



Nano carbon black-based screen printed sensor for carbofuran, isoprocarb, carbaryl and fenobucarb detection: application to grain samples



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ABSTRACT

An electrochemical screening assay for the detection of phenyl carbamates (i.e. carbaryl, carbofuran, isoprocarb and fenobucarb) was developed and applied to grains samples (i.e. durum wheat, soft wheat and maize). Nano carbon black (CB) was strategically employed to realize an effective, reproducible, fouling resistant, low cost, delocalisable screen printed sensor (CB-SPE). CB-SPEs morphology (SEM and FEM) and electrochemical property (CV and EIS) were studied. The final pesticides analysis protocol consist of: (i) extraction of the analyte (just by mixing), (ii) alkaline hydrolysis (10 min R.T.), (iii) DPV detection directly of 100 μL of extract on the CB-SPE surface. Linear range between 1.0×10^{-7} and 1.0×10^{-4} mol L^{-1} , good determination coefficients ($R^2 \geq 0.9971$) and satisfactory sensitivity ($\geq 3.90 \times 10^{-1}$ $\text{A M}^{-1} \text{cm}^{-2}$) and LODs ($\leq 8.0 \times 10^{-8}$ mol L^{-1}) were obtained for all the analytes. Excellent recoveries (78–102%) and accuracy (relative error vs. HPLC-MS/MS between 9.0% and -7.8%) resulted from the analysis of grains samples. The proposed CB-SPE based approach has demonstrated to be able to detect carbaryl at Maximum residue limits levels (MRLs), allowing class selective detection of commonly employed phenyl carbamates in food samples.

1. Introduction

Globalization, abatement of borders and the dislocation of productions have revolutionized the foodstuff trade, making more challenging the food safety control and monitoring. At the same time, the use of pesticides has improved crop yields and preservation of agricultural products, nevertheless contributing to food and environment contamination [1]. Indeed, the use of pesticides is a controversial issue, due to their known ability to cause a large number of negative health and environmental effects [2] and for the non-harmonised policies for regulation among nations [3]. The use of pesticides in cereals is widely reported, and the trend in the use is expected to increase substantially in the next few decades [1,4]. Among pesticides, carbamates are widely used in grains. Carbamates exposure have been associated with endocrine-disrupting activity, reproductive disorders, negative effects on cellular metabolic mechanisms and mitochondrial function [2]. Moreover, carbamates result to be cytotoxic and genotoxic, and there are evidence of increased risk for dementia, and non-Hodgkin's lymphoma [2,5]; they can also induce immunotoxicity [6]. Hence, the accessibility of analytical methods for the detection and quantification of these compounds, both for environmental and food safety control, is highly required. In recent years, chromatography coupled to mass

spectrometry have represented the most employed technique for pesticides analysis in food [7,8], as well as in grains [9,10]. However, despite the high performance of these techniques, they are often associated to various limitations as: time consumption, laboriousness, requirement of expensive equipments and highly trained technicians, etc [11]; moreover they require accurate extraction and clean up steps [12]. For this reasons, there is the need for complementary, easy to use, screening techniques [13]. The past two decades have been dominated by bio-sensors advancements [13–15] and, more recently, nanotechnology have become active part of several (bio)sensors and (bio) assay formats also for the detection of pesticides [11,16–20]. Recently, different strategies were proposed for the carbamates direct detection exploiting nanomaterials modified electrodes. Carbaryl detection was achieved employing glassy carbon (GCE) electrodes modified with MWCNTs/ cobalt phthalocyanine [21] and graphene oxide-ionic liquid composite [22] in natural water and fruit samples, respectively. The same analyte was also analyzed in tomato samples with a low silica X zeolite modified carbon paste electrode (CPE) [23], and using a graphene-modified boron-doped diamond electrode, in this case in apple juice [24]. A molecularly imprinted polymer reduced graphene oxide and gold nanoparticles modified GCE electrode was employed for carbofuran detection in vegetable samples [25]. Carbofuran and carbaryl

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in fruit and vegetable samples were also determined using a GCE electrode (CoO)-decorated with reduced graphene oxide [26]. During the “graphene epoch”, another material appeared in the sensor scene: nano carbon black (CB). The CB nanospheres exhibit excellent conductivity, unique electrochemical properties, extreme ease of use and cost-effectiveness (about 1 euro/kg). Recently, several works have been reported on the CB based sensors development; different strategies have been employed to construct sensors and biosensors [16,20,27], and different new devices [28–30] have been proposed and exploited for several application [20,29,31–34]. Despite the different approaches employed the CB exhibited in all cases remarkable proprieties in sensor improvements, proving to be a ductile and useful nanomaterial.

In this work, an electrochemical multianalyte screening method for the detection of carbaryl, carbofuran, isoprocarb and fenobucarb was developed and applied to maize, hard and soft wheat samples. A nanosphere CB modification of screen printed electrode (SPE) was strategically employed, optimized and characterized, in order to increase the sensitivity, selectivity and to reduce the fouling of the sensor. The sample extraction was optimized in order to obtain satisfactory recovery with the minimum treatment. The final analysis protocol resulting consist of: (i) extraction of the analyte (just by mixing), (ii) alkaline hydrolysis (10 min at room temperature), (iii) DPV detection (performed directly placing 100 μL of extract on the electrode surface). The data were compared with UHPLC-MS/MS. The proposed assay results to be quick, user friendly with a minimal waste production and able to be used in delocalized analysis.

2. Materials and methods

2.1. Chemicals and solutions

Carbamates standards: carbaryl, carbofuran, isoprocarb, and fenobucarb and their respective hydrolysed form 1-naphthol, 2,3-dihydro-2,2-dimethyl-7-hydroxy benzofuran, 2-isopropylphenol, 2-sec-butylphenol were purchased from Sigma Aldrich (St Louis, MO, USA). Disodium hydrogen phosphate anhydrous, sodium dihydrogen phosphate hydrate, sodium acetate, potassium ferrocyanide, potassium ferricyanide, potassium chloride, methanol, acetonitrile and N,N-dimethylformamide were purchased from Sigma from Sigma Aldrich (St Louis, MO, USA). CB N220 was obtained from Cabot Corporation (Ravenna, Italy). Stock solutions of carbamates standards and their hydrolysed forms were prepared at a concentration of 1.0×10^{-2} mol L⁻¹ in methanol and stored at -18°C in the dark. Milli-Q water (Millipore, Bedford, MA, USA) was used for all the experiments.

2.2. Samples

Wheat and maize samples were purchased in a local mills consortium (Cereal Abruzzo S.r.l., Mosciano S. Angelo, TE, Italy), different samples were used: durum wheat (HW), organic durum wheat (HWO), soft wheat (SW), organic soft wheat (SWO) and maize (MZ).

2.3. Apparatus and measurements

All electrochemical measurements were performed, on a portable PalmSens 4 Potentiostat / Galvanostat / Impedance Analyzer (Palm Instruments BV, Houten, Netherlands) using commercial screen printed electrodes (Dropsens C110) having a carbon working electrode of 4 mm in diameter. Structure and morphology of the CB nanospheres, as well as surface coverage of the electrodes were analyzed by high resolution scanning electron microscopy (HR-SEM) using a Hitachi S3000N (Hitachi, Japan). Sample shaking was carried out by a SSL1 orbital shaker from Stuart equipment (Belfast, UK). Pesticides were chromatographically determined by UHPLC Nexera LC20AD XR from Shimadzu (Kyoto, Japan) using a Kinetex XB-C18 column (100×2.1 mm) packed with core-shell 1.7 μm particles (Torrance, CA,

USA). Identification and quantification were carried using a triple quadrupole mass spectrometer 4500 Sciex Qtrap (Toronto, ON, Canada).

2.4. Preparation of the modified SPE electrodes

CB dispersion volume, concentration and solvent were optimized in order to obtain the most effective electrodes in terms of sensitivity and reproducibility. The final SPE modification was obtained employing 1.0 mg mL⁻¹ CB dispersed in DMF:H₂O 1:1 (v/v). CB was dispersed in an ultrasonication bath for 60 min to obtain a CB nanospheres suspension, then the electrode was modified by drop casting 10 μL and allowing drying and solvent evaporation.

2.5. SPE electrochemical characterization

Electroactive area and heterogeneous transfer constant calculation were performed by cyclic voltammetry (CV) using 1 mmol L⁻¹ ferricyanide solution K₃[Fe(CN)₆] in 0.1 mol L⁻¹ KCl. Effective electrodes working area (A) were determined from the slopes of the I_p vs v^{1/2} graphs using the Randles-Sevcik equation. To this aim 1 mmol L⁻¹ K₃[Fe(CN)₆] CV at scan rates of at 5, 10, 25, 50, 75, 100, 150 and 200 mV s⁻¹ were recorded and diffusion coefficient (D) of 7.603×10^{-6} cm² s⁻² was used [35,36]. The Nicholson method [37] was used to calculate the heterogeneous rate constants (k^0) considering α equal to 0.5 and I_{pa}/I_{pc} close to unity. Electrochemical impedance spectroscopy (EIS) was carried out using 5 mmol L⁻¹ Fe(CN)₆^{4-/3-} in 0.1 M KCl. Nyquist plots ($-Z_{re}$ vs. Z_{im}) were employed to analyze the impedance results, obtained using a sinusoidal wave with amplitude of ± 10 mV in the frequency range 10^{-2} – 10^5 Hz at open circuit potential.

2.6. CV and DPV of the pesticides

CVs and DPV were used for the electrochemical sensing of the target pesticides hydrolysed form, the measurements were carried out by depositing 100 μL of the analytes solution on the sensor surface. CVs of pesticides hydrolysed form were performed individually and in mixture, with a scan rate of 0.050 V s⁻¹ in the potential range of -0.50 V and $+0.80$ V (vs. pseudo Ag/AgCl) at different pHs: 9.0 and 7.0 in phosphate buffer (0.01 mol L⁻¹) and at pH 4.5 in acetate buffer (0.01 mol L⁻¹). DPVs of the analytes were performed individually and in mixture, employing different amounts (10%, 20% and 30%) of acetonitrile and methanol. The simplex method was used for the optimization of the DPV conditions, with the final aim to maximize the sensitivity. The DPV were performed in the potential range of 0 to $+0.6$ V with a pulse width of 50 ms, and the final DPV pulse amplitude and scan rate were 20 mV and 50 mV s⁻¹, respectively. DPV of the sample extracts were performed after the extraction/hydrolysis step described in Section 2.7.

2.7. Pesticides extraction-hydrolysis / recovery studies

One gram of grain sample was weighed into a 15-mL Falcon flask, and 2.5 mL of extracting solution (MeOH) was added. The mixture was stirred (with an orbital shaker) at room temperature for 15 min. The supernatant was collected by a syringe and filtered with a phenex PTFE syringe filter (0.2 μm pore size). Before the CB-SPE DPV analysis, hydrolysis of the CMs was carried out on 100 μL of the extract by addition of 100 μL of NaOH to a final concentration of 60 mmol L⁻¹. Reaction was carried out for 10 min at room temperature under stirring. The resulting extract was brought to a final volume of 1 mL with 800 μL of 30 mmol L⁻¹ NaH₂PO₄. The pH of the solution was ≈ 7.0 . In order to study the effectiveness of the extraction procedure, 1 g of each blank sample was weighed and spiked with the appropriate amount of pesticide standard solution, to reach a final concentration of 0.25, 0.50 and 0.75 mg L⁻¹. After 24 h, the samples and the unfortified blank samples

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