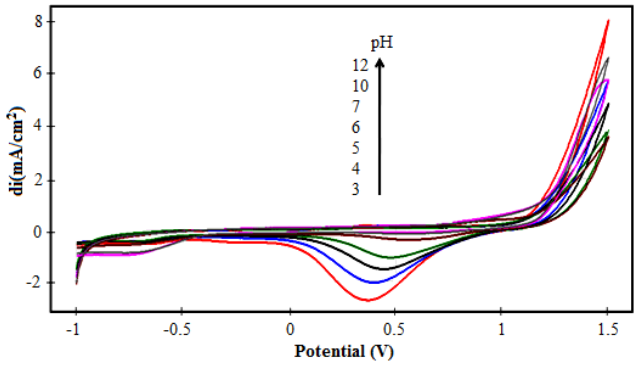

Fig. 8. Effect of pH on the Diquat reduction at the C.P.E-Cu surface.

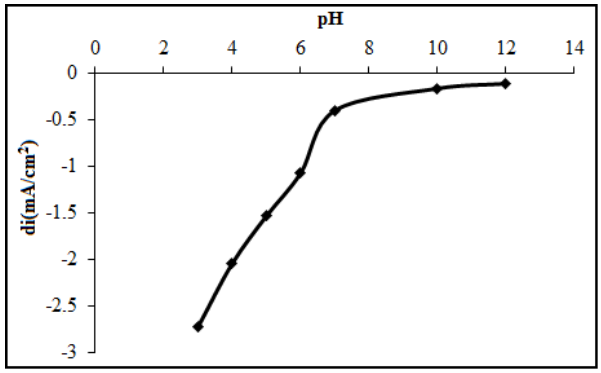

Fig. 9. The influence of pH on the current of the reduction peak.

Effect of concentration

The curve of the influence of the concentration of Diquat on the current of the peak was obtained under optimal conditions. Fig. 10 shows the cyclic voltammograms recorded on the C.P.E-Cu surface in the range between $4.0 \cdot 10^{-5}$ and $1.2 \cdot 10^{-4}$ mol L^{-1} of Diquat. The cathodic peak current increases with the increase of Diquat concentration. It has been illustrated that the cathode peak potentials shift towards negative values, indicating that the Diquat molecule is adsorbed over the electrode surface. Fig. 11 and 12 show the linearity between peak currents and peaks potentials versus the Diquat concentration on the C.P.E-Cu surface. The reactivity of the C.P.E-Cu towards the Diquat electroanalysis is improved by the copper. The detection limit (DL) and quantification limit (QL) were calculated on the cathodic peak current using the following equations: DL = 3 s/m, QL = 10 s /m (s: Standard deviation of the peak currents nine runs; m: Slope of the calibration curve). The DL and QL were calculated as $9.48 \cdot 10^{-6}$ mol L^{-1} and $3.16 \cdot 10^{-6}$ mol L^{-1}, respectively. The relative standard deviation for nine measurements was calculated as 5.77 % for Diquat concentration of $0.8 \cdot 10^{-4}$ mol L^{-1}. The DL obtained by C.P.E-Cu is compared with the results of other electrodes in the literature (Table 1) [20-23]. Fig. 13 indicates the behavior of impedance diagrams obtained at the C.P.E-Cu in the presence of several concentrations of Diquat.

Fig. 10. CVs recorded at the C.P.E-Cu surface for different concentrations in Na_2SO_4 (0.1 M, pH 3), 100 mV s^{-1}.

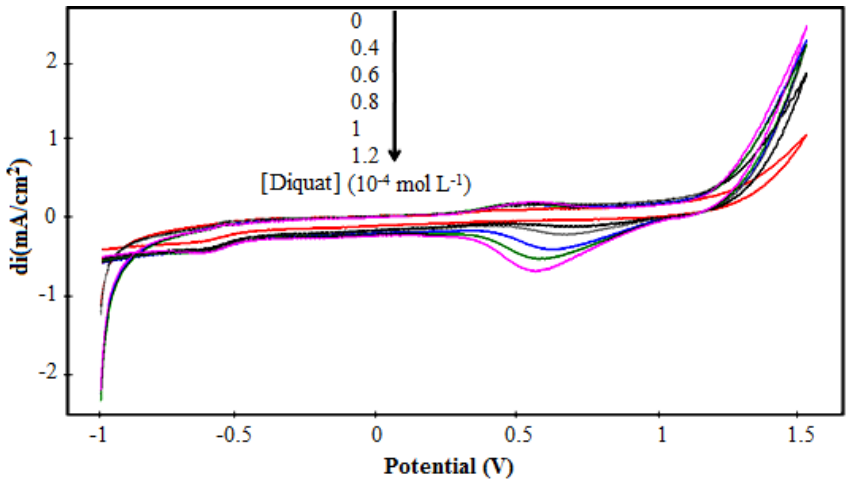

Table 1. Comparison of the different electrodes using for Diquat electroanalysis.

Electrodes	Analytical method	Detection limit	pH	References
Clay Modified Carbon Paste Electrode	Cyclic voltammetry	5.33×10^{-8} mol L^{-1}	3	[20]
Carbon nanomaterials thin film	Cyclic voltammetry	1.1×10^{-7} mol L^{-1}	7	[21]
Gold microelectrodes	Square wave voltammetry	2.81×10^{-3} mol L^{-1}	7	[22]
Natural Phosphate Modified Carbon Paste Electrode	Cyclic voltammetry	9.24×10^{-8} mol L^{-1}	3	[23]
C.P.E-Cu	Cyclic voltammetry	9.48×10^{-6} mol L^{-1}	3	Present work

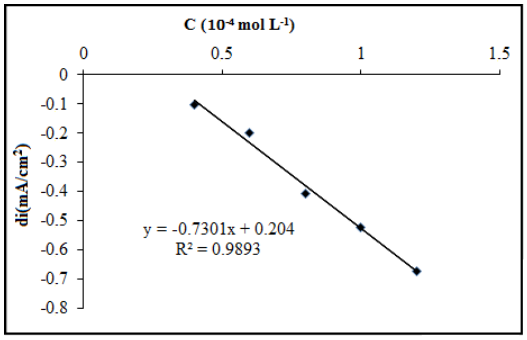

Fig. 11. Evolution of the reduction peak current as a function to the Diquat concentration.

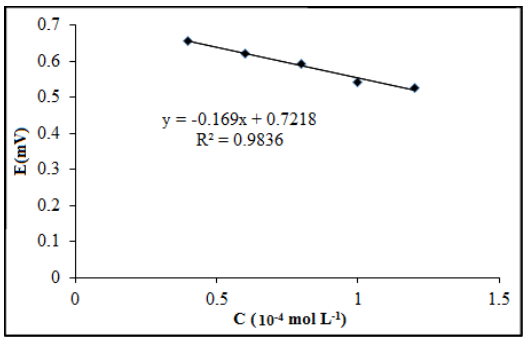

Fig. 12. Evolution of the reduction peak potential as a function to the Diquat concentration.

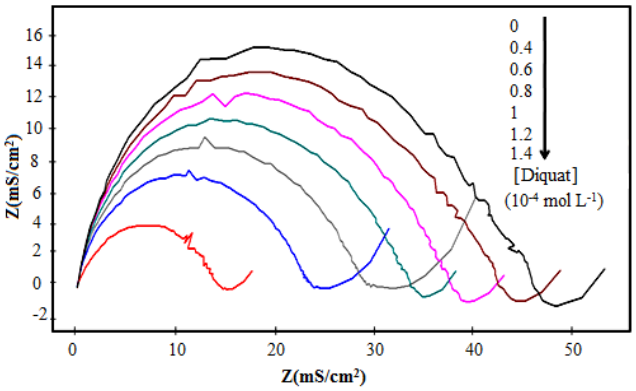

Fig. 13. EIS obtained for different concentrations of Diquat at the C.P.E-Cu surface, Na_2SO_4 (0.1 M, pH 3).

Analytical application

We crushed the apple (250g) and extracted 20 mL of its juice and passed it through the electrochemical cell with 30 ml of background electrolyte. And under the optimized conditions, we added determined concentrations of Diquat. The apple juice solutions were used without any pretreatment. The C.P.E-Cu was applied to the direct determination of Diquat in apple juice samples using the cyclic voltammetry method. Then, the calibration plot of the apple juice samples under optimized conditions is linear with an excellent correlation coefficient (R^2 = 0.9874) (Fig. 14). Consequently, the limit of detection obtained is $6.24 \cdot 10^{-6}$ mol L^{-1}. The relative standard deviation calculated is 4.11 % after nine measurements in the solution of $3.0 \cdot 10^{-5}$ mol L^{-1} of Diquat. This shows the possibility to detect Diquat in apple juice samples.

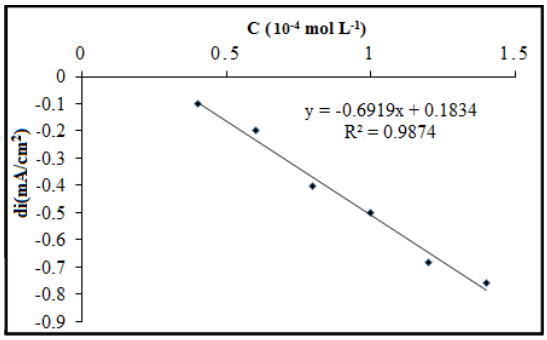

Fig. 14. Linearity between the peak current and added Diquat concentration in optimal conditions.

Conclusion

At the surface of C.P.E-Cu, Diquat can produce an irreversible cathodic peak at 0.6 V in 0.1 M Na_2SO_4 (pH 3). The C.P.E-Cu exhibits excellent electrocatalytic performance toward the reduction of Diquat. A large negative shift in the reduction potentials of Diquat has been observed. The catalytic evaluation was carried out by cyclic voltammetry. So, to obtain the detection limit of Diquat, cyclic voltammetry method was used to detect the Diquat in aqueous media. The C.P.E-Cu is characterized by excellent adsorption of Diquat. The linearity between the cathodic peak current and the Diquat concentration was linear in the range between $4 \cdot 10^{-5}$ and $1.2 \cdot 10^{-4}$ mol L^{-1}. The DL is $9.48 \cdot 10^{-6}$ mol L^{-1}. Besides, the results indicated the feasibility to determine the Diquat in real samples such as apple juice.

Conflicts of Interest

The authors declare no conflicts of interest.

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