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ORIGINAL PAPER

# Development of an adsorptive catalytic stripping voltammetric method for the determination of an endocrine disruptor pesticide chlorpyrifos and its application to the wine samples

**Füsun Okçu Pelit · Hasan Ertaş · F. Nil Ertaş**

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**Abstract** A very sensitive voltammetric method for the determination of an endocrine disruptor Chlorpyrifos (CP) insecticide at ng $mL^{-1}$ level was described. The pesticide was accumulated at a hanging mercury drop electrode (HMDE) and a well-resolved reduction peak was observed at −1.2 V (vs. Ag/AgCl) in pH: 2.0 media containing 5% aqueous ethanol solution. A systematic investigation of the solution parameters and operational parameters which affect the stripping response were carried out with differential pulse voltammetry. With an accumulation potential of −0.5 V and an accumulation time of 60 s, the detection and quantification limits were found to be 0.14 and 0.45 ng $mL^{-1}$, respectively. The remarkable sensitivity of the method was attributed to a catalytic process as concluded from cyclic voltammetry. The degree of interference from diverse ions and some other pesticides on the differential pulse stripping signal for CP was evaluated. The method developed was adapted for wine samples. The matrix effect of red wine was eliminated by means of liquid–liquid extraction (LLE) followed by solid-phase extraction (SPE) with satisfactory recovery values. This method offers a very sensitive and inexpensive way for determining CP residues in red wines.

**Keywords** Chlorpyrifos · Voltammetry · Wine · Solid-phase extraction · Endocrine disruptor

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## 1 Introduction

Viticulture has great importance in Turkey's agricultural structure. Although vineyards are spread all over the country, production is mainly concentrated in Aegean, Mediterranean, and Central Anatolian regions. Turkey is the sixth country in the world from the view point of the area planted grapevines. However, only a small portion of the harvest is used for wine production [1].

The grapevine is subject to attack by numerous plant and animal parasites. The most frequent diseases caused by fungi are *downy mildew*, *powdery mildew*, and *gray mold* in grapes [2]. Pesticides are used on agricultural commodities such as grapes and wine grapes and as a result, a part of pesticides left on the grapes at harvest, particularly late-season fungicides, can be carried into the wine [3]. For pesticide residues in wine no uniform maximum residue limits (MRLs) have been established yet. However, there is a worldwide trend toward setting specific, lower MRLs for pesticides in wine, which would range from 0.01 to 2 mg $kg^{-1}$ for different pesticides [4].

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) is a member of organophosphorus class insecticides and defined as an endocrine disruptor [5, 6]. It is widely used for the control of *Lobesia Botrana* in grapes [7]. Like the other organophosphorothioate pesticides, acute toxic effects of CP exposure are primarily due to the inhibition of acetylcholinestease [8].The potential harm effect of chlorpyrifos (CP) to ecosystems is considerable and numerous methods have been developed for its determination [9]. Analysis of Chlorpyrifos in different food matrixes is conventionally carried out by gas chromatography (GC) by using NPD [10], ECD [3], and MS detectors [11–13]. Liquid chromatography (HPLC) [14], immunoassay-based techniques, such as enzyme linked

immunosorbent assay (ELISA) [15], and liquid chromatography determinations combined with ELISA have also been reported [16, 17]. Major techniques for extraction and concentration of pesticides prior to the chromatographic separation in wine are liquid–liquid extraction (LLE) and solid-phase extraction (SPE), solid-phase micro extraction (SPME). In developing countries, routinely adopting the chromatographic analysis method is, however, financially limited for these kinds of analyses. Thus, development of reliable and fit for purpose methods of analysis for mixtures of pesticides with the use of simple and relatively inexpensive instrumentation is an appropriate objective. Hence, electroanalytical techniques provide an inexpensive alternative for pesticide analysis [18–24].

In fact, electrochemical methods are not frequently used for analysis of pesticides in complex matrices. Pesticide residue analysis by voltammetric methods is carried out especially in commercial formulations [25–27], water [28–33], and soil samples [34–38]. To date, a few studies were reported describing voltammetric determination of pesticide residues in food sample including liquid–liquid extraction and clean-up stages prior to the analysis [29, 39].

Chlorpyrifos is known to be electroactive and its differential pulse polarographic (DPP) behavior was investigated [40]. Adsorptive property of the molecule was utilized in stripping voltammetric determination of CP in commercial formulations and treated waste water samples [41].

This paper deals with the development of an adsorptive catalytic stripping voltammetric method for the sensitive detection of the CP at an HMDE. The application of the method for the determination of trace amounts of CP residue in red wine samples was also elucidated. This is of particular importance since no data are available in the literature for the determination of CP in wine samples by a voltammetric method. Determination of trace amount of pesticide residues in wine is difficult task since such complex matrices hinder an accurate evaluation and therefore, a pre-separation step is required for handling the samples. Thus, the effectiveness of LLE and SPE steps on recovery percentages was also examined in this paper.

## 2 Experimental

### 2.1 Instrumentation

Voltammetric studies were carried out with a Metrohm 694 VA Processor and Stand. A three electrode system was used including Ag/AgCl (saturated KCl) reference and platinum auxiliary electrodes. The working electrode was a hanging mercury drop electrode (HMDE). All experiments were carried at pulse amplitude of 50 mV and a scan rate of 100 mV $s^{-1}$.

Solid-phase extractions were applied by using cartridges (3 mL) containing 500 mg of Florosil, (Supelco, Oakville, Canada). A mechanical vacuum pump under a 20 in. Hg vacuum (Edwards E2M2, Crawley, UK) was used in SPE experiments. High speed homogenizer (Waring Commercial Laboratory) and nitrogen evaporator (Turbovax, USA) were used during the extraction. The samples were stirred by using an IKA basic vibratory stirrer (IKA Labortechnik, HS501). pH measurements were made by using Mettler Toledo Seven Multi pH-Meter (Switzerland).

### 2.2 Reagents

All reagents and chemicals used were of analytical grade. Universal Britton Robinson buffer solutions (BR) were prepared by mixing equal molar (0.04 M) of phosphoric, boric, and acetic acid solutions and by drop wise addition of 0.2 M NaOH to provide a wide range (2–10) of pH. Various electrolyte ion solutions of 1.0 M were prepared by dissolving the required amount of salts in a definite volume of double-distilled water. Procymidone, Penconazole, Bromopropylate, Lambda-Cyhalotrin, Iprodione, and Chlorpyrifos pesticides were supplied by Dr. Ehrenstrofer Laboratories and stock solution of which (500 μg $mL^{-1}$) was prepared by dissolving an appropriate amount of the pure solid reagents in absolute ethanol.

Analytical grade cyclohexane, ethyl acetate, acetonitrile, chloroform, dichloromethane, diethyl ether, petroleum ether, heptane (Lab Scan) ethanol, hexane, toluene, isooctane, and acetone (J.T.Beaker) reagents were used for the sample preparation. Analytical grade $HClO_4$, $H_3PO_4$, $CH_3COOH$, $H_3BO_3$, $H_2SO_4$, HCl, $HNO_3$, and Titrisol buffer solutions were supplied by Merck.

The wine sample used was a red wine obtained commercially from the local market. This sample contains 12.8% (v/v) ethyl alcohol. The measurements were made at laboratory temperature and all the solutions were allowed to reach at this temperature prior to measurement.

### 2.3 Procedures

#### *2.3.1 Voltammetric measurement procedure*

An aliquot of buffer solution (20 mL) containing 5–25% ethanol was placed in the voltammetric cell. The solution was purged with nitrogen for 5 min and a new drop was initiated. The analyte was deposited via adsorption onto the HMDE surface by applying the potential at −0.50 V for 1 min. Then, the potential was scanned from −0.50 to −1.25 V until otherwise stated. The precision of the method was calculated from sequential eight analyses as RSD%. In the sample analysis, the standard addition method was used in order to eliminate the matrix effects.

The wine samples were spiked with small volumes of CP standard solution to be 100 ng $mL^{-1}$ in the cell and further additions were made. The procedure was applied to five parallel red wine samples.

### 2.3.2 *Preparation of wine sample for analysis*

20 mL of wine sample was placed in an extraction bottle, and mixed with 10 mL of n-heptane by stirring for 30 min at a rate of 350 rpm. In clean-up step, 5 mL of the organic phase taken from the above step was passed through the Florosil column and the analyte retained in the column was eluted by 3 mL of Petroleum Ether. The column was dried under vacuum and elute was dried under a nitrogen flow. The residue was dissolved in 0.5 mL EtOH by using vortex stirrer and diluted with 4.5 mL Titrisol buffer.

## 3 Results and discussion

### 3.1 Optimization of experimental and instrumental parameters

Early studies for voltammetric determination of CP were initiated with a dropping mercury electrode (DME) and the DP polarogram of CP standard solution was recorded at 1 s of drop time. In DP, polarogram of CP in pH 2.0 BR buffer solution revealed that the reduction peak of CP cannot be characterized definitely as it is located very close to hydrogen-evolution peak. Therefore, hanging mercury drop electrode (HMDE) was used and a well-separated reduction peak was obtained at −1.10 V in pH 2.0 BR medium.

To investigate the effect of pH on the peak shape, the analysis was carried out in BR buffer solutions over a pH range of 2.0 to 10.0 each containing 25% ethanol as described earlier [40]. Figure 1 illustrates the dependence of the peak height of the CP on the pH. As the medium was made more alkaline, the peak potential has shifted from −1,110 to −1,206 mV indicating a pH dependent reduction process. Considering the structural effects on the reduction mechanism, even the pyridine moiety is electroinactive in nature, the mesomeric effect of the three Cl atoms in CP molecule increases the localization of the electrons in the pyridine system and results in a reduction of the C=N centre [41]. The reduction reaction was attributed to the reduction of this centre of the pyridine ring via $2e^-$ and $2H^+$. This explains the decline in the peak current at high pHs. Best results were obtained in acidic media and pH 2.0 BR buffer solutions. More acidic regions were avoided as the reduction peak of CP is located very close to hydrogen-evolution peak.

A small volume of ethanol is usually added to the buffer solution to maintain appropriate solubility of the pesticide molecule. In this study, the effect of the optimum ethanol percentage was found to be 5% (Fig. 1 inset). The decrease in the peak height of the CP in high ethanol percentages could be explained by the less affinity of CP to mercury rather than the solution. Since adsorption of the CP on mercury drop strongly affects the reduction peak characteristics, further studies were focused on the adsorption parameters, namely deposition time and the potential.

The effect of deposition potential on the peak height of 1.0 μg $mL^{-1}$ CP was investigated at pH 2.0 BR buffer solution containing 5% ethanol. Since a strong adsorption was observed at −0.50 V in the plot of the peak current versus the deposition potential (Fig. 2), this potential was selected for further studies.

Deposition of CP on the HMDE should be carefully controlled for avoiding saturation and maintain linearity with increased analyte loading. Figure 3 shows the effect of deposition time on the adsorptive cathodic stripping voltammetric (AdCSV) peak heights of CP deposited on an HMDE. Since the concentration of CP is high (1.0 μg $mL^{-1}$), a deposition time of 60 s would be adequate. However, a longer deposition period can be used for the more sensitive regions.

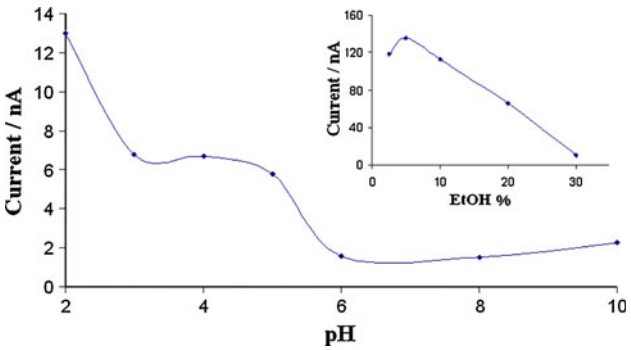



**Fig. 1** The effect of pH on the peak current of 0.6 μg $mL^{-1}$ CP recorded at HMDE in BR buffer solutions containing 25% ethanol. *Inset figure* represents the dependence of the peak current on the ethanol percentage

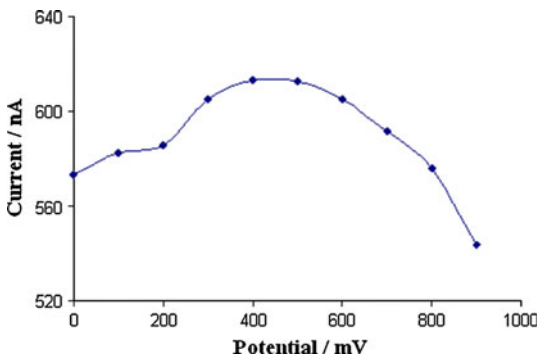



**Fig. 2** Effect of deposition potential on the peak height of 1.0 μg $mL^{-1}$ CP in BR buffer solutions containing 5% ethanol (Deposition time = 60 s)

The composition of the electrolyte solution is another significant parameter which affects the adsorption as well as the reduction of CP. Replacing the BR buffer solution with 0.01 M HCl, $HNO_3$, $H_2SO_4$, $HClO_4$, and $H_3PO_4$ solutions to obtain a more sensitive peak, it was observed that the most sensitive one was recorded in 0.01 M $HClO_4$ solution, and further studies were carried out with this electrolyte.

The effect of solution temperature on the CP peaks was also studied over a range of 20 to 40 °C and maximum peak current was obtained at 25 °C (data not shown). It is concluded that the decreasing current observed at higher temperatures indicates the thermal desorption or volatilization of CP molecule.

### 3.2 Cyclic voltammetric behavior of CP molecule at HMDE

Cyclic voltammetry (CV) is a useful tool for mechanistic studies. As can be seen from Fig. 4, 1.2 μg $mL^{-1}$ of CP molecule gives a reduction peak at −1,200 mV in pH 2.0 medium at a scan rate of 100 mV $s^{-1}$. No anodic peak was observed as an irreversible reduction occurred.

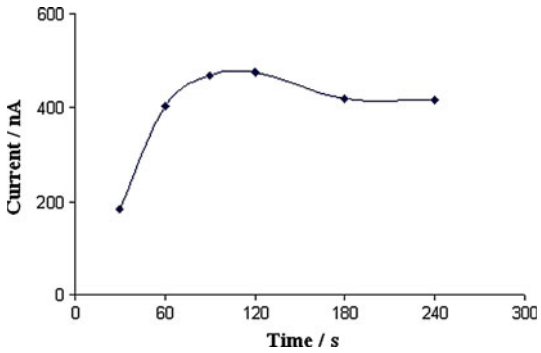



**Fig. 3** Effect of deposition time on the AdCSV peak height of 1.0 μg $mL^{-1}$ CP in BR buffer solutions containing 5% ethanol (Deposition potential = −0.5 V)

The reduction peak has shifted to more negative potentials with increasing scan rate ($v$). The plot of peak potential versus log ($v$) which exhibits a linear relationship with a good correlation for CP corresponds to the fact that the analyte is transferred to the mercury drop by diffusion (Fig. 5).

On the other hand, the peak currents for very low concentrations were much larger than expected from Randles–Sevcik equation, indicating that another process is involved beside the diffusion. As pointed out in a former study [30], a relatively high peak current indicates a possible hydrogen-evolution catalytic process over pyridine moiety. Further experiments were designed to cover diagnostic tests depending on the scan rate. Figure 6 shows that the ratio of "peak current $v^{-1/2}$"decreases at higher scan rates and the peak current reaches a stable value at lower scan rates (Fig. 6 inset). Both findings confirm that a catalytic process is involved.

Moreover it was observed that, the peak current of the CP is strongly dependent on the drop size of HMDE. The peak current measured experimentally increases 26 times, although the drop size changes 1 to 9 with the surface area changing 0.15 to 0.60 $mm^2$ as specified in the instrumentation manual. This means that as greater the surface area where the CP molecules are adsorbed is greater the catalytic effect.

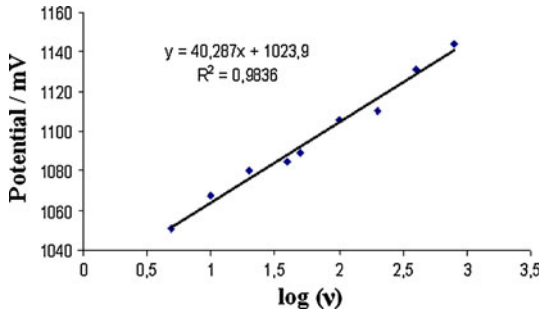
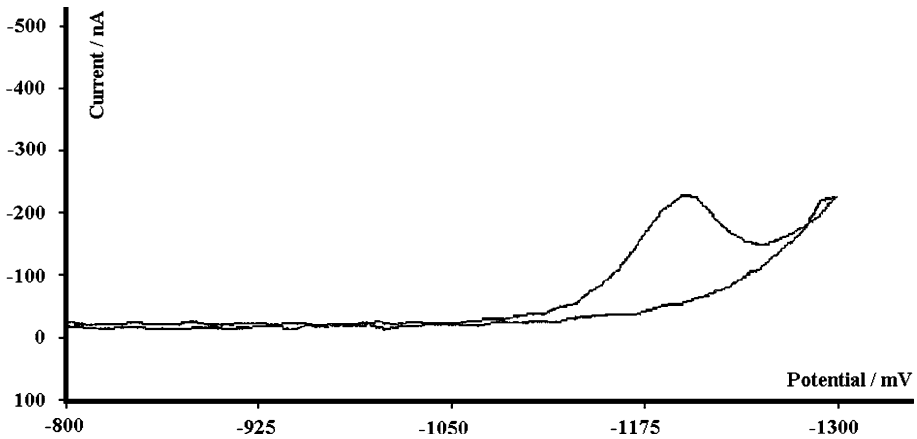



**Fig. 5** The plot of potential versus log $v$

**Fig. 4** The CV voltammograms of 1.2 μg $mL^{-1}$ CP at pH 2.0 medium recorded at an HMDE for a scan rate of 1,000 mV $s^{-1}$



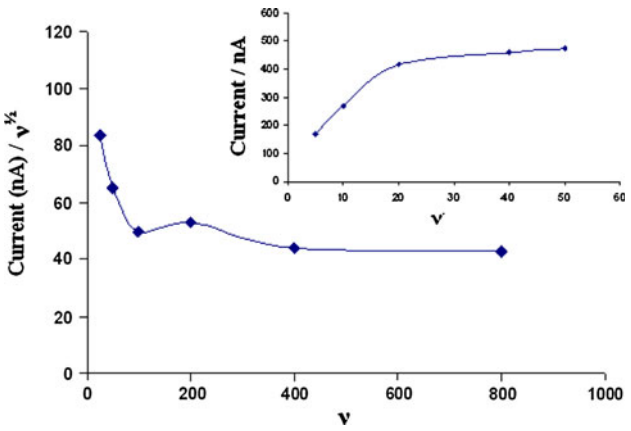



**Fig. 6** The plot of current/$v^{1/2}$ versus $v$. *Inset figure* shows the dependence of peak current on $v$ for lower scan rates

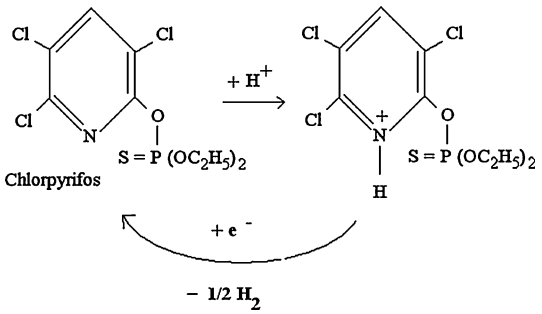



**Fig. 7** The mechanism proposed for CP reduction at an HMDE

As a result, the reduction mechanism of CP can be evaluated as a catalytic process. Pyridine moiety of the CP molecule undergoes protonation leading to pyridinium ion and then it is reduced with the regeneration of pyridine as hydrogen gas is liberated (Fig. 7). Finally, the overall reaction is the reduction of the hydrogen ion to hydrogen molecule. However, this occurs at a potential significantly lower than that for the normal reduction of the hydrogen ion and forms an independent peak whose height is controlled by the concentration of the CP. Although catalytic currents are usually of poor reproducibility, they do offer greater sensitivity as the magnitude of the current is two orders larger than that of diffusion currents. This mechanism differs from that proposed earlier [40, 41] and implies the high sensitivity of the method. Lower ethanol percentages utilized in this study would also contribute to the sensitivity as it affects the adsorption characteristics. Medium pH is another effect which indicates the presence of the catalytic process since hydrogen ion is reduced.

### 3.3 Analytical characteristics

A calibration curve of the peak current versus concentration was plotted in pH 2.0 $HClO_4$ solutions containing 5% EtOH with a drop size of 6 of hanging mercury electrode. Figure 8 shows the voltammograms obtained for a range of 20–100 ng $mL^{-1}$ CP. Similar calibration curve was also plotted for the more sensitive concentration region of 0.2–1.2 ng $mL^{-1}$. The slope and the intercept of the curve were found to be 66.21 ± 7.28 nA mL $ng^{-1}$ and 0.69 ± 0.08, respectively. Each point of the two calibration curves is the average mean value of three measurements. LOD is the lowest concentration that can be distinguished from the noise level. The LOD and LOQ values were calculated as 0.14 and 0.45 ng $mL^{-1}$, respectively, and the RSD value at this level was found to be 7.4% ($n = 8$).

### 3.4 Interference studies

Metal ions tend to do interference by forming complexes with the organic analyte or simply being reduced with a potential close to the analyte. Therefore, the effect of several metal ions was investigated in the presence of $3 \times 10^{-7}$ M CP in pH 2.0 $HClO_4$ solution containing 5% ethanol. Copper, lead, cadmium, and zinc ions were added into the cell to give a tenth, the same or ten fold of the CP concentration. Ten-fold copper, lead, and cadmium ions have led a decrease in the peak current less than 8%. In contrast to those ions above, zinc ion severely hinders the signal since it is reduced at a very close potential to that of CP molecule. Nevertheless, the wine samples require a pre-separation step for removal of organic residues as well as the inorganic constituents in the sample matrix.

To study the selectivity of the method, possible interference of other pesticides, which might be used in grapevine, was studied. Procymidone (PRO), Iprodione (IP), Penconazole (PNC), Bromopropylate (BRP), and Lambda-Chyhalothrin (LB) pesticides were usually detected in Turkish wine samples as reported in a former study [42]. Voltammetric measurements were carried out in Titrisol buffer solution containing 5% ethanol and spiked with CP to be 0.5 μg $mL^{-1}$ in the cell. Results have revealed that PRO, IP, PNC, and LB pesticides have no electro-active properties under the experimental conditions. On the other hand, BRP standard has given a single peak close to a large reduction signal of hydrogen at −1.2 V. The peak current of CP at 0.5 μg $mL^{-1}$ concentration level has decreased to the half of the initial one in the presence of equal concentrations of BRP.

In fact, most organic residues tend to be surface active and result in a certain loss in the signal. Yet, pre-separation step was applied in wine analyses where the analytes are separated mostly by their polarities. By applying an appropriate separation technique, this interference can be eliminated. Moreover, this finding indicates that both pesticide residues can be determined simultaneously in wine sample.

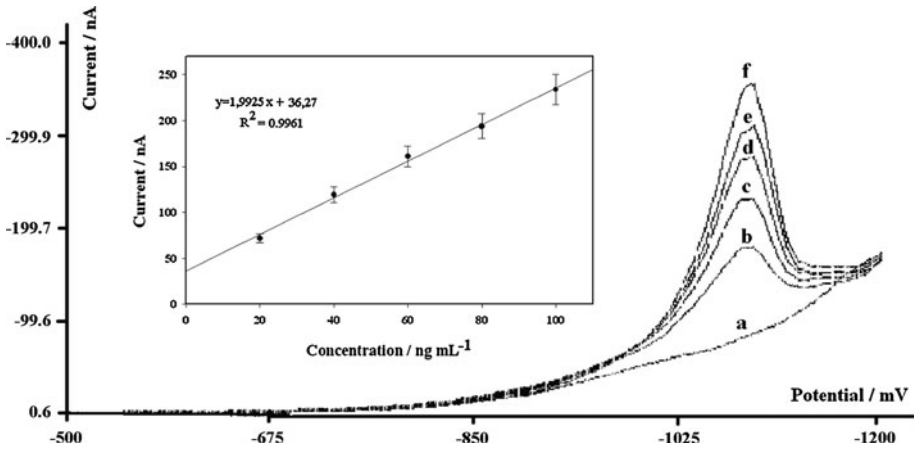



**Fig. 8** The DP voltammograms and corresponding calibration graph for CP in higher concentration range at pH 2.0 $HClO_4$ solution containing 5% ethanol (Deposition potential = −0.5 V, Deposition time = 30 s)

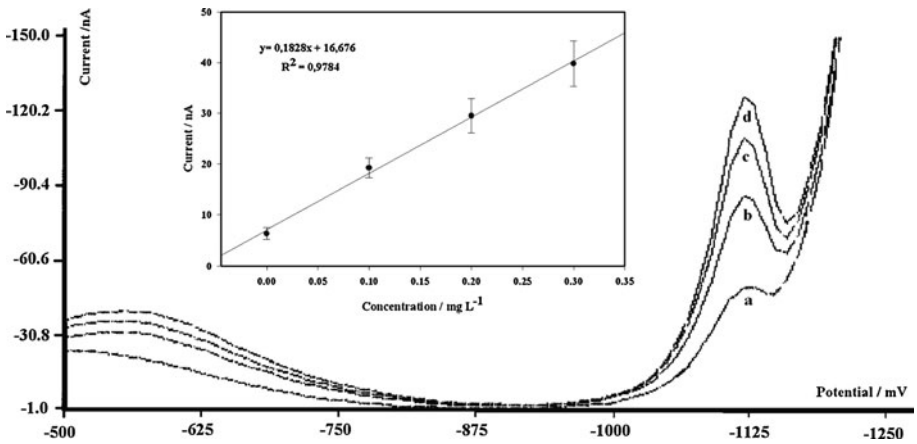



**Fig. 9** The standard addition DP voltammogram of **a** wine sample and after addition of CP standard to be **b** 0.1, **c** 0.2, and **d** 0.3 μg $mL^{-1}$

### 3.5 Application of the method for wine samples

The complex matrix of the wine samples requires a pre-separation step for the determination of the pesticides. Pesticide residue analysis in food is usually carried out by means of multi-residue-methods for extraction and clean-up stages followed by a final determination step. In this study, various separation techniques including liquid–liquid extraction (LLE) with different solvents and solid-phase extraction (SPE) with different cartridges were tested in the clean-up step prior to the voltammetric measurement of CP. LLE step was optimized by determining recovery ratios for different solvents, namely n-heptane, petroleum ether, cyclohexane, toluene, diethyl ether, dichloromethane, chloroform, and ethyl acetate. For this purpose, a synthetic wine sample containing 12% EtOH and 0.5 μg $mL^{-1}$ CP was placed in an extraction bottle and LLE step was applied according to the procedure given in Sect. 2. Recovery percentages were found to decrease accordingly with the polarity index of the extraction solvent and then n-heptane was chosen as it gives the best result. However, this step alone does not fulfill the requirements in eliminating the matrix effects and additional clean-up process is needed. Therefore, as a further step, solid-phase extraction (SPE) cartridges including Florosil sorbents were utilized. Elution was made by Petroleum Ether and elute was dried under nitrogen stream. The residue was dissolved in small amount of ethanol and diluted with pH 2.0 Titrisol buffer. The procedure was applied to five parallel red wine samples. Voltammograms were recorded for the samples prepared in this way (Fig. 9) and by using standard addition method. Thus, the CP content of sample was calculated as $0.060 \pm 0.006$ μg $mL^{-1}$ ($n = 5$). The accuracy of the method was tested upon recovery studies. Red wine samples were spiked with 0.05 μg $mL^{-1}$ of CP and recovery ratios were found in a range of 84–110%.

## 4 Conclusions

In this paper, electrochemical behavior of chlorpyrifos pesticide was investigated by differential pulse adsorptive stripping voltammetry on an HMDE. The reduction

mechanism of the CP was elucidated as a catalytic process via pyridine moiety of the molecule. Excellent sensitivity of the method inherited from the catalytic process was utilized in the determination of the CP in sub ppb levels. Based on this, a convenient procedure for the determination of the CP residue in wine samples is proposed. The complex matrix effect was eliminated by using both LLE and SPE steps with very satisfactory recovery values. Hence, this electroanalytical technique provides an inexpensive, simple, sensitive, and rapid alternative for electroactive pesticide analysis in wine samples with a sufficient precision and accuracy.

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## References

1. Karabayır C (2009) Wine sector in Turkey. IGEME, Export Promotion Centre of Turkey, Ankara, Turkey, p 2
2. Simon D, Helliwell S, Robards K (1998) Anal Chim Acta 360:1
3. Oliva J, Navarro S, Barba A et al (1999) J Chromatogr A 833:43
4. Hyötylainen T, Lüthje K, Rautiainen-Rama M et al (2004) J Chromatogr A 1056:267
5. Viswanath G, Chatterjee S, Dabral S et al (2010) J Steroid Biochem Mol Biol 120:22
6. Jeong S-H, Kim B-Y, Kang H-G et al (2006) Toxicology 220:189
7. Guardino X, Obiols J, Rosell MG et al (1998) J Chromatogr A 823:91
8. Zhao Q, Dourson M, Gadagbui B (2006) Regul Toxicol Pharmacol 44:111
9. Eaton DL, Daroff RB, Autrup H et al (2008) Crit Rev Toxicol S2:1
10. Rastrelli L, Totaro K, De Simone F (2002) Food Chem 79:303
11. Serrano R, Lopez FJ, Roig-Navarro AF et al (1997) J Chromatogr A 778:151
12. Richter P, Sepulveda B, Oliva R et al (2003) J Chromatogr A 994:169
13. Liu S, Pleil JD (2002) J Chromatogr B 769:155
14. Abu-Qare AW, Abou-Donia MB (2001) J Chromatogr B 757:295
15. Brun EM, Garces-Garcia M, Puchades R et al (2005) J Agric Food Chem 53:9352
16. Velasco-Arjona J, Manclus JJ, Montoya A et al (1997) Talanta 45:371
17. Giraudi G, Rosso I, Baggiani C et al (1999) Anal Chim Acta 392:85
18. De Sauza D, Machado SAS (2005) Anal Bioanal Chem 382:1720
19. De Sauza D, De Toledo RA, Gali A et al (2007) Anal Bioanal Chem 387:2245
20. Zhang Y, Kang T-F, Wan Y-W et al (2009) Microchim Acta 165:307
21. Lopes IC, De Sauza D, Machado SAS et al (2007) Anal Bioanal Chem 388:1907
22. Ibrahim MS, Al-Magboul KM, Kamal MM (2001) Anal Chim Acta 432:21
23. Lin MS, Jan BI, Leu H-J et al (1999) Anal Chim Acta 388:111
24. Drevinek M, Horak V (1997) J Electroanal Chem 423:83
25. Santos LBO, Abate G, Masini JC (2004) Talanta 62:667
26. Navalon A, El-Khattabi R, Gonzalez-Casado A et al (1999) Microchim Acta 130:261
27. Thriveni T, Kumar JR, Lee JY et al (2009) Environ Monit Assess 151:9
28. El Bakouri H, Palacios-Santander JM, Cubillana-Aguilera L et al (2005) Chemosphere 60:1565
29. Ni Y, Qiu P, Kokot S (2004) Talanta 63:561
30. Santos LBO, Masini JC (2008) Anal Chim Acta 606:209
31. Barroso MF, Nunes OC, Vaz MC et al (2005) Anal Bioanal Chem 381:879
32. Erdoğdu G (2008) J Anal Chem 63(8):762
33. Papp Z, Svancara I, Guzsvany V et al (2009) Microchim Acta 166:169
34. Oudou HC, Alonso RM, Bruun Hansen HC (2004) Anal Chim Acta 523:69
35. Manisankar P, Viswanathan S, Pusphalatha AM et al (2005) Anal Chim Acta 528:157
36. Manisankar P, Selvanathan G, Vedhi C (2005) Appl Clay Sci 29:249
37. Tavares O, Morais S, Paiga P et al (2005) Anal Bioanal Chem 382:477
38. Erdoğdu G, Titretir S (2007) J Anal Chem 62(8):777
39. Thriveni T, Kumar JR, Sujatha D et al (2007) Food Chem 104:1304
40. Al-Meqbali A.S.R, El-Shahawi M.S, Kamal M.M (1998) Electroanalysis 10(11):784
41. El-Shahawi MS, Kamal MM (1998) Fresenius J Anal Chem 362:344
42. Okçu F (2009) Voltammetric and chromatographic method development for pesticide residues in some food products. PhD Thesis, Ege University, Turkey