Talanta 115 (2013) 172–177

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Sensitive determination of paraquat by square wave anodic stripping voltammetry with chitin modified carbon paste electrode

H. El Harmoudi [a,b], M. Achak [a,b], A. Farahi [a,b], S. Lahrich [a], L. El Gaini [b], M. Abdennouri [a], A. Bouzidi [c], M. Bakasse [b], M.A. El Mhammedi [a,*]

[a] *Equipe de Chimie Analytique et Modélisation Statistique, Université Hassan 1er, Faculté Polydisciplinaire, BP 145, Khouribga, Morocco*
[b] *Equipe d'Analyse des Micropolluants Organiques, Faculté de Sciences, Université Chouaib Doukkali, Morocco*
[c] *Laboratoire de Sciences de l'Environnement et Développement, Université Hassan 1er, Faculté des Sciences et Techniques, Settat, Morocco*

ARTICLE INFO

Article history:
Received 19 November 2012
Received in revised form
30 March 2013
Accepted 1 April 2013
Available online 29 April 2013

Keywords:
Chitin
Olive oil
Olives
Paraquat
Square wave anodic stripping voltammetry

ABSTRACT

A novel analytical approach has been developed and evaluated for the quantitative analysis of paraquat herbicides which can be found at trace levels in olive oil and olives. The aim of this work is to optimize all factors that can influence this determination by a carbon paste electrode modified with chitin (Chit-CPE). The best responses were obtained with square wave potential in diluted Na_2SO_4 as supporting electrolyte. The influence of various parameters on the Chit-CPE was investigated. Under the optimized working conditions, calibration graphs were linear in the concentration ranges of 5.0×10^{-9}–1.0×0^{-5} mol L^{-1}. For 180 s preconcentration, detection limits of 2.67×10^{-10} mol L^{-1} (peak 2) was obtained at the signal noise ratio (SNR) of 3. To evaluate the reproducibility of the newly developed electrode, the measurements of 1.0×10^{-5} mol L^{-1} PQ were carried out for seven times at Chit-CPE and the relative standard deviation was 5.2%. The analytical methodology was successfully applied to monitor the paraquat content in olives and olive oil.

1. Introduction

Paraquat (1,1-dimethyl-4,4-bipyridinium dichloride), a fast-acting non-selective contact herbicide, is widely used to control broad-leaved weeds in growing corn, fruit trees and vegetables. It is also used as a desiccant before harvesting and for destroying marijuana plants. Accidental and occupational exposures of agriculture workers are the primary hazards for human health. During the past few decades, paraquat (PQ) has proved to be a popular agent for intentional poisonings. Paraquat is extremely toxic to humans (LD50 35 mg/kg) and animals (rats: LD50 is 110–150 mg/kg), by all means of exposure. Since recently, the use of PQ has been restricted [1–4]. There is no specific treatment for PQ poisoning. Hence the management of poisonings is to relieve symptoms and treat complications [5]. Paraquat is an herbicide that is used in weeding many crops and there have been many authenticated cases of detection of its residues in water sources [6]. Its residues constitute a potential danger for health since it is a highly persistent molecule when present in the environment. This fact increases the contamination risk when paraquat is overused. Therefore, there is an urgent need to determine paraquat in the environment, air and food. PQ is polar, highly soluble in water and has a low volatility. According to its properties, this compound is usually determined by ion-pair HPLC with UV detection [7], this latter being the method recommended by the Environmental Protection Agency (EPA) [8].

Standardized analytical methods for paraquat determination in environmental samples, mainly based on gas and liquid chromatography [9–11] or mass spectrometry (MS) [12–15], and more recently, on electrophoretic methods, with either UV detection [16] or mass spectrometry [17] have certain disadvantages because they require rather complicated and expensive instruments and time-consuming procedures, especially for in situ applications or in decentralized laboratories. Electroanalytical stripping techniques, however, prove to be the ideal alternative in such a case [18–20].

Literature has so far reported different electroanalytical approaches in order to determine paraquat [21,22]. They are mainly based on the stripping voltammetry technique [23–25]. An increase in the sensitivity of electroanalytical methods, using chemically modified electrodes (CMEs), can be achieved by its combination with an effective method of pre-concentration. The basic carbon electrode materials most frequently used for electrochemical measurements are glassy carbon and carbon paste electrode (CPE) [25–27].

The main objective of this work was to develop a procedure for the determination of paraquat by square wave anodic stripping voltammetry (SWASV) using a carbon paste electrode modified

---

[*] Corresponding author. Tel.: +212 68858296; fax: +212 23485201.
E-mail address: elmhammedi@yahoo.fr (M.A. El Mhammedi).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.04.002

with commercial chitin particles (Chit-CPE). The advantages of using this electrode include the availability of a wide potential range of CPE for analysis, the easily renewable surface and the simplicity of fabrication. Among the different inorganic solids, chitin has advantages because it is biocompatible, biodegradable, antibacterium and almost non-toxic [28]. Its high hydrophilicity and its high chemical reactivity are attributed to a large number of functional groups [26].

All experimental variables involved in the stripping method were investigated in detail in order to identify the best working conditions. A fast, sensitive method for determining paraquat in oils (especially olive oil) is described. In principle, considering the extreme lipophobicity of the bipyridyl herbicides, it is quite unlikely to find such residues in olive oil. Nevertheless, they could appear at ppb levels. This is particularly critical in the case of organic oils which are, by definition, supposed not to contain pesticides. Therefore, we must ensure that such oils fulfill the legislation.

2. Experimental

2.1. Equipment and reagent

A stock solution of 10^{-3} mol L^{-1} PQ was prepared by dissolving the corresponding amount of paraquat chloride in bidistilled water. A working solution of 10^{-4} mol L^{-1} PQ was prepared daily from the stock solution, by dilution in bidistilled water. pH was adjusted by adding H_2SO_4 or NaOH. All chemicals used in these experiments were extremely pure (used without further purification). They were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies.

Electrochemical measurements were carried out by using an eDAQ e-corder/potentiostat EA163 controlled by eDAQ EChem data acquisition software. A voltammetric cell with three electrodes was used: a carbon paste electrode modified with the chitin as the working electrode (WE), a platinum electrode as the auxiliary electrode (AE) and an Ag/AgCl/Cl^- (3 M) as the reference electrode (RE). A pH-meter sensION™, (pH31) with the glass-Ag/AgCl/KCl (3.00 mol L^{-1}) combined electrode, was used for adjusting pH values.

2.2. Working procedure

The working electrode was constructed from 1 mm diameter bar of carbon which was partially inserted into PTFE cylindrical tubing of approximately 5 mm internal diameter, forming a cylindrical cavity. A chemically modified carbon paste electrode (Chit-CPE) was prepared by mixing amounts of chitin and carbon paste thoroughly until obtaining a uniformly wetted paste. Portions of the resulting composite material were then packed into a home built electrode assembly consisting of the cavity (geometric area 0.1256 cm²) of PTFE tube electrode of a plastic pipette tip. Electrical contact was established with a bar of carbon.

The electrode, after having been washed with distilled water and heated at room temperature, was transferred into the sample cell (10 mL). Two-step procedures were followed for the analytical determination of the concentration of paraquat in aqueous samples. The working electrode was first immersed in a Na_2SO_4 solution containing paraquat at open circuit. Where the accumulation of paraquat ions was achieved chemically, the electrochemical experiments were performed in 0.1 mol L^{-1} Na_2SO_4 electrolyte solutions at Chit-CPE.

Several supporting electrolytes namely ($NaClO_4$, Na_2SO_4, CH_3COOH, and $HClO_4$) were tested. Each of the four considered electrolytes was tested working in SWASV. After recording the voltammogram of the blank, the test solutions were spiked with paraquat solution (10^{-4} mol L^{-1}). The best electrochemical response, measured in terms of the highest analytical signal and improved reproducibility, was obtained in Na_2SO_4. This means that 0.10 mol L^{-1} of Na_2SO_4 was used throughout the experimental program as the supporting electrolyte.

The appropriate solutions of paraquat were transferred into the electrochemical cell and the optimization of the analytical procedure for SWASV was carried out following a systematic study of the experimental parameters that affect the SWASV responses; such as, the pH of the medium, frequency, amplitude, deposition potential and deposition time. After the optimization of the voltammetric conditions, analytical curves were obtained by the standard addition method. Recovery experiments were then performed by adding a known amount of PQ to the supporting electrolyte, followed by standard additions from the paraquat stock solution and by plotting the resulting analytical curve. All measurements were performed in triplicate under ambient conditions.

The analytical utility of this procedure was assessed by applying it to the determination of paraquat in realistic samples containing this herbicide. The experiments were carried out by adding a known amount of paraquat to the supporting electrolyte followed by standard additions from the diquat stock solution and by plotting the resulting analytical curve. The supporting electrolytes were prepared by addition of 0.1 mol L^{-1} Na_2SO_4 to fresh oil and olive samples.

3. Result and discussion

The voltammetric response of paraquat at the chitin modified carbon paste electrode Chit-CPE was investigated using cyclic voltammetry (Fig. 1). The results show two voltammetric peaks toward the negative and the positive sweep direction as indicated in the literature [20,26,29–31]. According to the experiment undertaken, the electrochemical process related to peaks presents a totally reversible behavior indicated by the presence of direct and reverse currents with similar values of peak current. In addition, the difference between peak potential for forward and reverse scans, presented values about 58 mV. This indicates of the transfer of one electron during the redox process, a behavior similar to that published in previous literature reports [21,22,25]. The two peaks can hence be used, with great success, for the electroanalytical determinations of paraquat residues in different samples.

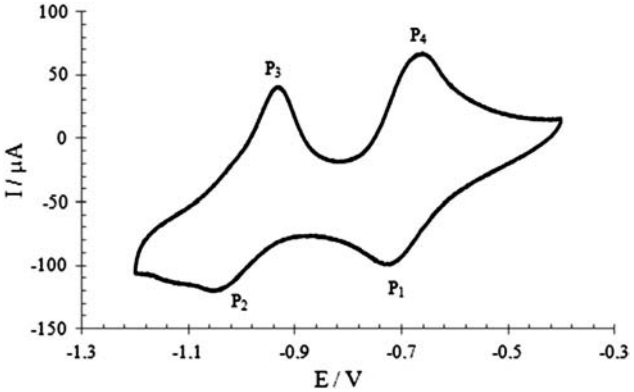

Fig. 1. Cyclic voltammogram for 5.0×10^{-4} mol L^{-1} of paraquat in 0.10 mol L^{-1} of Na_2SO_4, pH 6.0, scan rate, 50 mV s^{-1} on the Chit-CPE.

3.1. Optimization of experimental variables

The influence of the experimental variables (frequency, amplitude, pulse height, deposition potential and deposition time) which were involved in the SWASV determination of paraquat was investigated (Fig. 2). The effect of frequency (υ) on the current intensity (Ip) of paraquat on Chit-CPE was evaluated in the range from 5 to 50 Hz. The signal increased up to 50 Hz. Nevertheless, the maximum acceptable value to be in a SWASV program, which is 50 Hz and which corresponds to 0.02 s of duration for each step, was used in the present experimental study. The amplitude influence was investigated in the range from 1 to 100 mV.

The results obtained demonstrated that a height of the paraquat peak increased linearly as a consequence of the increase of amplitude values up to 50 mV. According to this value, the paraquat signal remained stable due to peak broadening and the signal noise increased. The pulse height was studied in the range from 1 to 50 mV. The stripping signal underwent an increase up to 4 mV, where the highest peak intensity was obtained. A slight decrease of the signal was observed after 4 mV.

In agreement with the high peak current values, good shapes of the signal and better signal to noise ratio, the selected optimal values were 4 mV, 50 mV and 50 Hz for pulse height, amplitude and frequency respectively.

The effect of deposition potential was evaluated in the range from −0.9 V to −1.3 V. The highest voltammetric signal was obtained with a deposition potential of −1.0 V, which is chosen as the optimal value. In this case, no irreversible changes were observed on the surface of the modified working electrode when more negative potentials were applied. But the paraquat signal intensity was affected as a result of the height peak increase of the undesirable signal.

Using the optimized parameter values, the influence of deposition time on the peak currents was finally tested in the range from 0 to 140 s. The height of the paraquat peak increased as a consequence of the increase of deposition time, up to 90 s. Longer deposition times resulted in smaller signals probably due to electrode saturation.

The decrease in proton concentration as pH increases from 2.0 to 9.5 is shown to have a pronounced effect on the SWASV response of paraquat (Fig. 3). Up to a pH of 7.5, the peak currents show an increase for peak 1 and peak 2. This could be explained by the fact that at low pH, amine groups in the chitin easily form protonation that induced an electrostatic repulsion of paraquat ions and a competition between paraquat and H$^+$ for binding sites.

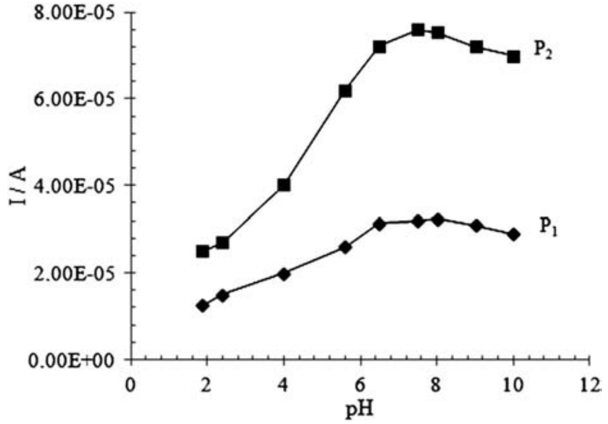

Fig. 3. Influence of pH on SWASV oxidation peaks for 1.5×10^{-5} mol L^{-1} PQ in 0.1 mol L^{-1} Na$_2$SO$_4$ at Chit-CPE, tp=3 min.

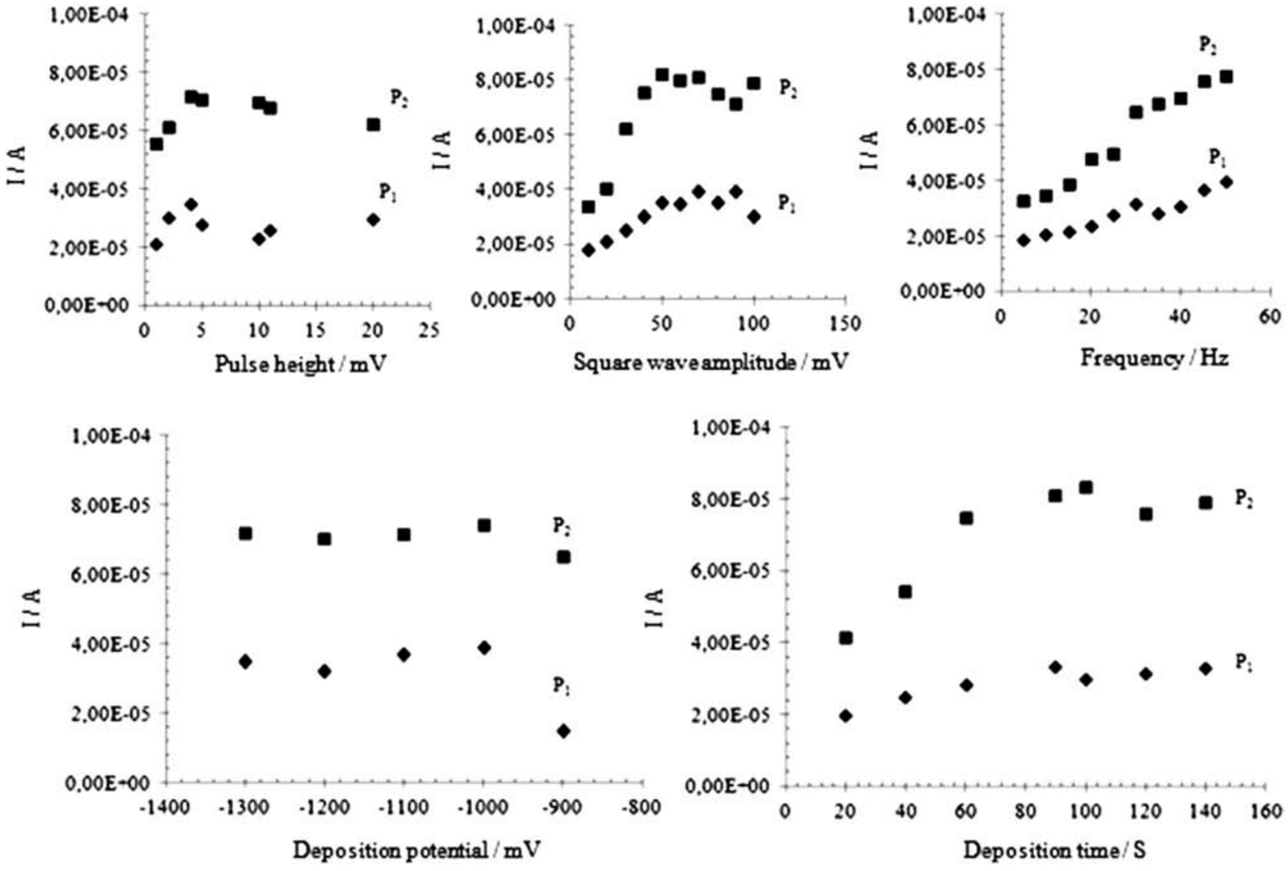

Fig. 2. Influence of the experimental variables (pulse height, amplitude, frequency, deposition potential and deposition time) involved in the SWASV method and response to PQ 1.0×10^{-5} mol L^{-1} in 0.1 mol L^{-1} Na$_2$SO$_4$ at the chitin-modified carbon paste electrode.

The peak potentials do not, however, seem to be affected by the concentration of H^+, suggesting the absence of any protonation step in the reduction mechanism, which is in agreement with published works [22,25]. Therefore, pH 7.5 was chosen for subsequent measurements.

For an open potential, the effect of accumulation time on the extraction efficiency was examined in the range of 30–420 s with constant stirring speed. The intensity of the peak P_1 and peak P_2 of PQ generally increased with extraction time until 180 s (Fig. 4). After 180 s, no dramatic increase of the current intensity was observed with additional extraction time. Moreover, long extraction time may result in solvent drop dissolution in water and consequently leads to poor sensitivity and precision. From a comprehensive view, an extraction time of 180 s was selected for subsequent experiments.

The dependence of anodic current response on the chitin loading in the carbon paste in pH 7.5 conditions is shown in Fig. 5. The current response increases with the increase of the amount of chitin until a chitin/CP ratio of 2% by weight (w/w). The anodic peaks currents decreased significantly when more than 2% (chitin, w/w) is used in the electrode preparation. This probably occurs due to the conductive reduce of area of the electrode surfaces. Hence a 2% chitin of ratio (Chitin/CP) by weight was used throughout this work.

3.2. *Repeatability, linearity and detection limit*

Calibration data were obtained for paraquat solutions under optimum experimental conditions described above. Fig. 6 shows some of the typical SWASV voltammograms recorded on the Chit-CPE after being in contact with different paraquat concentrations for 180 s. A calibration graph was then constructed from the observed peak currents (Table 1). A linear fit was applied over the range of 1.5×10^{-9}–1.0×0^{-5} mol L^{-1} with a correlation coefficient (R^2) of 0.9826. The limit of detection (LOD) for PQ, based on a signal-to-noise ratio (S/N) of 3, was 2.67×10^{-10} mol L^{-1}. The precision of this method was determined by the analysis standard solution at 1.0×0^{-5} mol L^{-1} and 5.0×10^{-8} mol L^{-1} of PQ for seven times continuously, and the relative standard deviation (RSD) was 5.2% and 6.02% for peak 2 respectively.

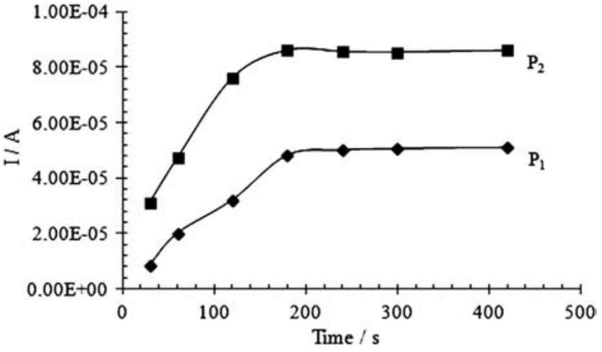

Fig. 4. Effect of accumulation time on charge transfer of 1.0×10^{-5} mol L^{-1} PQ in 0.1 mol L^{-1} Na_2SO_4, pH 7.5 at Chit-CPE.

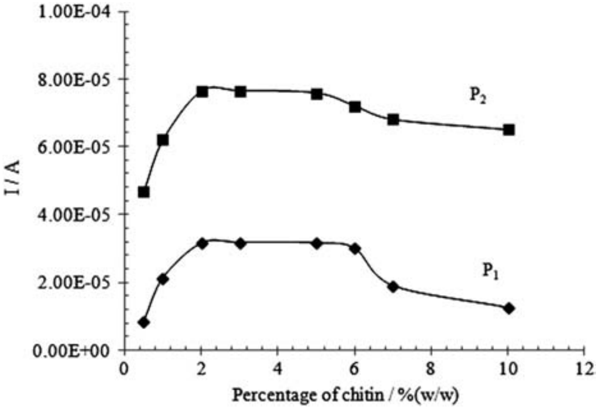

Fig. 5. Influence of the content of chitin in carbon paste mixture percent (w/w) on SWASV peak currents of 1.0×10^{-5} mol L^{-1} paraquat in 0.1 M Na_2SO_4 (pH 7.5), *t*P=3 min.

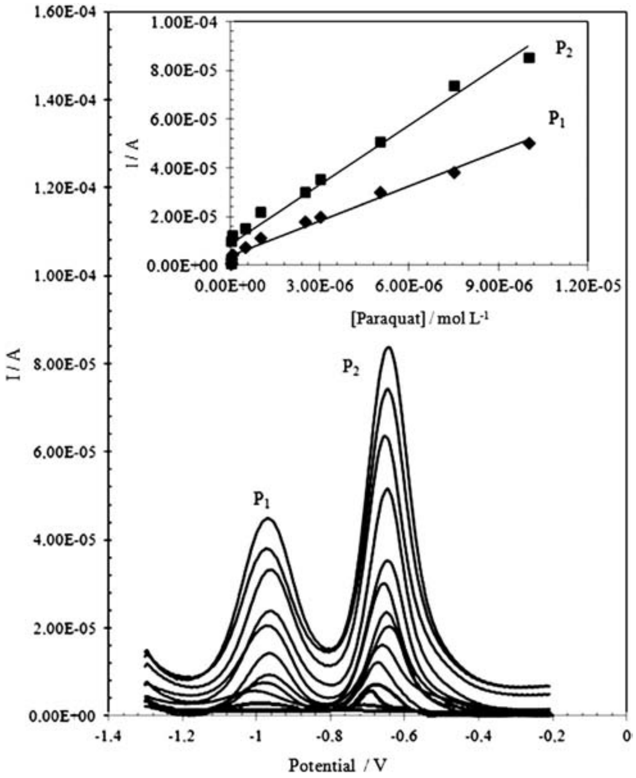

Fig. 6. Calibration curve and respective stripping voltammograms for increasing concentrations of PQ from 1.5×10^{-9} to 1.0×10^{-5} mol L^{-1} in Na_2SO_4 0.1 M by using the SWASV optimized method at the Chit-CPE.

Table 1
Results obtained from linear regression curves (Fig. 5) for the determination of paraquat in pure electrolyte on Chit-CPE using SWASV.

Parameter	Peak 1	Peak 2
Equation	I(A)=4.7618C+4E-06	I(A)=8.1296C+9E-06
R^2	0.9898	0.9826
S (blanc)	12.412E-09	7.235E-10
Slope (AL mol^{-1})	4.7618	8.1296
DL (mol L^{-1})	7.82E-09	2.67E-10
QL (mol L^{-1})	26.066E-09	8.90E-10
Sensibility (AL mol^{-1})	6.02E+07	5.2E+07

To evaluate the analytical performance of the proposed method, figures of merit were determined. Table 2 shows a comparison between our simple proposed assays with other methods toward the detection of paraquat. The results indicate that the Chit-CPE has excellent reproducibility. The results obtained here show that the proposed SWASV method is fast, sensitive and better suited than conventional methods like spectrophotometry or chromatography, to characterize fast variations in concentration of dilute paraquat aqueous solutions. Most of these techniques are either suffering from the instability of the reagent and the instrumental system or require extensive sample

Table 2
Detection of paraquat reported at some analytical methods.

Methods	DL (μg L^{-1})	DSR (%)
CE–MS hydrodynamic injection [17]	2000	7
CE–MS electrokinetic injection [17]	30	17
CSEI-sweeping-MEKC [32]	0.001	<22
SPE–LC–MS–MS [13]	0.03	7.9
Chit-CPE	0.049	<6.02

CE–MS: capillary electrophoresis–mass spectrometry.
SPE–LC–MS–MS: on-line solid-phase extraction–liquid chromatography–tandem mass spectrometry.
CSEI-sweeping-MEKC: micellar electrokinetic chromatography (MEKC) using sweeping and cation-selective exhaustive injection (CSEI).

Table 3
Results obtained from recovery curves of paraquat in spiked olive and olive oils samples considering peak 1 and peak 2 on Chit-CPE and SWASV.

Sample	Recovered concentration ($\times 10^{-6}$ mol L^{-1})		Recovery (%)		R.S.D. (%)	
	P1	P2	P1	P2	P1	P2
Olive	9.1	9.44	91.0	94.4	6.1	5.90
Olive oils	9.3	9.75	93.0	97.5	5.71	5.34

pretreatment. Moreover, after careful analysis of the results obtained for the detection and quantification limits, it is apparent that the use of the Chit-CPE provides an alternative method for electrochemical detection of paraquat, with the possibility of its employment for analytical determination of other pesticides that are frequently determined at mercury electrodes. These latter have the inconvenience of being highly toxic, or chromatographic and spectrophotometric methods. This presents difficulties involving limited sensitivity and/or specificity and require laborious and time-consuming sample preparation procedures; such as, cation exchange chromatography, ion-pair liquid–liquid extraction (LLE) and/or solid phase extraction [32–34].

The proposed electrode was stored at room temperature, and its response was studied every week. The response was 92% of its initial value after 45 days which shows long-term stability and very good sensitivity for the analysis of real samples.

3.3. Practical application

Olive oil products have a great importance in the sustainable economy of important regions in Morocco. It is obtained from the fruit of the olive without any further treatment. The most extensively applied agrochemicals in olive plantations of Mediterranean countries are far herbicides and insecticides.

In Morocco, the paraquat is one of the most widely used herbicides in olive cultures. Due to its permitted use in such cultures, the methodology proposed was applied in order to evaluate the occurrence of matrix effects in the electroanalytical determination of paraquat residues directly in the samples. The paraquat residues can persist to the harvest stage, making possible the contamination of the olives used to produce the olive oil. This can cause the presence of trace amounts of these pesticides in olive oil samples. The United States Environmental Protection Agency (EPA) proposed that maximum contaminant limits (MCL) for paraquat in drinking water is 3 μg L^{-1}. There is currently no legislation on the MCL values of paraquat in oils. However, values of 1 mg L^{-1} PQ in olives are commonly accepted [35].

3.3.1. Olive samples

A representative 20 g portion of olives (including the seed of the crop) previously homogenized was weighed and transferred to a glass mortar, where it was fortified homogenously with 2 ml of the bidistilled water because of its solubilizing effect of paraquat [36]. The mixture was then gently blended in the mortar for 30 min to assess the homogeneity of the sample. The mixture samples were used after filtration step, to prepare the supporting electrolyte (by adding 0.1 mol L^{-1} Na_2SO_4) and corresponding analytical curves were again obtained applying for SWASV experiments. The recovery studies were realized by adding an appropriate volume of paraquat standard solution (1×10^{-5} mol L^{-1}) to electrochemical cell. The recovery results obtained, in triplicate, were related to the interference effects of the constituents of each sample (Table 3). The statistical calculations for the assay results showed suitable precision of the proposed voltammetric method. There were no significant differences between the calculated and added concentrations at the 95% confidence level and within an acceptable range of error. The results of relative standard deviations (5.9%) and the recovery percentage (94.4%) that were obtained for peak 2, were considered satisfactory compared to those obtained using other analytical methods, considering that neither the extraction or preparation stages of the samples are necessary in the proposed methodology. The slight decrease in the values of the recovery reflects an electrochemical process involving depression due to competitive effects between analytes, fouling of electrode or passivation of analyte response.

3.3.2. Oils samples

Due to the high polarity of the paraquat, a water solution partition was selected for extraction. The extraction procedure was as follows: 20 ml of oil are dissolved in 30 mL of bidistilled water. The system is shaken for 30 min, centrifuged and the lower aqueous phase is taken for direct analysis. The samples were used in preparing the supporting electrolyte (adding 0.1 mol L^{-1} Na_2SO_4) and the analytical curves were again obtained by SWASV experiments. No paraquat was detected in these original samples. So they were spiked with appropriate amounts of paraquat and were adjusted to a pH 7.5 value. The analytical sensitivities, defined by the slope of the analytical curves, were compared with that obtained with purified water, where it is possible to observe that the peak current values for the paraquat reduction process displayed some influence from the components of the samples employed, characterized by a decrease in the slope of the curves obtained. It was found that peaks currents iP1 and iP2 versus paraquat added into real samples increased linearly. These results indicate that the proposed methodology is suitable for the determination of paraquat in these samples. As summarized in Table 3 for spiked samples, the analytical response of analyte in SWASV determination slightly decreased compared to those obtained in pure electrolyte. The results of relative standard deviations and percentage signal that were obtained for peak 2, were considered satisfactory compared to those obtained using other analytical methods [11]. The mean percentage recoveries of added PQ were found to be 98% using Liquid Chromatography (HPLC) in oils samples in confidence interval of 95%. These results demonstrate the applicability of the procedure for paraquat determination in oils samples. The proposed methodology has therefore proven to be applicable for use in complex samples.

4. Conclusion

Initially, the electrochemical behavior of paraquat was evaluated using the voltammetric results at carbon paste electrode modified with chitin. The voltammetric response showed two oxidation waves associated to the partial oxidation of paraquat molecule. The influence of the experimental variables which were involved in the SWASV determination of paraquat was investigated. The results indicate that the method developed for the analytical determination of paraquat using chitin modified paste electrode is applicable for the determination of the pesticide at 2.67×10^{-10} mol L^{-1} levels with very good precision. The use of SWASV is faster and more sensitive than other conventional techniques in confidence interval of 95%.

The analytical utility of this procedure was assessed by applying it to the determination of paraquat in olives and oils samples containing this herbicide. The slight decrease in the values of the recovery of obtained paraquat reflects an electrochemical process involving adsorption of reagents and/or products. This can be inhibited by the presence of other components in the samples used.

In this way, the use of carbon paste electrode in conjunction with SWASV in determining paraquat proves to be a very suitable and efficient analytical methodology which permits its application in a variety of different natural matrices.

References

[1] J.T. Stevens, D.D. Summer, Classes of Pesticides, in: W.J. Hayes, E.R. Laws (Eds.), Herbicides in Handbook of Pesticide Toxicology, 3, Academic Press, NY, 1991.

[2] P. Houzé, F.J. Baud, R. Mouy, C. Bismuth, R. Bourdon, J.M. Scherrmann, Hum. Exp. Toxicol. 9 (1) (1990) 5–12.

[3] M. Mirjana Djukic, D. Marina Jovanovic, Milica Ninkovic, Ivana Stevanovic, Katarina Ilic, Marijana Curcic, Jelena Vekic, Chem.-Biol. Interact. 199 (2012) 74–86.

[4] You Hwan Jo, Kyus eok Kim, Joong Eui Rhee, Gil Joon Suh, Woon Yong Kwon, Sang Hoon Na, Hasan B. Alam, Resuscitation 82 (2011) 487–491.

[5] W.C. Robbe III, W.J. Meggs, Insecticides, Herbicides, Rodenticides, in: J.E. Tintinalli, G.D. Kelen, J.S. Stapczynski, O.J. Ma, D.M. Cline (Eds.), Emergency Medicine: A Comprehensive Study Guide, sixth ed.,McGraw-Hill, New York, 2004 (Chapter 182).

[6] L. Ritter, K. Solomon, P. Sibley, K. Hall, P. Keen, G. Mattu, B. Linton, J. Toxicol. Environ. Health A 65 (2002) 1–142.

[7] C. Fuke, T. Arao, Y. Morinaga, H. Takaesu, K. Ameno, T. Miyazaki Legal, Medicine 4 (2002) 156–163.

[8] J.W. Hodgeson, W.J. Bashe, J.W. Eichelberger, Method 549.1, Revision 1.0, Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency, 1992.

[9] Norberto C. Posecion, Enrique M. Ostrea, Dawn M. Bielawski, J. Chromatogr. B 862 (2008) 93–99.

[10] Rafael Menck de Almeida, Mauricio Yonamine, J. Chromatogr. B 853 (2007) 260–264.

[11] Marıa A. Aramendıa, V. Borau, Fernando Lafont, Alberto Marinas, Jose M. Marinas, Jose M. Moreno, Juan M. Porras, Francisco J. Urbano, Food Chem. 97 (2006) 181–188.

[12] V.Y. Taguchi, S.W.D. Jenkins, P.W. Crozier, T.D. Wang, J. Am. Soc. Mass. Spectrom. 9 (1998) 830–839.

[13] R. Castro, E. Moyano, M.T. Galceran, J. Chromatogr. A 914 (2001) 111–121.

[14] D.K. Blake, R.T. Gallagher, B.H. Woollen, Chromatographia 55 (2002) 183–185.

[15] L. Grey, B. Nguyen, P. Yang, J. Chromatogr. A 958 (2002) 25–33.

[16] O. Nuneez, E. Moyano, M.T. Galceran, J. Chromatogr. A 946 (2002) 275–282.

[17] O. Nunnez, E. Moyano, M.T. Galceran, J. Chromatogr. A 974 (2002) 243–255.

[18] José A. Ribeiro, Cátia A. Carreira, Hye Jin Lee, Fernando Silva, Ana Martins, Carlos M. Pereira, Electrochim. Acta 55 (2010) 7892–7896.

[19] Xiulan Sun, Cai Li, Zaijun Yan, Zhilei Wei, Yinjun Fang, Guoxiao Ren, Yaru Huang, Electrochim. Acta 56 (2011) 1117–1122.

[20] D. De Souza, S.A.S. Machado, Anal. Chim. Acta 546 (2005) 85–91.

[21] D. De Souza, S.A.S. Machado, Quim. Nova 26 (2003) 644.

[22] A. Walcarius, L. Lamberts, J. Electroanal. Chem. 406 (1996) 59.

[23] E. Alvarez, M.-Teresa Sevilla, J.M. Pinilla, L. Hernandez, Anal. Chim. Acta 260 (1992) 19–23.

[24] L.T. Hu, I.W. Sun, Talanta 53 (2000) 443.

[25] Xiaoliang Ye, Yonge Gu, Chunming Wang, Sens. Actuators B: Chem. 173 (2012) 530–539.

[26] M.A. El Mhammedi, M. Bakasse, A. Chtaini, J. Hazard. Mater. 145 (1–2) (2007) 1–7.

[27] C. Jeon, W. Holl, Hydrometallurgy 71 (2004) 421–428.

[28] G. Crini, Prog. Polym. Sci. 30 (2005) 38–70.

[29] M.A. El Mhammedi, M. Bakasse, R. Bachirat, A. Chtaini, Food Chem. 110 (4) (2008) 1001–1006.

[30] M.A. El Mhammedi, M. Achak, M. Bakasse, R. Bachirat, A. Chtaini, Mater. Sci. Eng. C 30 (6) (2010) 833–838.

[31] O. Nuennez, J.-B. Kim, E. Moyano, M.T. Galceran, S. Terabe, J. Chromatogr. A 961 (2002) 65–75.

[32] S. Hara, N. Sasaki, D. Takase, S. Shiotsuka, K. Ogata, K. Futagami, K. Tamura, Anal. Sci. 23 (2007) 523–526.

[33] M. Luque, A. Ríos, M. Valcárcel, Analyst 123 (1998) 2383–2387.

[34] R.A. Braithwaite, Hum. Toxicol. 6 (1987) 83–86.

[35] FAO/WHO, 1971 Evaluation of Some Pesticide Residues in Food, AGP:1971/M/9/1; WHO Pesticide Residues Series, No. 1, 1972b.

[36] E. Halfon, S. Galassi, R. Brouggemann, A. Provini, Chemosphere 33 (1996) 1543–1562.