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Carbon nanotube β-cyclodextrin modified electrode as enhanced sensing platform for the determination of fungicide pyrimethanil

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ABSTRACT

A sensitive electrochemical sensor was successfully developed based on a glassy carbon (GC) electrode modified by a combination of multi-walled carbon nanotubes (MWCNT) with β-cyclodextrin (β-CD) incorporated in a polyaniline film, and applied to detect and determine the fungicide pyrimethanil in pome fruit (apples). The β-CD/MWCNT modified GC electrode displayed a detection limit of 1.04 μM (0.21 mg/kg) which is below the maximum residue levels set for pyrimethanil in pome fruit and citrus fruit by EU regulations. The results indicate that the β-CD/MWCNT modified GC electrode exhibits efficient electrocatalytic oxidation of pyrimethanil with high reproducibility, repeatability and stability. Furthermore, the obtained results were in excellent agreement with those obtained using an established HPLC procedure.

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1. Introduction

Plants make up the majority of the earth's living environment. Directly or indirectly, plants make up all the food on which humans and animals depend. The European and Mediterranean area is characterized by a great diversity of cultivated and wild species. Different species of cereals, fruit orchards and vineyards are grown over a large proportion of cultivated land in most European countries. The Mediterranean Diet, recently nominated as World's Intangible Cultural Heritage by UNESCO, emphasizes primarily plant-based foods such as fruits, vegetables, nuts, healthy fats, e.g. olive oil, and drinking red wine in moderation. Some of these food crops can be affected by a range of pests and diseases, causing significant losses to farmers and threatening food security. It is estimated that diseases, insects and weeds together interfere with the production of, or destroy, between 31 and 42% of all crops produced worldwide annually (Agrios, 2005). Over the last century, the control of plant diseases and other plant pests has depended increasingly on the extensive use of pesticides (Agrios, 2005). Some of these chemicals are applied to protect food crops from the pests at various stages of cultivation and during post-harvest storage. However, the risk of residues remaining on the food is of major concern in food safety issues. To regulate the safety of foods, government agencies have set tolerance levels or maximum residue limits (MRLs) for pesticide residues on food commodities (European Food Safety Authority [EFSA], 2015; Environmental Protection Agency [EPA], 2015).

Pyrimethanil, *N*–(4,6–dimethylpyrimidin–2–yl)aniline (Scheme 1), belongs to the anilino–pyrimidine class of fungicides and has been used worldwide for pre-harvest foliar application or for post-harvest commodity treatments (EFSA, 2011). This broad-spectrum fungicide is effective against diseases caused by *Botrytis*, *Monilinia*, *Venturia* and *Penicillium* spp. and other pathogens (Gullino, Leroux & Smith, 2000; Kanetis, Forster, & Adaskaveg, 2007; Sholberg, Bedford, & Stokes, 2005). The application rates of pyrimethanil during the growing season are in average 600 g ha^{-1} in apple orchards or 1 kg ha^{-1} in vineyards (EFSA, 2011). The metabolism of pyrimethanil in primary crops was investigated and it was shown that metabolites of pyrimethanil were present at levels significantly below those of the parent (EFSA, 2011). Consequently, the residue definition for foliar and post-harvest treatment in all crop groups was defined as pyrimethanil only, for both enforcement and risk assessment (EFSA, 2011). Currently,

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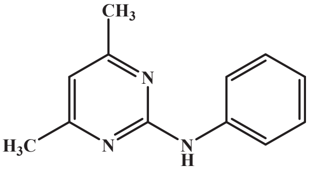


Scheme 1. Molecular structure of pyrimethanil (PYR).

pyrimethanil residues are most commonly monitored using gas chromatography or high performance liquid chromatography (HPLC) coupled with either selective detectors or mass spectrometry (Navickiene & Ribeiro, 2004; Gulaboski & Pereira, 2009; Vaquero-Fernández, Sanz-Asensio, Fernández-Zurbano, López-Alonso, & Martínez-Soria, 2013; Yáñez-Sedeño, Riu, Pingarrón, & Rius, 2010). However, these methods are in general time-consuming, labour-intensive and not environmentally friendly. Thus, it is very necessary to develop simple, rapid and low cost methods for the determination of pesticide residuals in fruits.

Electrochemistry provides powerful and versatile tools for food analysis owing to their simplicity, rapidity, affordability and miniaturization for on-site detection (Gulaboski et al., 2009). The use of electrochemical sensing approaches has been widely exploited as an inexpensive method to sensitively detect a variety of compounds, including pesticides. The physical and catalytic properties make carbon nanotubes (CNT) ideal for use as electrode materials in sensors. CNT-based sensors in general exhibit low limits of detection and fast response due to the signal enhancement provided by high surface area and rapid electrode kinetics (Vashist, Zheng, Al-Rubeaan, Luong, & Sheu, 2011; Yáñez-Sedeño et al., 2010). Composite materials formed with CNT have also been prepared with the aim of improving operational characteristics of the resulting sensors in terms of selectivity, stability or sensitivity. Nanocomposites of β-cyclodextrin (β-CD) and multiwalled CNT (MWCNT) deposited on a glassy carbon electrode (GCE) have recently been successfully used to study and quantify many organic molecules owing to the synergistic effect of both materials (Rahemi et al., 2012, 2013; Shen & Wang, 2009). The great significance of cyclodextrins lies in their ability to selectively form inclusion complexes (host–guest complexes) with many organic and biological molecules.

A number of reports have recently appeared highlighting the synergetic performance of PANI–CNT composites in certain applications including sensors (Gajendran & Saraswathi, 2008). The electrochemical properties of these PANI-CNT composites are greatly enhanced compared to the individual components (Gajendran and Saraswathi, 2008). Recently it has been shown that the sensitivity of PANI–CNT composite sensors can be improved by incorporation of CDs (Rahemi et al., 2012, 2013). The usefulness of CDs is related to their unique structures and to the fact that CDs retain their analyte-recognizing and entrapping properties under a relatively broad range of experimental conditions (Szente & Szemán, 2013). The interfacial architecture and electrochemical activity of PANI/CNT-modified electrodes after incorporating CDs and the resulting recognition effects were already reported (Rahemi et al., 2012, 2013; Shen & Wang, 2009).

The purpose of the present study is the establishment of an analytical methodology for the determination of pyrimethanil (PYR) residues in fruits using a polyaniline-β-CD/MWCNT-modified glassy carbon electrode. The chemical recognition of pyrimethanil by β-CD is combined with the added advantage of a faster electron transfer process due to the functionalised MWCNT, dispersed in the conducting PANI matrix. The new analytical methodology developed has been employed for the direct oxidative determination of pyrimethanil in apples by cyclic voltammetry.

2. Experimental

2.1. Reagents

Multi-walled carbon nanotubes (MWCNTs) were obtained from NanoLab (USA). Pyrimethanil, aniline and β-cyclodextrin (β-CD) were supplied by Sigma–Aldrich Química (Sintra, Portugal). All other chemicals and reagents (Sigma–Aldrich Química) employed were of analytical grade and were used as received without any further purification.

All solutions were prepared with deionised water (Milli-Q-50 18 MΩ cm). Buffer solutions employed for voltammetric determinations were 0.1 mol L^{-1} in the pH range 3–9.

HPLC–grade methanol was supplied by Carlo Erba. The solvents were filtered through a 0.45–μm filter before use.

2.2. Apparatus

Voltammetric experiments were performed using an Autolab PGSTAT 12 potentiostat/galvanostat (Metrohm Autolab, Netherlands). All measurements were conducted in a one-compartment glass electrochemical cell equipped with a three-electrode system arrangement. The working electrode used was a bare or a modified glassy carbon electrode (GCE, d = 2 mm), the counter electrode was a platinum wire, with a saturated Ag/AgCl reference electrode completing the circuit. All measurements were carried out at room temperature.

The pH measurements were performed using a Crison pH-meter (Crison, Spain) equipped with a glass electrode.

HPLC analysis (Navickiene & Ribeiro, 2004) was performed using a Shimadzu LC-20AD Prominence Liquid Chromatograph (Shimadzu, Tokyo, Japan) with a diode array detector (SPD-M20A). Separation was performed on a prepacked Nucleosil 100-5 C18, analytical column (250 mm × 4.6 mm, 5 μm, Macherey–Nagel, Duren, Germany) and the mobile phase consisted of methanol–water (70:30, v/v). It was delivered isocratically at 1 mL min^{-1} at room temperature.

The chromatographic data was processed using the software package LabSolutions (Shimadzu, Japan).

2.3. Preparation of MWCNT modified GCE

The preparation and characterization of the PANI-β-CD/fMWCNT modified GCE has been previously described (Rahemi et al., 2012). Briefly, two milligrams of (–COOH) functionalised MWCNT (fMWCNT) was dispersed by using ultrasonic agitation in 1 mL aqueous β-CD solution (2%) to give a 2 mg mL^{-1} black suspension. Before surface modification, the 2 mm bare GCE was carefully polished to a mirror finish with an aqueous slurry of alumina powder (BDH Chemicals, VWR, USA) on a microcloth pad and then ultrasonically cleaned in ultra-pure water and ethanol alternately to remove traces of alumina and possible contaminants. Subsequently, a solution of aniline (0.011 mol L^{-1}) was electropolymerized on the cleaned GCE, in a sulphuric acid aqueous solution (0.025 mol L^{-1}), sweeping the potential between −0.1 V and 1.0 V vs. Ag/AgCl at a scan rate of 50 mV s^{-1} for 50 cycles. After preparation of the polyaniline film on the GC electrode surface, an aliquot of 6 μL (2 mg mL^{-1}) of the MWCNT or fMWCNT dispersion was drop cast onto the GCE surface and dried in air at ambient temperature. Finally, the surface of the PANI-β-CD/MWCNT modified GCE was gently washed with water to remove the loosely attached β-CD/MWCNT.

The PANI-β-CD/fMWCNT film coated GC sensor was activated in acetate buffer solution (pH 4.0) by cyclic voltammetric sweeps between +0.5 and + 1.3 V vs Ag/AgCl until stable cyclic voltammograms were obtained.

For the cleaning of the PANI-β-CD/fMWCNT film coated GC sensor, successive cyclic voltammetric sweeps in 0.1 mol L^{-1} acetate buffer (pH 4.0) solution were performed until unchanged cyclic voltammograms were obtained (six cycles).

2.4. Analytical determination of pyrimethanil

2.4.1. Calibration

A 10 mM stock standard solution of pyrimethanil was prepared in ethanol. Standard solutions used to establish the calibration curve were prepared directly in the voltammetric cell by adding accurate volumes of the stock standard solution to the selected acetate buffer pH 4.0 supporting electrolyte solution in order to obtain concentrations between 10 and 80 μM. Calibration curves were obtained by plotting the peak current vs. pyrimethanil concentration.

The limit of detection (LOD) was calculated according to IUPAC recommendations (Mocak, Bond, Mitchell, & Scollary, 1997), using an S/N ratio of three. Method precision was checked on different days, within day ($n = 5$) and between days ($n = 5$) for three different concentrations.

The accuracy of the proposed method was determined by recovery assays and by comparing the results with those obtained from a previously published HPLC method (Navickiene & Ribeiro, 2004).

The selectivity of the sensor was investigated by assessing its response to pyrimethanil in apple samples spiked with increasing amounts of other fungicides commonly found in plant protection products containing PYR, as well as with 2-amino-4,6-dimethylpyrimidine, the major PYR environmental degradation product. The current responses obtained from the analysis of PYR without and with the addition of the potentially interfering compounds were compared.

2.4.2. Recovery assays

An apple sample was obtained at a local market. A representative portion of the sample was chopped in a food chopper and 100 g portions were stored in closed containers in a freezer. A 10 g portion of apple sample was weighed, spiked with PYR fungicide and mixed and homogenized using an ultrasonic bath for 15 min. Then 10 mL ethyl acetate-*n*-hexane (50:50 v/v) and 2 g of sodium chloride were added and homogenized for 30 min. The resulting suspension was filtered and evaporated to dryness using a Buchi rotavapor. The residue obtained was redissolved in methanol (HPLC) or ethanol (PANI-β-CD/MWCNT modified GCE) and analysed.

3. Results and discussion

3.1. Electrochemical behaviour of pyrimethanil

Cyclic voltammetry was employed for investigation of the electrochemical properties of pyrimethanil on the bare GC electrode and PANI-β-CD/fMWCNT electrode. The potential was scanned from +0.75 to +1.25 V vs Ag/AgCl in 0.1 mol L^{-1} acetate buffer solution (pH 4.0), containing 40 μM of pyrimethanil. Fig. 1 shows the CV response obtained using a scan rate of 20 mV s^{-1} at a bare GC electrode and PANI-β-CD/fMWCNT. At the bare GC electrode, a weak and broad oxidation peak is obtained for pyrimethanil at 0.99 V. At the PANI-β-CD/fMWCNT, the electrochemical response increased significantly, occurring at a less positive potential of 0.95 V. In both cases the results showed no reduction peak was observed in the reverse scan suggesting that the electrochemical reaction was an irreversible process.

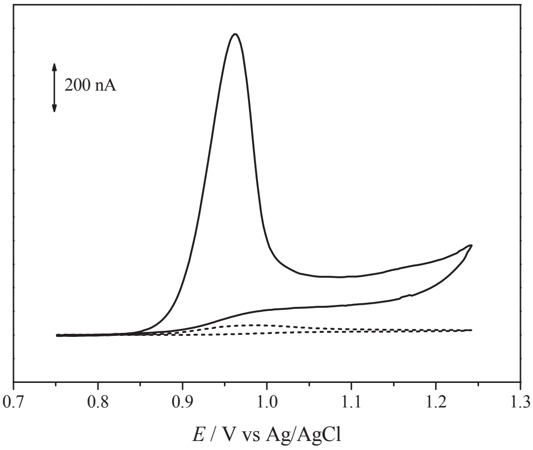


Fig. 1. Cyclic voltammograms of 40 μM solutions of pyrimethanil at (●●●) GC electrode and (–) PANI-β-CD/fMWCNT/GCE in pH 4.0 acetate buffer electrolyte. Scan rate: 20 mV s^{-1}.

The signal amplification observed can be attributed to the higher available surface area provided by MWCNT. Furthermore, the presence of β-CD in the PANI/MWCNT film-modified electrode can promote the formation of an inclusion complex between β-CD and pyrimethanil. The ability of β-CD to form an inclusion complex with pyrimethanil can lead to a signal enhancement due to the higher concentration of pyrimethanil at the PANI-β-CD/fMWCNT film electrode surface. The pyrimethanil-β-CD complex in the PANI-β-CD/MWCNT film would then dissociate and diffuse rapidly through the porous layer of MWCNT to the GC surface, promoting the electrochemical reaction of pyrimethanil.

3.2. Effect of pH and scan rate

Cyclic voltammograms of pyrimethanil in different pH electrolytes were recorded at the PANI-β-CD/fMWCNT electrode. Fig. 2 shows the effect of pH on the anodic peak potential, E_{pa}, of pyrimethanil at the PANI-β-CD/fMWCNT electrode. The E_{pa} vs pH plot shows that the peak potential is dependent on pH in the interval investigated, from 3.1 to 8.0. The oxidation peak shifted negatively as pH increased indicating that protons participate in the electrode reaction. The slope of the dotted line, ca. 57 mV per pH unit, shows that the mechanism of this oxidation process in aqueous media involves the same number of electrons and protons. The

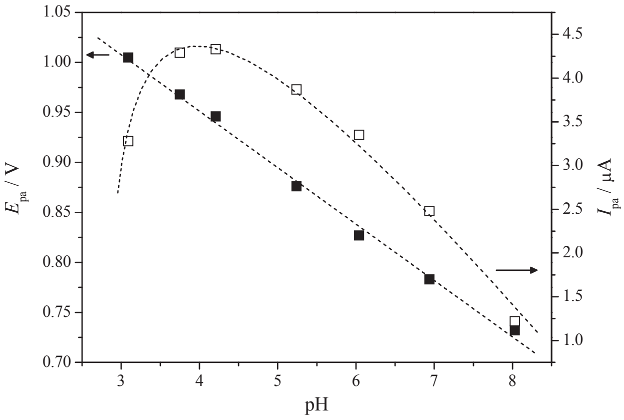


Fig. 2. Plot of anodic peak potential, E_{pa} (filled symbols) and anodic peak current, I_{pa} (open symbols) vs. pH from cyclic voltammograms of 40 μM solutions of pyrimethanil at PANI-β-CD/fMWCNT film electrode in different buffer electrolytes as a function of pH. Scan rate: 20 mV s^{-1}.

voltammetric behaviour observed is consistent with the oxidation mechanism suggested in the literature for aniline derivatives. The primary intermediate formed by one-electron abstraction is the cation radical which can undergo either dimerization or deprotonation (Hammerich & Lund, 2000). The predominant coupling is tail-to-tail coupling that results in the formation of benzidine derivatives (Scheme 2) (Jaworski & Kalinowski, 2007).

The effect of electrolyte pH on the current response of pyrimethanil at the PANI-β-CD/fMWCNT electrode was also investigated. A plot of anodic peak current, I_{pa}, vs. pH shows that the highest peak current is obtained around pH 4 (Fig. 2). Therefore, acetate buffer pH 4.0 was chosen for subsequent analytical experiments.

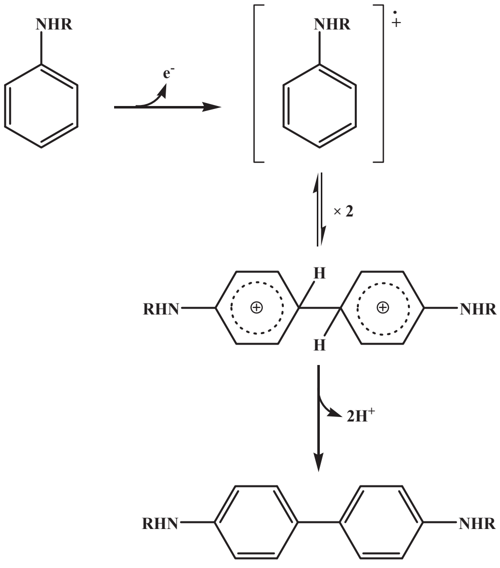
Important information concerning the electrochemical mechanism can be obtained from the relationship between peak current and scan rate. Cyclic voltammograms of pyrimethanil at different scan rates were recorded at the PANI-β-CD/fMWCNT electrode in pH 4.0 acetate buffer solution. A linear relationship was observed between the peak current and the square root of scan rate in the range 10–120 mV s^{-1}, which revealed that the electrode reaction mechanism of pyrimethanil is a diffusion-controlled process. Further evidence that there are no effects from adsorption of the electroactive species was obtained by immersing the PANI-β-CD/fMWCNT film electrode at open circuit in solutions of 40 μM pyrimethanil in pH 4 buffer solution. No significant changes to the anodic peak current corresponding to pyrimethanil oxidation were observed after 1 min accumulation.

3.3. *Pyrimethanil quantification*

Cyclic voltammetry experiments, using the developed PANI-β-CD/fMWCNT film electrode, were carried out in triplicate, with the optimized experimental parameters, in order to construct an analytical curve for the determination of pyrimethanil.

Linear calibration plots with a sensitivity of 0.158 ± 0.012 A M^{-1} were obtained for PYR concentrations ranging from 10 to 80 μM (Fig. 3). A limit of detection (LOD) of 1.04 μM (0.21 mg/kg) was calculated using the 3 S/N ratio, as recommended by IUPAC (Mocak et al., 1997).

Postharvest disease is one of the most important constraints that affects fresh fruit quality and marketing values. PYR has been shown to be an effective fungicide for postharvest management of both blue and grey mould decay of apples, and of citrus green mould (Sholberg et al., 2005; Smilanick, Mansour, Gabler, & Goodwine, 2006). The maximum residue levels (MRLs) set for PYR in pome fruit and citrus fruit are 7 mg/kg and 8 mg/kg, respectively (Commission Regulation (EU), 2014). Thus, the LOD calculated is adequate for the method to be used for residue monitoring purposes in these fruits, considering the established MRLs. No other study regarding PYR quantification based on electrochemical (bio)sensors has been reported so far.



Scheme 2. Proposed mechanism for the electrochemical oxidation of pyrimethanil.

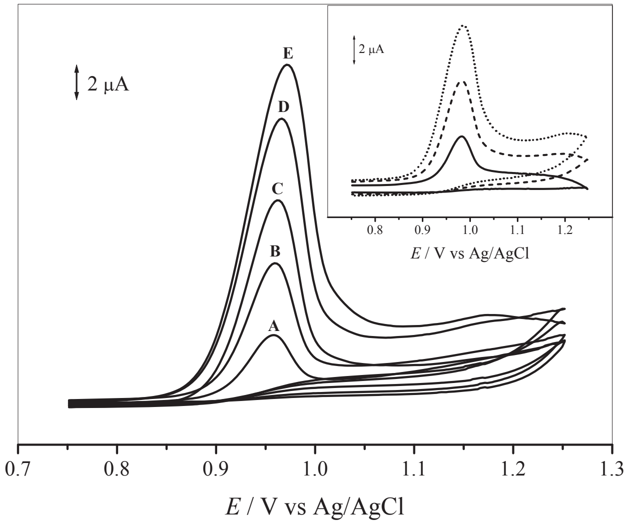


Fig. 3. Cyclic voltammograms of pyrimethanil standard solutions with concentrations of: (A) 10, (B) 20, (C) 40, (D) 60 and (E) 80 μM at PANI-β-CD/fMWCNT film electrode in pH 4.0 acetate buffer electrolyte. Inset: Cyclic voltammograms obtained for the determination of PYR at concentrations of 2, 8 and 16 mg/kg in spiked apple samples. Scan rate: 20 mV s^{-1}.

The intra-day repeatability and the reproducibility of the method were evaluated by repeatedly ($n = 5$) measuring pyrimethanil, at three concentrations (10, 40 and 80 μM) on the same day and over five consecutive days. RSD maximum values of 1.8 and 2.4% were found for repeatability and the reproducibility, respectively.

The developed sensor was used for the quantification of pyrimethanil in apple samples acquired locally. The accuracy of the proposed methodology was evaluated by recovery assays performed at three spiking levels (2, 8 and 16 mg/kg) by the standard addition method (Fig. 3, inset). Recoveries between 97.1% and 104.0% of PYR from apple samples were achieved (Table 1).

The accuracy of the proposed voltammetric method was assessed by comparing the results found with those obtained using a previously-published chromatographic procedure (Navickiene and Ribeiro, 2004). Five independent measurements were carried out, for both the CV and HPLC methods. These results, summarised in Table 1, show that the data from the CV method agree well with those from chromatography. The *F*- and *t*-test yielded no significant differences between the HPLC and the proposed analytical method at a 95% confidence level. Both methodologies have comparable precision and accuracy. However, the PANI-β-CD/fMWCNT film electrode proposed here makes possible the simple determination of PYR in a short time and at a lower cost.

3.4. *Operational lifetime and selectivity*

The stability of the PANI-β-CD/fMWCNT/GC modified electrode was assessed over a 5-day period. After this period of time, the sensor exhibited ca. 93% of its initial response.

To investigate the effects of common interfering substances on the determination of pyrimethanil (8 mg/kg) in apple samples with

Table 1
Results obtained for the analysis of pyrimethanil (PYR) in spiked apple samples using the proposed cyclic voltammetric method and HPLC.

Method	PYR added (mg/kg)	PYR found (mg/kg)[a]	Recovery (%)	RSD (%)	*t*-test[b]	*F*-test[b]
CV	2.0	2.08	104.0	3.2	0.09	2.48
	8.0	7.77	97.1	1.8	0.15	0.49
	16.0	15.9	99.2	2.8	0.64	1.33
HPLC	2.0	2.10	105.0	1.3		
	8.0	7.72	96.5	0.9		
	16.0	16.3	101.9	2.1		

[a] Average of five replicate measurements.
[b] Tabulated *t*- and *F*- values, at $P = 0.05$, are 2.31 and 6.39, respectively.

Table 2
Influence of interfering substance on anodic peak current for PYR determination at PANI-β-CD/fMWCNT film electrode in pH 4.0 acetate buffer electrolyte, concentration of PYR 8 mg/kg, 1:1 mass ratio PYR:interferent, expressed as percentage change in response.

Interferent	Change in current response (%)
Ca^{2+}	+1.2
Mg^{2+}	−1.1
NO_3^-	−2.1
PO_4^{3-}	+3.2
Fluquinconazole	+4.1
2-Amino-4,6-dimethylpyrimidine	−4.6

the use of the new sensing platform, controlled amounts of the interfering substances were added individually. Different amounts of Ca^{2+}, Mg^{2+}, NO_3^-, PO_4^{3-}, fluquinconazole, a fungicide commonly found in plant protection products containing PYR, and 2-amino-4,6-dimethylpyrimidine, the PYR major environmental degradation product, were investigated for possible interferences. At mass ratios of 1:1, no significant interference was observed (signal change less than 5%) (Table 2).

The easy preparation, good repeatability and reproducibility, high stability, and short analysis time for the sensor developed in this work are clearly important characteristics for analytical purposes and fully demonstrate its usefulness.

4. Conclusions

A novel approach for quantification of fungicide pyrimethanil in fruit samples was developed, based on the use of a PANI-β-CD/fMWCNT/GC modified electrode.

The PANI-β-CD/fMWCNT/GC film displayed a good electroanalytical performance for PYR quantification in apples, with high sensitivity, linearity, accuracy, repeatability, reproducibility and stability. Since the PANI-β-CD/fMWCNT/GC film is easy to prepare and inexpensive, it represents an interesting alternative for food safety screening purposes, complementing or even replacing the established chromatographic procedures and allowing a faster estimation of fungicide residues. The results obtained by the proposed electroanalytical methodology for PYR in apple samples were in excellent agreement with those obtained using the HPLC procedure.

The combination of host–guest electrostatic interactions with the catalytic and electronic properties of MWCNT embodies a new approach towards constructing electrodes for the quantification of pesticides in foods.

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