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Talanta

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Separation of a binary mixture of pesticides in fruits using a flow-through optosensor

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ARTICLE INFO

Article history:

Received 13 February 2013

Received in revised form

31 May 2013

Accepted 6 June 2013

Available online 14 June 2013

Keywords:

SIA

Automation

Plaguicide

MRL

On-line separation

ABSTRACT

A flow-through optosensor is here proposed for the determination of mixtures of two widely used pesticides, carbendazim and *o*-phenylphenol, in fruits. The pesticides are separated on-line using an additional amount of solid support, C_{18} silica gel, in the flow-through cell. The resolution is performed due to the different retention/desorption kinetics of the analytes when interacting with the C_{18} microbeads. Therefore, both separation and determination are integrated in the same cell, considerably simplifying the system. In addition, the use of Sequential Injection Analysis provides a high degree of automation and minimum wastes generation. After the analytes are separated, their native fluorescence is measured, obtaining linearity in the 2.0–30 and 1.1–20 $mg\ kg^{-1}$ ranges for carbendazim and *o*-phenylphenol. The detection limits are 0.60 and 0.33 $mg\ kg^{-1}$ for carbendazim and *o*-phenylphenol respectively. The proposed method fulfills the maximum residue limits (MRLs) established in Europe and USA for these pesticides in cherries, pineapple, and mango: 5–10 $mg\ kg^{-1}$. In order to demonstrate the suitability of the method, several samples have been analyzed and the obtained results compared with a chromatographic method.

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1. Introduction

In the last years, the detection of environmental hazardous chemicals has been rising in demand. Pesticides (herbicides, fungicides or insecticides) are substances intended for preventing, destroying, repelling or mitigating any pest. Their worldwide use can lead to their accumulation in soil, water, atmosphere, and agricultural products, and they can therefore exist in harmful levels, posing an environmental threat. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species [1]. As a result, the development of new analytical methods for the determination of these compounds in a wide variety of samples is today a high-interest research area.

Carbendazim (CBZ) and *o*-phenylphenol (OPP) are two widely used fungicides, mainly used for the post-harvest treatment of fruits and vegetables. Hence many analytical methodologies have been described for their reliable determination in a wide range of matrices. Modern analytical methods for their quantitation usually involve liquid chromatography [2–8] or gas chromatography [9–11] coupled to mass spectrometry detection. These methodologies present unique outstanding properties for multi-residue analysis in complex matrices, due to their high sensitivity and

selectivity. In recent years, optical [12,13] and electrochemical [14,15] methods have also been utilized for the analysis of CBZ. Compared to chromatography, these methods focus in only a small number of analytes and specific applications. Among them, the design of flow-based analytical methods is a field of special interest due to their intrinsic favorable characteristics, especially their low-cost and low wastes generation [16,17]. In order to improve other features of flow methods, such as sensitivity and selectivity, a possible modification is the implementation of Solid-Phase Spectroscopy (SPS) in flow analysis, which is called flow-through optosensing. In these systems, the target compound is retained on an appropriate solid support, placed in the flow-through cell, and its detection is performed directly on these microbeads, therefore improving the selectivity and sensitivity [16,18,19].

A high percentage of the flow optosensors described in scientific literature have focused in the analysis of pharmaceuticals and water samples [20–22], although that tendency has changed in the last few years, observing applications in the alimentary field for both contaminants and natural compounds [23–25]. Although multi-parametric sensors have been previously described [26–29], they have been mainly applied to the determination of the target compounds in clinical or water samples, and very rarely in food products [24].

In this manuscript we present a bi-parameter flow-through optosensor for the determination of two widely used pesticides,

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carbendazim (CBZ) and *o*-phenylphenol (OPP), in fruits. The most common strategy for the on-line separation of the analytes in the flow-system consists in using a mini-column filled with the same solid support used in the flow-through cell and placed just before the cell [24,26,28,30]. In addition, a less used approach consists in using an extra amount of solid support in the flow-cell [27,31]. In both cases, the separation of the analytes is achieved due to their differences in the sorption/elution process on the solid support microbeads. However, performing the separation directly in the flow-cell clearly simplifies the flow manifold and has been the selected strategy in this work. This is the first time that a bi-parameter flow-through optosensor, separating the analytes without using a pre-column, is described with applications in the alimentary field.

Sequential Injection Analysis (SIA) has been chosen as the flow methodology, increasing the automation and robustness of the developed method. Using QuEChERS [32] as the extraction procedure, CBZ and OPP can be fluorimetrically detected after their on-line separation. The proposed method fulfills the maximum residue limits (MRLs) established in Europe and USA for these pesticides in cherries, pineapple and mango: 5–10 mg kg⁻¹ [33,34]. In addition no matrix-effect has been observed, therefore avoiding the use of matrix-matched standards for the proposed applications.

2. Experimental

2.1. Reagents and solutions

CBZ and OPP (Sigma, Alcobendas, Madrid, Spain) stock solutions of 100 µg mL⁻¹ were prepared by weighing the appropriate amount of analyte and dissolving in methanol (MeOH). The solutions remained stable for at least 1 month when kept away from light at about 4 °C. These stock solutions were used to prepare the working standard solutions by suitable dilution with deionized water.

MeOH, sodium chloride and anhydrous magnesium sulfate were obtained from Panreac (Barcelona, Spain); all of them were reagent grade. Ammonia and acetonitrile (HPLC grade) were obtained from Sigma. Primary-secondary amine (PSA) (Supelclean PSA SPE bulk packing) was obtained from Supelco (Bellefonte, PA, USA). C₁₈ bonded phase silica gel beads (Waters, Milford, USA) with 55–105 µm of average particle size, were used as solid support. All the pesticides used in the interference study were obtained from Sigma.

2.2. Apparatus and instruments

A FIALab-3500 automatic analyzer (FIALab Instruments, Inc., the USA) was used to construct the manifold (Fig. 1). The analyzer includes two 5-mL syringe pumps, a holding coil, a peristaltic pump and an 8-port multiposition valve, being all the components computer-controlled by FIALab 5.0 software. The analyzer was connected to a Cary-Eclipse Luminescence Spectrometer (Varian Inc., Mulgrave, Australia) for luminescence measurements. A Hellma flow cell 176.052-QS (25 µL inner volume and 1.5 mm light path length) was used. The cell was filled with C₁₈ solid support microbeads, as slurry suspension in methanol, with the aid of the peristaltic pump. The outlet of the cell was blocked with glass wool, avoiding the movement of the solid support but allowing the flow of solutions. An additional amount of solid support was used in the cell as a strategy to separate the analytes, just above the detection area. The manifold is shown in Fig. 1, representing only the components of the FIALab that have been used in the method, for simplicity's sake.

A T18-basic Ultra-Turrax from IKA (Spain) was used for the homogenization of the analyzed samples.

An HPLC method was selected as reference method. CBZ and OPP separation was carried out using an HPLC system (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA), consisting of vacuum degasser, autosampler, and a binary pump. A reversed phase C₁₈ analytical column of 50 × 2.1 mm² and 2.6 µm particle size (Kinetex, Phenomenex) was used for the separation, at ambient temperature. Mobile phases A and B were water with 0.1% formic acid (v/v) and acetonitrile, respectively. A linear gradient from 10% B to 70% B in 15 min was used, with a flow-rate of 0.35 mL min⁻¹. The HPLC system was connected to an ion trap mass spectrometer (Esquire 6000, Bruker Daltonics, Billerica, MA, USA) equipped with an electrospray interface. CBZ was determined in positive-ion mode, [M+H]⁺ at *m/z* 192 with a fragment at *m/z* 160. OPP was determined in negative-ion mode, [M-H]⁻ at *m/z* 169.

2.3. Sample treatment

The QuEChERS method [32] was selected for the extraction of CBZ and OPP from the selected samples (cherries, pineapple and mango), being all of them obtained from local markets.

An Ultra-Turrax was used for sample homogenization. Pineapples were peeled before being ground, stones were removed from mangos before grinding them, and cherries were directly ground.

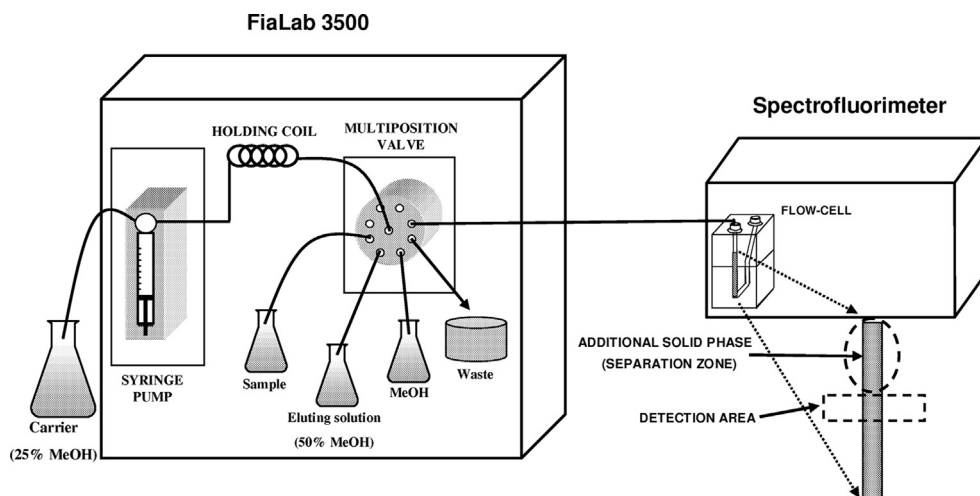


Fig. 1. SIA manifold.

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