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Determination of Diazinon in fruit samples using electrochemical sensor based on carbon nanotubes modified carbon paste electrode

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ABSTRACT

A carbon paste electrode is modified with carbon nanotubes. That's application for voltammetric detection of Diazinon (DZN) is reported in this study. Pesticides are meant to destroy the pests and are classified into different groups. The presence of pests residues impact our health and cause several health issues such as skin and nerves system diseases. Diazinon(oo-diethyl-o-(2-isopropyl-6methyipyrimidin-4-yl)-momothiophosphate) (DZN) is one of the most common organophosphate pesticides (Ops) that are extensively used for control pests in soil, on plants, fruits, and vegetable pests. The electrochemical behavior of CNT/CPE was studied by cyclic voltammetry (CV) and Differential pulse voltammetry (DPV). The chemical parameters influencing the response are optimized for detection of DZN. These are pH value, amount of modifier and scan rate. The fabricated electrochemical sensor displayed a linear and sensitive response to DZN within the concentration range of 1×10^{-10} to 6×10^{-8} M. The detection limit found to be 4.5×10^{-10}. This sensor was successfully used to determine DZN in food samples.

1. Introduction

Ops are the most toxic compounds, which are commonly used as pesticides, insecticides and chemical warfare agents. They are applied as pesticides and insecticides to repel pests in many countries, Because of their effectiveness (Ensafi et al., 2017), low cost and widespread availability (Amare et al., 2014). These compounds are used commonly to eliminate a vast range of pests on fruits and vegetables (Tefera et al., 2015). Pesticides play an important role in preventing or reduction of diseases caused by pests. Therefore, they can increase the farm production (Zhao et al., 2015). However unusual usage of pests can cause enhancement of the excessive residues. The presence of residues of these pesticides in ground waters and foodstuffs are of major concern for human and environment (Geremedhin et al., 2013). They can lead to unfavorable effects on the environment and human health because of their toxicity (Liu et al., 2017). These pesticides are toxic because they have a strong prevention effect on the activity of acetylcholine esterase enzyme (ACHE) which is mainly contained in cholinergic neurons. As a consequence, the ACHE can accelerate the rate of hydrolysis of acetylcholine into cholin and acetate. The disincentivization of ACHE activity makes extreme aggregation of acetylcholine in the body which disarranges the physiology of the nerve system and leads to death (Xiaojuan Liu, Song, Hou and Li, 2017). OPs compounds have also been developed as extremely powerful neurotoxic chemical-warfare agents (CWAs) (Lin et al., 2004). DZN is an Ops which is widespread used in agriculture (Motaharian et al., 2016), and controls pests in soil, vegetables and fruits (Khadem et al., 2017). DZN acts as disincentiver for ACHE, so that causes an unusual aggregation of ACHE. The complications of this toxicity are headache, depression, heart disease, serious neurological disorders (Dhull et al., 2013) and eventually death (Motaharian et al., 2016). The pesticides residues can enter into the food chain and cause diverse problems (Sassolas et al., 2012). They are the most important pollutants and need to be controlled due to their toxicity and durability. So, because of the mentioned harmful effects, quick detection of them is very important (Zhao et al., 2015). Accordingly, various techniques such as gas chromatography (GC) (Andreescu et al., 2002), high performance liquid chromatography (HPLC) (Erdoğdu, 2003; Lee et al., 2002; Gupta et al., 2011) liquid chromatography coupled with mass spectroscopy (GC-MS) (Gupta et al., 2014b), fluorescent (Gupta et al., 2015), strip voltammetry (Gupta et al, 2012), inductively coupled plasma (ICP) Gupta et al., 2014 are used to determine pesticides owing to their sensitivity and precision (Wei and

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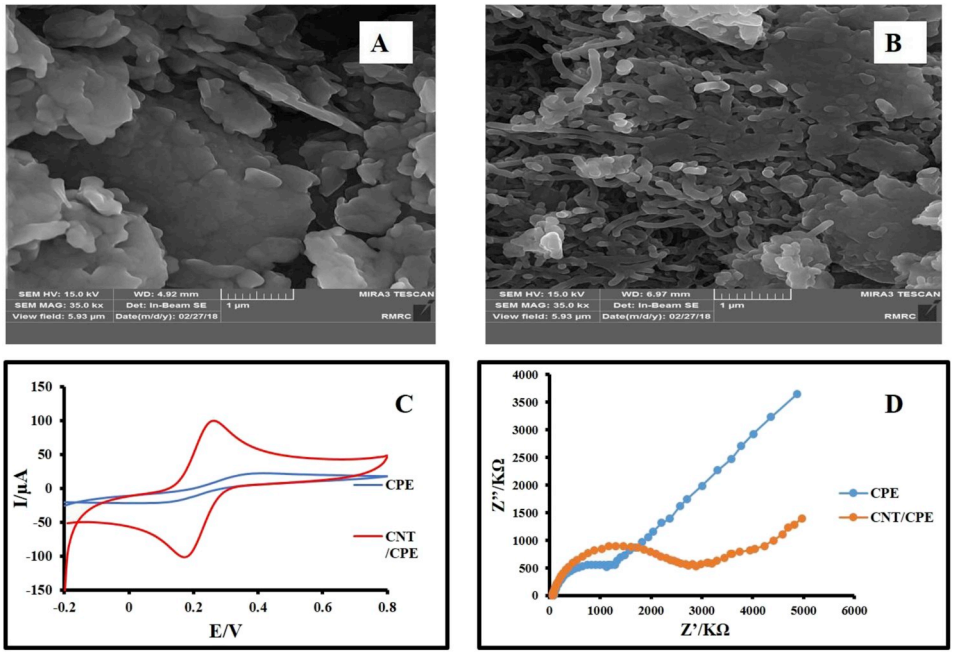

Fig. 1. FESEM image of A) CPE B) CNT/CPE C) Cyclic voltammograms and D) EIS at bare and CPE/CNT in 1 mM $Fe(CN)6^{-3/-4}$ solution at scan rate of 100 mV/s.

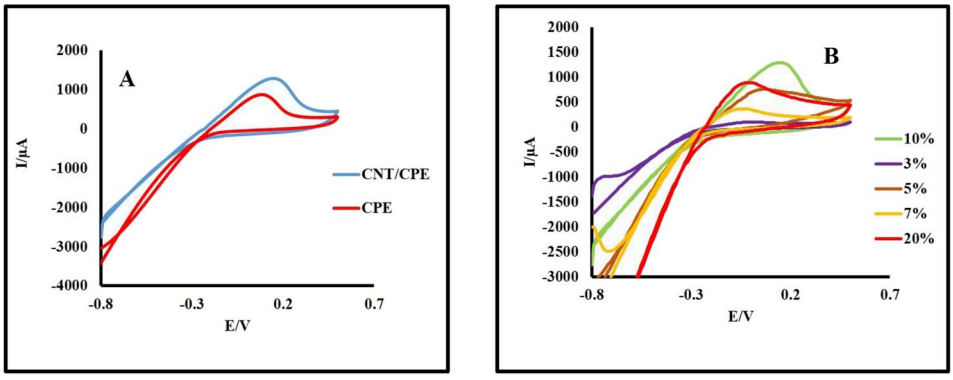

Fig. 2. A) Cyclic voltammograms of 0.01 M Diazinon solutions at CPE and CNT/CPE acetate buffer pH 5.25 B) Effect of CNT on peak current of DZN in acetate buffer solution (pH 5.25) at 100 mV/s.

Feng, 2017). Electrochemical methods have many advantages over other techniques for detection such as reproducibly, good stability, high sensitivity, measuring trace level of samples and cost-effectiveness (Tefera et al., 2015; Motaharian et al., 2016). Modification of the electrode area can greatly improve the sensitivity and selectivity (Shabani-Nooshabadi et al., (2019)) of electrochemical sensors and excludes surface sediment (Li et al., 2004; Tefera et al., 2015). Chemical modification of electrodes is a very adequate method for detection of Ops (Liu, 2011). These promising future technologies are appropriate alternative to solve the problems of low electron transfer (Karimi-Maleh et al., 2015) in electrochemical sensors and high over potentials of process (Deroco et al., 2017). Various materials can be used for modification of electrodes area, such as carbon nanotubes, metal oxides and polymers (Tefera et al., 2015). Carbon nanotubes (CNTs) are tubular molecules formed of carbon atoms and have two different types of structures including single wall and multi walls. They have specific tube frame and many incomparable properties such as excellent electrical conductivity and great chemical stability (Amare et al., 2014). They are significant groups of nanomaterial which are applied for modifying bare electrodes (Tefera et al., 2015; Ruoff et al., 2003). Modification of the electrode layers with nanoparticles (Gupta et al., 2014a) such as CNTs for use in sensors have been chosen because of desirable mechanical rigidity, high conductivity (Antoine et al., 2019), high surface area (Asfaram et al., 2015) in hydrous and anhydrous solutions (Tefera et al., 2015; Ruoff et al., 2003), good detection limit, great sensitives (Sanjay, Koyeli. 2018) and decrement of over potentials (Karimi-Maleh et al., 2012). Moreover, the accurate electronic behavior of CNTs shows that they have the capability to improve electron transfer reactions and have a great electrocatalytic efficacy as electrode materials. According to these fascinating properties, today CNTs are the best candidates for modifying electrodes (Amare et al., 2014). In another studies, different types of sensors for DZN detection have used. For example, analysis of DZN, using a Nafion coated GCE and SWV electrochemical technique (Erdoğdu, 2003; Lee et al., 2002). DZN detection with an electrochemical sensor based on MIP and SWV method was performed (Motaharian et al., 2016). Another electrochemical MIP sensor was used for determination of DZN (Khadem et al., 2017). The present paper explains the determination of DZN using CNT/CPE. CNT display high electro catalytic activity to DZN. A sensitive and selective response has been obtained after placing the electrode in acetate buffer solution containing suitable concentration of DZN. This modified electrode with excellent performance was successfully applied for the detection of Diazinon in fruit samples.

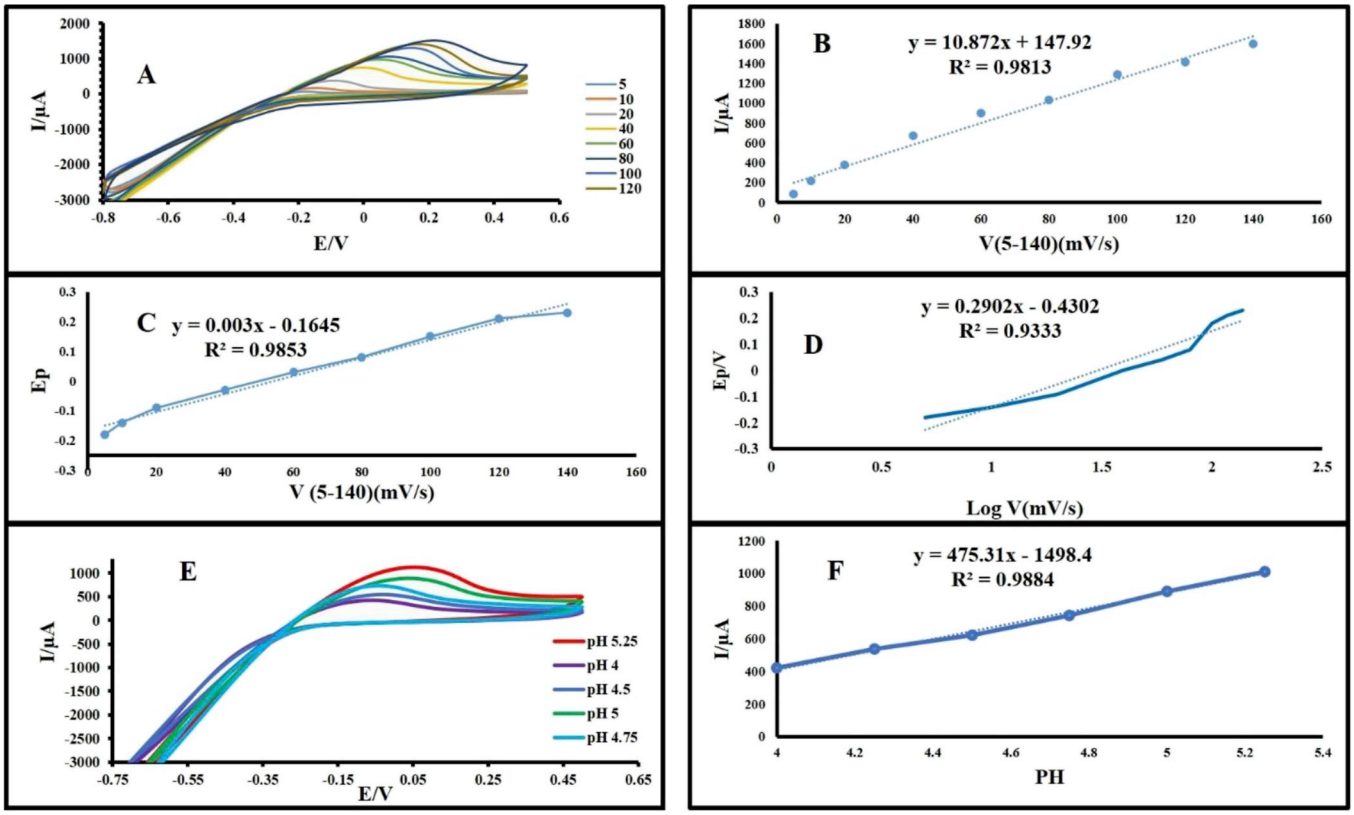

Fig. 3. (A) CVs of DZN at CPE/CNT in various scan rates (5–140). (B) Dependence of peak current on the scan rate. (C) The relation between E_p and scan rate. (D)The relation between Ep and LogV. (D) Dependency of peak current on the scan rate E) Effect of pH on the response of CNT/CPE to DZN. (F) Plot of peak current versus pH.

Table 1
Effect of interferents on detection of DZN at CNT/CPE

Interfent	[Interfent] (mol/lit)	Added	RSD%
K^{+1}	1 M	300 μL	4.7
Ca^{2+}	1 M	300 μL	6.1
Mg^{2+}	1 M	300 μL	5.3
Ni^{2+}	1 M	300 μL	6.1

Table 2
DZN determination in real samples.

Sample	DZN(mol/lit)	RSD%
Tomato	1 M	3.7
Apple	1 M	4.2
Cucumber	1 M	3.1
Spinach	1 M	4.6
Sweet peppers	1 M	4.3
Lettuce	1 M	3.5
Cabbage	1 M	3.2
Eggplant	1 M	5.1

2. Experimental method

2.1. Apparatus and materials

The electrochemical analyses were carried out by a Three-electrode system that contains an Ag/Agcl as reference electrode, a platinum wire auxiliary electrode and a CNT/CPE working electrode.

DZN was purchased from Partonar Company. Graphite powder, CNTs, acetic acid, sodium acetate and ethanol were supplied from Merck. DZN stock solution was prepared by dissolving DZN in ethanol and kept in the refrigerator. Acetate buffer solution was prepared using 1 M acetic acid and 1 M sodium acetate solutions and the pH of the solutions were adjusted with NaOH and HCl.

2.2. Preparations of the sensors

The unmodified electrode was prepared by mixing 70% graphite powder with 30% paraffin oil (ratio of C: Paraffin 70:30, w/w) then homogenized for 10min. The proper amount of CNT (modifier) was added to the paste and then homogenized in a mortar to prepare CNT/CPE electrode. The modified electrode was finally obtained by packing the prepared paste into a glass tube. Electrical connection was made by pushing a wire down the glass tube into the back of the mixture.

3. Results and discussion

3.1. Electrochemical characterization of CNT/CPE

Fig. 1A shows the FESEM image of carbon paste electrode. As can be seen at a surface of CPE, the layers of irregularly plates of graphite powder do exist. After addition of CNT to carbon paste, it can be seen that CNTs were distributed on the surface of electrode with special tubular structure (Fig. 1B). This image indicates that the CNTs were successfully modified on the CNT/CPE. The structure and properties of CNT/CPE and CPE were investigated using cyclic voltammetry (CV) technique in 5 mM $Fe(CN)6^{-3/-4}$ solution containing 0.1 M KCl. As shown in Fig. 1C, the CNT/CPE peak current was incremented compared with CPE. The reduction peak current was clearly increase from 22.207 μA at CPE to 97.288 μA at CNT/CPE. Furthermore, the peak to peak separation (ΔE_P) enhanced from 0.26 for CPE to 0.1 for CNT/CPE. This enhancement showed that CNT can improve the sensitivity and conductivity of the carbon paste electrode. For complementary information about the modified electrode, EIS was employed (Fig. 1D). EIS is an efficient method for monitoring the surface characteristics of

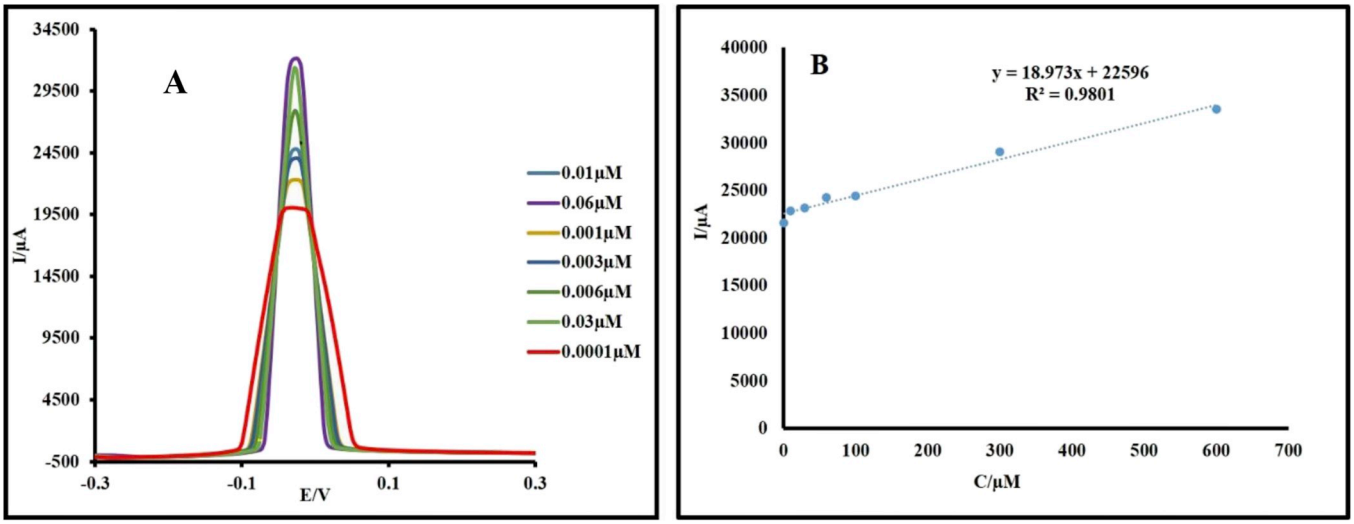

Fig. 4. (A) Voltammograms of DZN at various concentrations (B) Diazinon calibration curve.(In the concentration range of 1×10^{-8} to 1×10^{-10} M.

Table 3
The performance of the various reported electrochemical sensors for Diazinon detection.

Electrode	Modifier	Detection limit	Technique	Literature
glassy carbon	Nafion®-coated	75 nM	square-wave voltammetric	G. Erdo du 2002
carbon paste electrode	MIP nanoparticles	7.9×10^{-10} M	SWV	Ali Motaharian et al., 2016
gold electrode	acetylcholinesterase enzyme	10-6 ppm	CV	Mashuni1 et al., 2016
carbon paste electrode	Multi-walls carbon nanotubes and a molecularly imprinted polymer	1.3×10^{-10} M	square wave voltammetric	Monireh Khadem. et al., 2017
carbon paste electrode	Multi-walls carbon nanotubes	4.5×10^{-10}	DPV	this work

modified electrodes which presents the electron transfer resistance (Ret) at the surface of the electrodes. Herein, the differences in Nyquist plots were considered as a variable related to the modification of the electrode. As can be seen, in the CPE, a semi-circle was observed at the electrode surface. While as the electrode was modified by CNT, a smaller semi-circle was obtained, indicating that the use of CNT could decrease the electrode impedance because of the conductivity of it and accelerating the transfer of the electrons.

3.2. Electrochemical behavior of diazinon

To select the best peak potential, the cyclic voltammetric behavior of DZN was investigated by non-modified and modified carbon paste electrodes. The electrochemical behavior of DZN at CNT/CPE was examined in acetate buffer (pH 5.25) in the potential range of −0.8 to +0.5 at scan rate of 100 mV/s. As can be seen at Fig. 2A, DZN exhibited a favorable peak at 0.1 V. In this test, the presence of CNT improved the electrochemical response of the DZN and acted as an electrocatalyst.

3.3. Effect of varying amount of modifier

The quantity of CNT was optimized to obtain a better response. Fig. 2B Shows the effect of various amount of CNT added to CPE to achieve the best response of DZN. The peak current rise with increasing the amount of CNT up to 10 percent. Further addition of CNT resulted in reduction of the peak current.

3.4. Effect of scan rate

The influence of scan rate on the peak current of DZN on CNT/CPE was studied by cyclic voltammetry in the range of 5–140 mv/s. Fig. 3A Indicates that the peak current enhanced by rising of scan rate. Displaying a linear relationship between the scan rates and peak current of DZN (Fig. 3B). It can be attributed to the adsorption-controlled process of the reduction of DZN at CNT/CPE. Additionally, the peak potential shifted to more positive values with increasing scan rate. Moreover, a linear relationship with the correlation coefficient of (0.9853) between the peak potential of DZN and scan rate was obtained (Fig. 3C). Also there is a relationship between E_p and Logarithm of V according to equation (1)(Fig. 3D).

$$E_p = 0.5308 + 0.0392\log V \quad (1)$$

3.5. Effect of pH buffer solution

The effect of electrolyte pH on peak current was investigated using CV in acetate buffer over the pH range 4–5.25. The effect of pH is displayed in Fig. 3E and F, these Figures represents the cyclic voltammograms of DZN in acetate buffer solution with various pH values. Both the peak current and peak potential showed variation with buffer solution pH. The peak increased with pH until it reached to a maximum value at pH 5.25. As can be seen diazinon reduction potential positively shifts when pH increase from 4 to 5.25. In high pH values lack of proton can be an obstacle to diazinon reduction. Therefore, results showed this pH (pH 5.25) is the best value for determination of DZN and influence on the peak current. So, the peak potentials shift positively with increasing pH.

3.6. Effect of interferences

The applicability of this sensor for determination of DZN was investigated by studying the selectivity of the fabricated sensor. The CNT/CPE was inserted in to the solution of DZN with different ions. The 100-fold excess of calcium, potassium, magnesium and nickel were added to the defined concentration of DZN. Based on results, these ions had no interfering effect on signal till 100-fold concentration. Generally, the results show that CNT/CPE exhibits a well selectivity towards determination of DZN. Table 1 indicates the response of CNT/CPE for each ion.

3.7. Detection of pesticides in real samples

3.7.1. Real samples

The sensor was employed to detect DZN in real samples. Fruits and vegetables were bought from local market and washed with water. For prepared the real sample solution they were sliced to small pieces and mixed in a blender. Afterwards, different concentrations of DZN were sprayed onto the slices and the solution was diluted with acetate buffer, after that, were centrifuged at 9000 rpm for 10 min. The measurement results shown in Table 2.

3.8. Determination of detection limit

Fig. 4A Displays the DPV response of DZN at the surface of CNT/CPE. This test was performed to determine the DZN lowest limit of detection in the range of 1×10^{-10} to 6×10^{-8} M. It was calculated using related equation (equation (2)). The oxidation peak current of DZN increased significantly with enhancement of the DZN concentration. Thus, a linear relationship with the correlation coefficient of (0.9801) between the peak current of DZN and its concentration was attained (Fig. 4B) according to equation (3). To evaluate the sensor performance, in Table 3, the performance of the various reported electrochemical sensors for Diazinon detection was reported.

$$LOD = 3\delta/S \quad (2)$$

$$I_p = 18.973\ \mu A\, L\, mol^{-1}\ x\ [DZN]\ + 22{,}596 \quad (3)$$

4. Conclusions

DZN as a common pesticide can exist in the fruits and vegetables, so measuring of DZN was the aim of this work. In this research, a modified electrode was used for rapid detection of DZN. The CNT enhance the sensor response due to high surface area, as well as improving the electro-catalytic activity and increasing the electron transfer between the electrode and electrolyte. The suggested electrode was a suitable choice for determination of DZN in fruits samples with favorable limit of detection (LOD) without the interferences of other species. Therefore, the CNT/CPE could be a proper candidate for determination of DZN in real samples.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bcab.2019.101245.

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