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Development of an semi-automatic and sensitive photochemically induced fluorescence sensor for the determination of thiamethoxam in vegetables



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ABSTRACT

The determination of thiamethoxam (TMX), a widely known neonicotinoid pesticide, by a multi-commutated optosensing device implemented with photochemically induced fluorescence (PIF) has been developed. The combination of both methodologies allows, on one hand a quick on-line photo-degradation of TMX and, on the other hand, the preconcentration, quantification and desorption of the fluorescent photoproduct generated once retained on C₁₈ silica gel filling the flow-cell which was monitored at 353 and 407 nm for excitation and emission wavelengths, respectively.

The proposed analytical method presents a detection limit of 3.6 ng mL⁻¹ by using Multicommuted Flow Injection Analysis (MCFA) as flow methodology. Recovery experiments have been carried out in different kinds of vegetables at levels same or below the legislated maximum residue limit, demonstrating that this method combines advantages such as simplicity, high sensibility and high selectivity, in addition to fulfill the requirements for its applications in quality control. The obtained results in the analysis of real samples were in good agreement with those provided by a reference liquid chromatography (HPLC) method.

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1. Introduction

The quality and food safety are, due to a convergence of factors, two of the most important global issues in the food field. Nevertheless, modern agricultural production is highly based on the use of agrochemicals, such as pesticides, applied to crops at various stages of cultivation and during the post-harvest storage. One of these pesticides is thiamethoxam (TMX) which has been widely used in last years. For this reason, the European Union has established its maximum residue limit (MRL) [1] in fruits and vegetables in the 0.05–7 mg kg⁻¹ range, depending upon the type of food crop. Both foods are essentials and play basic roles in a healthful diet, so checking that they are below this range is vital. Specifically, the European Commission proposed to restrict the use of TMX (along with imidacloprid and clothianidin) for a period of 2 years from December 2013 [2]. This is the result of the disappearance of hundreds of millions of bees, a crisis that has been called the problem of colony collapse disorder, and could have been caused by the use of this insecticide, among others [3].

Currently, TMX is typically analyzed by liquid chromatography

(LC) [4–7], gas chromatography (GC) [8,9] and voltammetry [10], but information on residue determinations of TMX in leafy vegetables is very scarce. There is much interest in exploring inexpensive and reliable methods for the determination of TMX, being fluorescence methods a great proposal for these. TMX is not naturally fluorescent, and, therefore, it has to be converted into fluorescent species by a derivatization method. An alternative is the use of photo-induced fluorescence (PIF) which is based on the photochemical transformation of a non-fluorescent or weakly fluorescent analyte into strongly fluorescent photoproduct(s) by using UV irradiation [11–16].

By coupling PIF and Solid Phase Spectrometry (SPS), the selectivity and sensitivity of the method can be increased. The combination of both methodologies allows both photodegradation of TMX and sorption of the fluorescent photoproduct generated on a suitable support placed in a commercial flow cell. Moreover, the implementation of SPS with Flow Injection Analysis (FIA), called Flow Injection-Solid Phase Spectroscopy (FI-SPS), has become a promising research area which is based on the selective on-line retention of the analyte or a derivate on an appropriate solid support and the direct measurement of its light absorption or emission (PIF in this case). Multicommuted Flow Injection Analysis (MCFA) [17–19], which was designed making use of three-way solenoid valves automatically-controlled by a computer with

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home-made software, is a novel and interesting alternative to FIA. MCFIA, in addition to provide better results, has low-cost components, low consumption of reagents, high repeatability and sample throughput, robustness and simplicity of the system.

The objective of the study was the development of an original analytical approach based in the coupling of MCFIA-SPS-PIF methodologies. To our best knowledge, no photochemical reaction has been reported to date for the quantitative determination of TMX. The proposed system was successfully used to analyze this compound in different vegetables samples (spinach, lettuce and peppers). Taking into account that QuEChERS (quick, easy, cheap, effective, rugged and safe) [20] approach represents the most commonly applied extraction method for the determination of pesticide residues in food samples, this one has been used as sample pre-treatment to extract and separate TMX from some interfering substances present in the matrix of the selected applications.

2. Experimental

2.1. Instrumentation

Luminescence measurements were performed with a Cary-Eclipse Luminescence Spectrometer (Varian Inc., Mulgrave, Australia). The spectrometer was connected to a computer with a Cary-Eclipse (Varian) software package for data collection and treatment. Instrument excitation and emission slits were set at 10 and 10 nm, respectively. The detector voltage was 640 V.

A Hellma flow cell 176.752-QS (25 μ L of inner volume and a light path length of 1.5 mm) was used. The cell was filled with C₁₈ silica gel microbeads, and was blocked at the outlet with glass wool to prevent displacement of the resin particles.

MCFIA system was built using a four-channel Gilson Minipuls-3 (Villiers Le Bel, France) peristaltic pump with rate selector and methanol-resistant pump tubes type Solvflex (Elkay Products, Shrewsbury, MA, USA). An electronic interface based on ULN 2803 integrate circuit was employed to generate the electric potential (12 V) and current (100 mA) required to control the four 161T031 NResearch three-way solenoid valves (Neptune Research, MA, USA). The software for controlling the system was written in Java.

A home-made continuous photochemical reactor was constructed by coiling PTFE tubing (180 cm, 0.8 mm i.d.) around a low-pressure mercury lamp (15 W, 254 nm). It was placed into an aluminum box to permit the maximum reflectance of UV light. Since the aluminum foil allowed the heat dissipation, no cooling device was needed and all the experiments were carried out at room temperature.

PTFE tubing and fittings were used for connecting the flow-through cell, the rotary valves and the solutions reservoirs.

A Mili-Q-Plus ultra-pure water system from Millipore (Milford, MA, USA) was used to obtain the HPLC-grade water used during all the experiments. A Sonorex Digital 10 P (Bandelin Electronic, Berlin, Germany) ultrasonic bath, a pH-meter Crison GLP 21 (Crison Instruments, Barcelona, Spain) and a centrifuge Mixtasel-BL (Selecta, Barcelona, Spain) were also used.

For the validation of the proposed method, a high-performance liquid chromatography-ion trap-mass spectrometry (HPLC-ESI-IT-MS) method was used as reference. The HPLC system (consisting of vacuum degasser, autosampler, binary pump and diode array detector) (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA) was equipped with a reversed phase Kinetex core-shell C₁₈ analytical column of 50 \times 2.1 mm and 2.6 μ m particle size (Phenomenex, Torrance, CA, USA). A C₁₈ Security Guard Ultra cartridge (Phenomenex) of 2.1 mm i.d. was also placed before the analytical column. The wavelength range was set at 210–520 nm in the diode

array detector. One microliter of extract was injected in each analytical run. The best separation was achieved by using a mobile phase consisting of methanol–formic acid (100:0.1, v/v) (A) and water–formic acid (100:0.1, v/v) (B). The following gradient program, with a total run time of 16 min, was used: 30% A (0 min), 100% A (8 min) and 30% A (10–16 min). The mobile phase flow rate was 0.25 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 operating in positive ion mode. The identification of TMX was done by using the protonated molecule of TMX ([M+H]⁺, *m/z* 292). For the quantitation and construction of the analytical curve, the product ion at *m/z* 211 was used. The ESI conditions were as follows: capillary voltage 4000 V; nebulizer pressure 40 psi; dry gas 9 L min⁻¹; gas temperature 350 °C. A capillary exit voltage of 50.0 V was set. The instrument was operated in product ion scan MS/MS mode.

2.2. Reagents and solutions

TMX (99.6%) was purchased from Fluka (Sigma-Aldrich, Madrid, Spain). Stock solution of 150 μ g mL⁻¹ of this analyte was prepared in Mili-Q water (Sigma, Madrid, Spain). The solution was kept in dark at about 4 °C. Working solutions were prepared daily by suitable dilution with Mili-Q water.

MeOH, acetonitrile, acetic acid, hydrochloric acid (HCl), anhydrous sodium acetate, sodium hydroxide (NaOH), sodium carbonate 10-hydrate (Na₂CO₃ · 10H₂O), sodium hydrogen carbonate (NaHCO₃), ammonium chloride (NH₄Cl), ammonia (NH₃), graphitized carbon (GCB), primary secondary amine (PSA) and anhydrous magnesium sulfate (MgSO₄) were obtained from Sigma. Sodium Dodecyl Sulfate (SDS) and Triton X-100 were purchased from Panreac (Barcelona, Spain). All of them were analytical reagent grade. Isolute QuEChERS extraction kit was acquired from Biotage (Sweden).

Sephadex-SP C-25 in sodium form, Sephadex-QAE A-25, Sephadex-CM C-25, all of them 40–120 μ m average particle size (Sigma-Aldrich, Buchs, Switzerland) and C₁₈ bonded phase silica gel beads (Waters, Milford, USA) with 55–105 μ m of average particle size, were tested as solid supports.

2.3. Sample treatment

Vegetable samples were obtained from local markets. “Blank” extracts were used to prepare matrix-matched standards for optimization purposes. TMX was analyzed in 2 types of lettuce, spinach, red and green pepper. Before performing the extraction procedure, approximately 500 g of each sample were thoroughly ground, homogenized, and stored at 20 °C until use.

Two types of the QuEChERS extraction procedures were applied. The first one was used for pigmented vegetable samples (peppers and spinach). This one was based on the original QuEChERS extraction method [20] but modified to eliminate the high influence of the extracted pigments [21]. In this method, 10 g of sample were weighed in a 50 mL PTFE centrifuge tube. Acetonitrile (10 mL) was added and the samples were shaken vigorously for 5 min to ensure the solvent interacted adequately with the entire samples. The sample tubes were then stored in a freezer at –20 °C for 20 min, taken out and then vortexed vigorously for 1 min. After that, 4 g MgSO₄ and 1 g NaCl were added, and the samples were vortexed immediately for 1 min. The extracts were then centrifuged for 5 min at relative centrifugal force (RCF) 4000 rpm. Then, a volume of 1.5 mL of prepared aliquot from the upper layer was transferred into a 2 mL centrifuge tube containing an amount of sorbent (10 mg GCB+150 mg MgSO₄ for green pepper and 30 mg GCB+150 mg MgSO₄ for red pepper and spinach). Finally,

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