

Review

# Electrochemical studies and square wave voltammetry of paraquat at natural phosphate modified carbon paste electrode

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## Abstract

A square wave voltammetry (SWV) method for the determination of trace amounts of paraquat at carbon paste electrode modified with natural phosphate (NP–CPE) is proposed. Paraquat was accumulated onto natural phosphate at open circuit potential from aqueous solution. The reduction peaks of paraquat were observed around  $-0.7$  V and  $-1.0$  V (versus SCE). The response of paraquat at NP–CPE related to: the concentration of this herbicide, preconcentration time, natural phosphate loading and measuring solution pH, was investigated. It was observed that the increase of the cathodic peak currents using SWV, under the optimized condition, is linear with the increase of paraquat concentration in the range from  $2.3 \times 10^{-8}$  mol L<sup>-1</sup> to  $300 \times 10^{-8}$  mol L<sup>-1</sup>. The detection limit (DL, 3S.D.) and quantification limit (QL, 10S.D.) for peak 1 were about  $7.8 \times 10^{-10}$  mol L<sup>-1</sup> and  $2.59 \times 10^{-9}$  mol L<sup>-1</sup>, respectively, in pure electrolyte water with the relative standard deviation of 1.8% ( $n = 7$ ). The proposed method was successfully applied to the determination of paraquat in real water samples with satisfactory results.

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**Keywords:** Paraquat; Natural phosphate; Carbon paste electrode; Square wave voltammetry

## Contents

1. Introduction	2
2. Experimental	2
2.1. Reagents	2
2.2. Preparation of the NP–CPE	2
2.3. Instrument	3
2.4. Procedure	3
3. Results	3
3.1. Natural phosphate characteristics	3
3.2. Preliminary voltammetric characterization	3
3.3. Optimization of experimental conditions	4
3.4. Calibration graph	5
3.5. Application to natural samples water	5
4. Conclusion	6
References	6

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## 1. Introduction

Paraquat (1,1-dimethyl-4,4-dipyridinium chloride) (PQ) is a quaternary nitrogen herbicide introduced in 1962 is widely used for broadleaf weed control. It is a quick-acting, non-selective compound that destroys green plant tissue on contact and by translocation within the plant. It has been used as a crop desiccant and defoliant, and as an aquatic herbicide. Paraquat is also one of the most widely used herbicides, and held the largest share of the global herbicide market until recently overtaken by glyphosate. It is sold in about 130 countries for the use on large and small farms, plantations and estates and in non-agricultural weed control. Paraquat is used to control broad-leaved weeds and grasses, being less effective on deep rooted plants such as dandelions. It does not harm mature bark, and is thus widely used for weed control in fruit orchards and plantation crops, including coffee, cocoa, coconut, oil palms, rubber, bananas, vines, olives and tea, ornamental trees and shrubs and in forestry. Other uses include weed control in alfalfa, onion, leeks, sugar beet, and asparagus. It is used for weed control on non-crop land and can be used as a defoliant for cotton and hops before harvesting. Paraquat is used as a desiccant for pineapples, sugar cane, soya beans and sunflower [1]. A major problem is however caused by abusive and uncontrolled use of paraquat. This problem is related to paraquat high persistence in the environment. After it is slightly absorbed and binds quickly to the soil, paraquat easily leaches into water sources due to its high solubility ( $620 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ ) [2]. The toxic effects of paraquat are mainly due to the cation and the halogen anions which have little toxic effects [3]. A major concern is the accidental and deliberate ingestion of the active ingredient found in herbicide, especially where even small quantities are fatal. Exposure to the concentrated active ingredient is a problem during mixing and loading sprayers. The sharp poisoning can result in respiratory distress and affects the nervous system and the kidneys. Death is generally caused by an evolutionary pulmonary fibrosis and a proliferation of the pulmonary epithelium [4]. In developing countries, the unregulated conditions of use of herbicides make safe use very difficult. Although not fatal at spray strength (regular use) such as required in plantations, herbicides lead to health problems.

The high toxicity of the paraquat has made it necessary to develop a sensitive and rapid method for the determination of this herbicide. In the literature there are numerous methods reported for the determination of paraquat. Until now the analytic approach varies [5,6], including a biological dosage [7,8], spectrophotometry [9–12], chromatography CLHP (UV) or (CPG) [13–16], immunoassay [17,18], potentiometry [19,20] and polarography [21]. The electrochemical determinations of paraquat have been also performed at different electrode surfaces [22–26]. The reversible redox property of paraquat makes voltammetry [27] a suitable technique for the determination of this compound. Because paraquat is a cation, the selectivity and sensitivity of the voltammetric determination of this compound can be improved by using electrodes that are chemically modified with cation-exchange resin. For example, a carbon paste electrode modified with Amberlite XAD-2 resin was devel-

oped for the determination of paraquat by cathodic stripping voltammetry [28]. However, the detection limit ( $0.10 \text{ mg mL}^{-1}$ ) achieved by this method was not very satisfactory. Moreover, surfactants interfered strongly with this method. Recently, clay-modified glassy carbon electrodes GCEs were shown to be very promising for the determination of paraquat with a good detection limit of 0.5 ppb [29]. A voltammetry method coupled to the electron paramagnetic resonance spectroscopy (EPR) [30] was developed to determine cyanoparaquat in propylene carbonate. The cationic characteristic of paraquat was used [31] to analyze the electrochemical behavior of paraquat at carbon paste electrodes modified by zeolites using cyclic voltammetry, chronoamperometry, square wave voltammetry and chronocoulometry. A similar cationic characteristic of paraquat was used [32] for the electrochemical study of paraquat using a glassy carbon working electrodes. It was observed that the neutral two-electron reduction product of paraquat forms an insoluble deposit on the electrode surface. The formation of these deposits was studied by cyclic voltammetry, rotating ring-disk electrode voltammetry (RRDE) and double potential step chronocoulometry (DPSC).

In this paper, we report an efficient method for the detection of paraquat in good to high yields, using electrochemical methods as well as square wave voltammetry (SWV) and cyclic voltammetry (CV) at carbon paste electrode (CPE) modified by natural phosphate (NP). The cationic property of paraquat allows an effective accumulation of this compound onto the NP-CPE. During the past 5 years, we have studied the use of phosphate compounds [33] to promote organic transformation [34] and have shown that its mild basic and acidic proprieties can be exploited in many synthetic applications [35]. Among the different inorganic solids, NP has advantages because it is cheap, readily available, stable in water, non-toxic, and not a pollutant.

## 2. Experimental

### 2.1. Reagents

A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco) [36]. Prior to use this material was treated by techniques involving attrition, sifting, calcinations ( $900^\circ\text{C}$ ), washing, and recalcination. Solutions of paraquat (Sigma, St. Louis, MO, USA) were prepared by dissolving the herbicide, without further purification step. More diluted paraquat standards were obtained by dilution of this solution. Carbon paste was supplied from (Carbone, Lorraine, ref 9900, French). All other reagents used were of analytical grade. Bi-distilled deionized water (BDW) was used throughout the preparation of the solutions.

### 2.2. Preparation of the NP-CPE

The modified carbon paste electrodes were obtained by a mixture of natural phosphate (NP) by a paste carbon (CP), to give NP/CP ratios 12, 25, 50, 75 and 90% by weigh (w/w). The mixture paste was then incorporated into the electrode cavity (laboratory made,  $0.1256 \text{ cm}^2$  geometric surface area) and was

polished by smooth paper. Electrical contact was established by a bar of carbon. The resulting electrode is hereby denoted as NP–CPE. The electrodes modified with natural phosphate (NP–CPE) and carbon paste alone (CPE) were prepared in a similar way.

### 2.3. Instrument

Cyclic and square wave voltammetry were carried out with a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes; using NP modified carbon paste as the working, platinum plate for counter and saturated calomel (SCE) as reference electrodes. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

### 2.4. Procedure

The initial working procedure consisted of measuring the electrochemical response at NP–CPE at a fixed concentration of paraquat. Several supporting electrolytes were tested ( $\text{Na}_2\text{HPO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{HClO}_4$ ), the best electrochemical response measured in term of the highest analytical signal was obtained in  $0.1 \text{ mol L}^{-1}$  of  $\text{K}_2\text{SO}_4$ . This means that the latter was used throughout the experimental program as supporting electrolyte.

Standard solution of paraquat was added into the electrochemical cell contained 20 mL of supporting electrolyte. The mixture solution was kept quiet for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each electrochemical measurement. The square wave voltammetry was recorded in the range from  $-0.3 \text{ V}$  to  $-1.3 \text{ V}$ , for which the scan rate is  $1 \text{ mV s}^{-1}$ , step potential 25 mV; amplitude 5 mV and duration 5 s. Optimum conditions were established by measuring the peak currents in dependence on all parameters. The suitability of the electroanalytical method in the determination of paraquat in natural water was tested under optimal condition. All experiments were carried out under ambient temperature.

## 3. Results

### 3.1. Natural phosphate characteristics

The surface structure of natural phosphate was observed using scanning electron microscopy (Fig. 1). The treatment of NP describes above lead to a fraction between  $100 \mu\text{m}$  and  $400 \mu\text{m}$  that is rich in phosphate and as can be seen that compact natural phosphate appearance was evident. The treated NP has following chemical composition: CaO (54.12%),  $\text{P}_2\text{O}_5$  (34.24%),  $\text{F}^-$  (3.37%),  $\text{SiO}_2$  (2.42%),  $\text{SO}_3$  (2.21%),  $\text{CO}_2$  (1.13%),  $\text{Na}_2\text{O}$  (0.92%), MgO (0.68%),  $\text{Al}_2\text{O}_3$  (0.46%),  $\text{Fe}_2\text{O}_3$  (0.36%),  $\text{K}_2\text{O}$  (0.04%) and several metals in the range of ppm. The structure of the material is similar to that of fluoroapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ). The apatite lattice is very tolerant of substitutions and vacancies; for example Ca can be replaced by Sr, Pb,

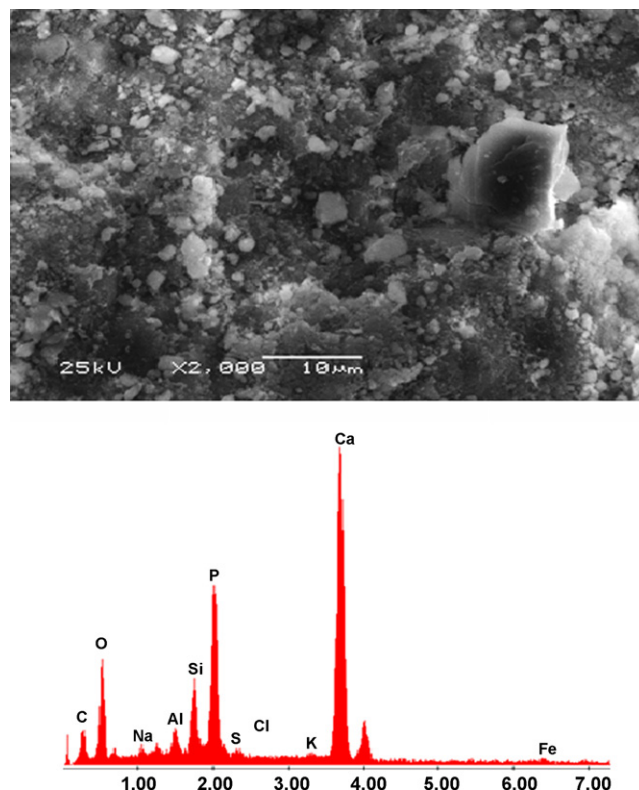


Fig. 1. Scanning electron micrograph of natural phosphate.

Co and Na.  $\text{PO}_4$  by  $\text{AsO}_4$ ,  $\text{SO}_4$  and  $\text{VO}_4$  and F can be replaced by OH and Cl. The natural phosphate presented a very low surface area (BET) at ca.  $1 \text{ m}^2 \text{ g}^{-1}$ .

### 3.2. Preliminary voltammetric characterization

The square wave voltammograms obtained for  $3 \times 10^{-4} \text{ mol L}^{-1}$  of paraquat herbicide present two redox peaks. The first one around  $-0.7 \text{ V}$  and the second at  $-1.0 \text{ V}$  versus SCE (Fig. 2). Peaks can be associated to the redox

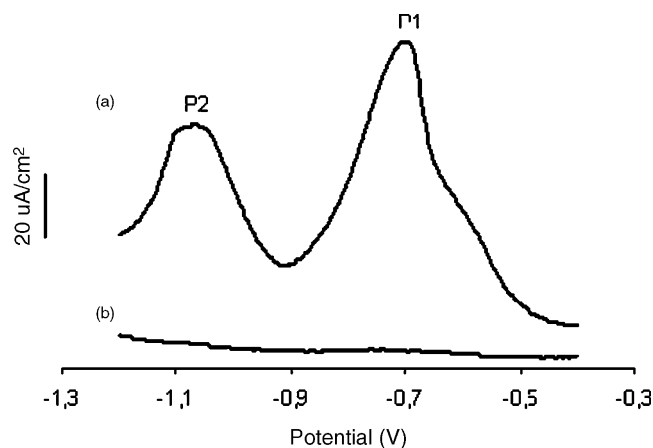
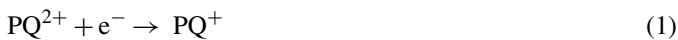
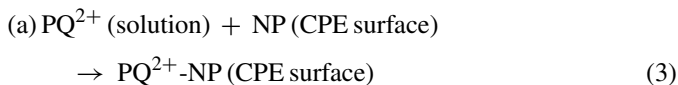


Fig. 2. Square wave voltammograms of  $3 \times 10^{-4} \text{ mol L}^{-1}$  of paraquat in  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$  at different carbon paste electrodes: (a) NP modified carbon paste electrode; (b) carbon paste electrode, accumulation time: 5 min; 10% of NP/CP ratio.

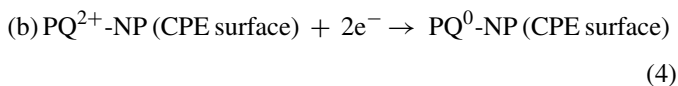
couple [37]:



Based on this work, the electrochemical process related to peaks present a totally reversible response. The two peaks can hence be used, with great success, for electroanalytical determination of paraquat residues in different samples. A control experiment was performed under the same conditions in the absence of natural phosphate; no redox peak was observed at low concentration of paraquat. The result indicates that the NP can greatly promote the preconcentration of paraquat at the carbon paste electrode and significantly increase the sensitivity of the determination of paraquat. The performance of the newly developed natural phosphate modified carbon paste electrode is based on the accumulation of paraquat from aqueous solution onto the surface of the modified electrode. The mechanism can be described as following:



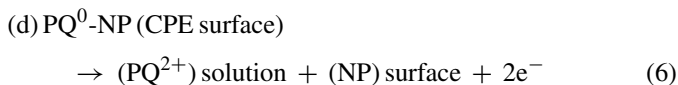
(the accumulation stage);



(the reduction stage);



(mass transport of  $\text{PQ}^{2+}$  to the electrode surfaces and subsequent reduction of the received paraquat)



(the stripping stage).

### 3.3. Optimization of experimental conditions

Scan rate can also influence the determination of paraquat by cyclic voltammetry. The peaks currents increased with the increase of scan rate. However, the shape of peaks became apparently large when more than  $50 \text{ mV s}^{-1}$  is used.

The effect of the initial pH on the paraquat determination at NP-CPE is shown in Fig. 3. We illustrate that as the pH increased the adsorbed amount of cationic paraquat increased in response to the increasing number of negatively charged sites that are available due to the loss of  $\text{H}^{+}$  from the electrode surfaces. As the pH increased, the peak currents increased at first, because NP can slowly dissolve in acidic solution and lose its ability of adsorption. It was reported that the decrease in proton concentration as pH increases from 1.8 to 11 is shown to exert a pronounced effect on the SWV and CV response of paraquat. Up to a pH of 5.0, the reduction peaks becomes reaches the maximally values. The peak potentials do not however seem to be affected by the concentration of  $\text{H}^{+}$ , suggesting the absence

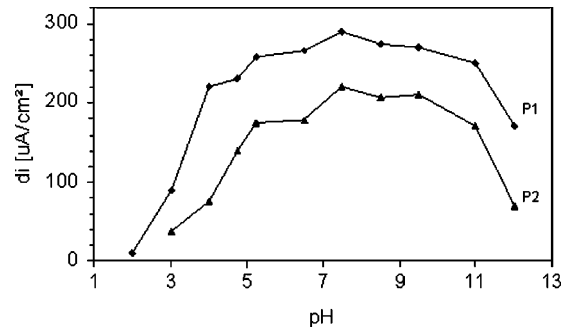


Fig. 3. Effect of the pH on SWV peak height of  $3 \times 10^{-4} \text{ mol L}^{-1}$  paraquat in  $\text{K}_2\text{SO}_4$  0.1 M, NP/CP = 50%,  $t_p = 15$  min, (a) peak 1 and (b) peak 2.

of any protonation step in the reduction mechanism reported in Eqs. (1) and (2) which is in close agreement with published works [21,24].

The use of NP as modifier of the carbon paste electrode can greatly increase the sensitivity of determination of paraquat, which is due to the adsorption of these heavy herbicide ions onto NP surfaces. Amount of NP can affect the electrochemical behaviors of paraquat at the carbon paste electrode. Fig. 4 shows the influence of NP loading on the voltammetric determination of paraquat. The redox peaks currents of paraquat increase with the increase of NP loading and reached the highest intensity from 50% of NP/CP ratio by weight (w/w). However, the continuous increase of NP amounts causes a decrease of peak currents, due probably to the decrease in the conductivity of the modified electrode. Then a 50% of ratio NP/CP (w/w) was used in further experiments.

An accumulation time can apparently influence the determination of paraquat (Fig. 5). Amounts of paraquat on the surface of modified electrode increased with the increase of accumula-

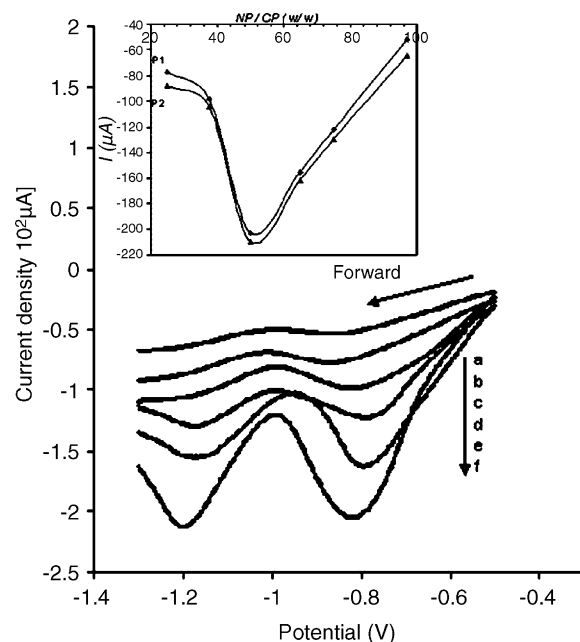


Fig. 4. Effect of NP loading on cyclic voltammograms of  $1.2 \times 10^{-4} \text{ mol L}^{-1}$  paraquat in  $\text{K}_2\text{SO}_4$  0.1 mol  $\text{L}^{-1}$  at NP-CPE,  $t_p = 15$  min.



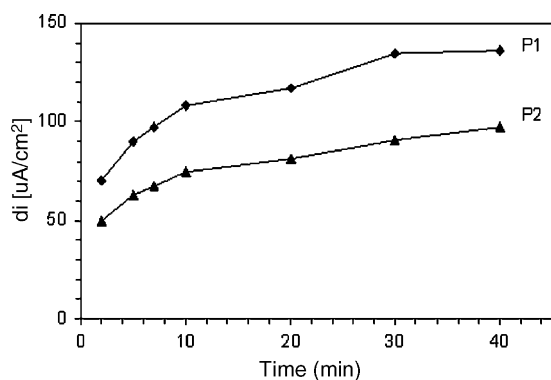


Fig. 5. Effect of accumulation time on SWV peak of  $1 \times 10^{-4} \text{ mol L}^{-1}$  paraquat in  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$  at NP-CPE (1–1).

tion time in the range of 0–10 min, which resulted in the increase of redox peak currents. With further increase of accumulation time, the peaks currents reached a flat caused by the complete coverage of active points on the surface of NP-modified carbon paste electrode by paraquat. Taking account of the sensitivity and the efficiency, accumulation time was 10 min in the following experiments.

### 3.4. Calibration graph

The square wave voltammetric determination of a series of standard solutions of paraquat was performed under the optimized working conditions described above. The results show that redox peak currents have a linear relationship with a concentration of paraquat in the range from  $2.3 \times 10^{-8} \text{ mol L}^{-1}$  to  $3 \times 10^{-4} \text{ mol L}^{-1}$  (Fig. 6). The linear correlation coefficients are 0.9729 and 0.9815 of P<sub>1</sub> and P<sub>2</sub>, respectively. According to Miller and Miller [38] the standard deviation of the mean current (S.D.) measured at reduction potential of paraquat for seven voltammograms of the blank solution in pure electrolytes was calculated from:

$$\text{S.D.} = \frac{1}{n-2} \sum_{j=0}^n (i_j - I_j)^2 \quad (7)$$

where  $i_j$  is the experimental value of the experiment number  $j$  and  $I_j$  is the corresponding recalculated value, at the same concentration using the regression line equation. The calculated S.D. was used in the determination of the detection limit (DL,  $3 \times \text{S.D./slope}$ ) and the quantification limit (QL,  $10 \times \text{S.D./slope}$ ). From these values, the detection and quantification limits were  $7.8 \times 10^{-10} \text{ mol L}^{-1}$  and  $2.59 \times 10^{-9} \text{ mol L}^{-1}$  for peak 1, respectively, and for peak 2 were found to be  $9.3 \times 10^{-10} \text{ mol L}^{-1}$  and  $3.09 \times 10^{-9} \text{ mol L}^{-1}$ , respectively. The precision, expressed as relative standard deviation (R.S.D.), was 1.70% for the first peak and 2.92% for the second peak.

### 3.5. Application to natural samples water

Finally, the proposed method was applied to the determination of paraquat in water samples. Under the optimized condition described above, the NP-CPE was applied for natural water

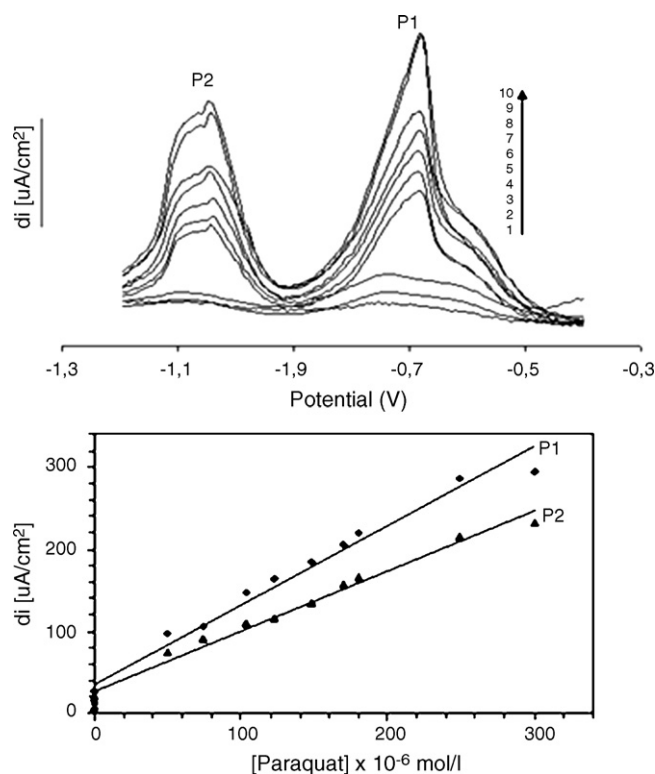


Fig. 6. Square wave voltammograms at NP-CP electrode with NP:CP=(1:1) and 10 min of preccentration time in  $\text{K}_2\text{SO}_4$   $0.1 \text{ mol L}^{-1}$  for different concentrations of paraquat; (1)  $2.3 \times 10^{-8} \text{ mol L}^{-1}$ , (2)  $6 \times 10^{-8} \text{ mol L}^{-1}$ , (3)  $5.04 \times 10^{-5} \text{ mol L}^{-1}$ , (4)  $1.02 \times 10^{-4} \text{ mol L}^{-1}$ , (5)  $1.22 \times 10^{-4} \text{ mol L}^{-1}$ , (6)  $1.48 \times 10^{-4} \text{ mol L}^{-1}$ , (7)  $1.7 \times 10^{-4} \text{ mol L}^{-1}$ , (8)  $1.8 \times 10^{-6} \text{ mol L}^{-1}$ , (9)  $2.49 \times 10^{-4} \text{ mol L}^{-1}$  and (10)  $3 \times 10^{-4} \text{ mol L}^{-1}$ .

samples collected in normal river waters (OUM ER RBIA, Tadmra-Azilal, Morocco). The support electrolytes were prepared by addition of  $0.1 \text{ mol L}^{-1}$  of  $\text{K}_2\text{SO}_4$  to a fresh water samples. The electroanalytical curves were obtained by using SWV in the range from  $2 \times 10^{-6} \text{ mol L}^{-1}$  to  $9 \times 10^{-5} \text{ mol L}^{-1}$  of paraquat. From Fig. 7, it was observed that peak currents versus paraquat

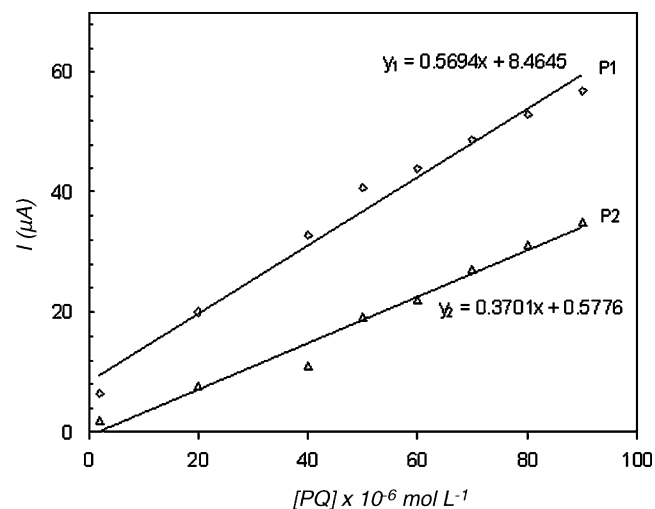


Fig. 7. Calibration curves for paraquat in electrolyte prepared with natural water samples and spiked with paraquat in the range from  $2 \times 10^{-6} \text{ mol L}^{-1}$  to  $9 \times 10^{-5} \text{ mol L}^{-1}$  under the experimental conditions presented in Fig. 6.

Table 1  
Results obtained from the linear regression curves (Fig. 7) for the determination of paraquat at HAP–CPE in natural waters

Parameters	Peak 1	Peak 2
$R^2$	0.9815	0.9712
Slop A ( $\text{mol L}^{-1}$ )	0.5736	0.0387
Standard deviation $\times 10^{-10}$ (A)	4.50	9.80
Relative standard deviation (%)	2.85	3.10

added into real sample solution increased linearly; hence the proposed methodology is suitable for the determination of paraquat in these waters. The statistical calculations for the assay results showed suitable precision of the proposed method (Table 1). It observed, however, the decrease of the sensitivity of NP–CPE due probably to the presence of inorganic mater, which can inhibit the adsorption process of paraquat onto natural phosphate.

The analytical procedure earlier described in the preceding sections was applied for domestic water artificially spiked by  $2 \times 10^{-5} \text{ mol L}^{-1}$  of paraquat. The domestic water samples were collected from different points of the TADLA-AZILAL region. The sampling points were selected based on different levels of organic matter. The amount of organic matter was evaluated by analysis of chemical oxygen demand (COD). The domestic water samples were used without any pretreatment, to prepare the support electrolyte (by adding  $0.10 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$ ). The Analytical histograms obtained by SWV for paraquat in electrolytes prepared with different domestic waters samples is shown in Fig. 8. The percentage of the signal ( $I\%$ ) studied according to the variation of the concentration of the organic matter (CDO) is defined by the equation:

$$I\% = \frac{I_p}{I_{p \max}} \times 100 \quad (8)$$

where  $I_p$  is the current of the peak in domestic water and  $I_{p \max}$  is the current of the peak in pure water. The results obtained for peak 1 and peak 2 presented the inverse dependence on the amount of organic matter presented in different samples. The presence of the organic substances in the matrix of the

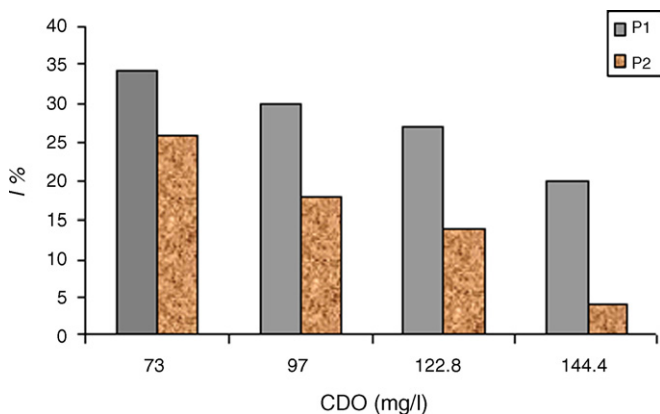


Fig. 8. Comparative histogram of the effect of CDO of the water samples on the response of the  $2 \times 10^{-5} \text{ mol L}^{-1}$  paraquat under the experimental conditions presented in Fig. 6.

samples has a considerable effect of accumulation of paraquat at NP–CPE; it is due probably to the immobilization of such compounds on natural phosphate surfaces.

#### 4. Conclusion

The application of natural phosphate in the preparation of modified carbon paste electrodes showed to be an interesting alternative in the electroanalytical determination of paraquat in real water samples. Measurements of paraquat in aqueous solution were carried out at NP–CPE using square wave voltammetry. Analytical results show that, under the optimized working conditions, the proposed sensor was able to detect  $7.8 \times 10^{-10} \text{ mol L}^{-1}$  of paraquat with a good sensitivity.

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