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Original article

Analysis of insecticide thiacloprid by ion chromatography combined with online photochemical derivatisation and fluorescence detection in water samples

Qamar Subhani [a], Zhong-Ping Huang [a], Zuo-Yi Zhu [a], Lu-Ye Liu [b], Yan Zhu [a,*]

[a] Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, China
[b] Thermofisher Scientific, Shanghai 2012303, China

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ABSTRACT

This study describes a novel application of ion chromatography coupled with post-column photochemically induced fluorimetry derivatisation in alkaline medium and fluorescence detection (IC-*hv*-FD) for the determination of neonicotinoid pesticide, thiacloprid. In an aqueous medium, this compound showed fluorescence with an excitation maximum at 236 nm and an emission maximum at 353 nm. The 10 mmol/L NaOH with 10% (v/v) acetonitrile solution pumped at flow rate of 1.0 mL/min was used for the chromatographic elution to isocratically separate thiacloprid on an Ion Pac® AS 11 (250 mm × 4 mm i.d; 13 μm particle size, Dionex) anion-exchange column. The linear concentration range of application was 0.04–10.0 mg/L, with a relative standard deviation (RSD, $n = 7$) of 1.7% (for a level of 2.0 mg/L) and detection limit (LOD, $S/N = 3$) of 9.9 μg/L. The procedure was applied with satisfactory results to the analysis of thiacloprid in ground and lake water samples. Pesticide average spiked recoveries ranged between 95.5% and 114.0%.

1. Introduction

Thiacloprid, (Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide (Fig. 1), is a second generation neonicotinoid pesticide launched by Bayer Crop Science under the brand name Calypso® in 2000 [1]. It acts as an agonist on the nicotinoid acetylcholine receptor (*n*AChR). The thiacloprid is applied directly to soil or sprayed over crop fields and hence, released directly to the environment; it could cause serious ambient contamination, principally in water, and pose human health risk [2]. Therefore the determination of levels of thiacloprid residues in ground and surface waters are of public interest.

Thiacloprid is unsuitable for the direct analysis by gas chromatography (GC) due to its low volatility and high polarity. High performance liquid chromatography (HPLC) in conjunction with different detectors, such as diode array detector (DAD) [3–6], mass spectroscopy (MS) [7–12] has been used for the determination of neonicotinoid pesticides in water and food. Liquid chromatography (LC) with DAD is restricted by detector unspecificity and insensitivity, and the significant interference from the sample matrices. In addition, HPLC–MS is fairly expensive and may not yet be available as a routine analytical method in a common analytical laboratory for pesticide residue.

In recent years, the use of photochemical reactions in order to improve the sensitivity, selectivity and simplicity of the fluorescence analysis of photoactive compounds has been reported [13–15]. The photochemical reactions have several advantages such as quicker reaction rate, lower dilution factor, fewer chemicals involved and it is not necessary to identify the structure of the fluorescent compound (s) formed after UV irradiation, provided that reproducible photo-chemically induced fluorescence (PIF) signals are obtained [16]. Unfortunately, no such methods have been reported in which photochemical derivatisations were coupled with a fluorescence detector (FD) for the determination of thiacloprid. Ion chromatography (IC) combined with post-column derivatisation and fluorescence detection (IC-*hv*-FD) for the determination of imidacloprid and carbendazim has been reported in our previous work [17]. Also, some papers have been found, which dealt with the determination of organic compounds in milk and blood using IC [18,19]. Ion chromatography can be advantageous over the HPLC mode under certain circumstances since the polymer based ion chromatographic column can be operated over a wider range of pH values (0–14). In the present work, for the first time, the thiacloprid was separated with ion chromatographic technique coupled with an online post column photochemical derivatisation and fluorescence detection.

* Corresponding author.
E-mail address: zhuyan@zju.edu.cn (Y. Zhu).

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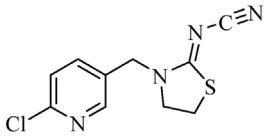

Fig. 1. Chemical structure of thiacloprid.

The present methodology is selective, sensitive, and has been applied in the determination of thiacloprid in water samples.

2. Experimental

Thiacloprid (98.5%, w/w) was obtained from Dr. Ehrenstorfer GmbH, Augsburg, Germany. HPLC grade acetonitrile (ACN) was purchased from Fisher Company Inc. (CA, USA). All other reagents were analytical grade obtained from Aladdin Co. (Shanghai, China). HPLC-grade water was purified with a Milli-Q (Millipore, Molsheim, France) system to a specific resistivity of 18.2 MΩ cm.

Stock standard solution (400 μg/mL) of the thiacloprid was freshly prepared by exactly weighing and dissolving the compound in water–ACN (90:10). The working solutions of different concentrations were prepared by dilution of the standard solution with mobile phase. The stock solution was stored in a refrigerator at −4 °C and working standard solutions were prepared daily.

The IC system consisted of a Dionex Ultimate 3000 series (Sunnyvale, CA, USA) equipped with a quaternary pump, automated sample injector, temperature controlled column compartment and an IonPac® AS11column (250 mm × 4 mm i.d; 13 μm particle size) preceded by an IonPac® AG11 guard column (50 mm × 4 mm i.d; 13 μm particle size) was used for separation. An ultimate 3000 RS fluorescence detector (Dionex, Sunnyvale, CA, USA) was used to record the fluorescence signals. The collection of data and integration were achieved by means of personal computer equipped with the Chromeleon® 6.8 software (Dionex, USA).

Our laboratory assembled the photochemical reaction unit, which equipped with a germicide UV-lamp (8 W, 254 nm) and a PTFE reaction tubing (1.5 mm o.d. × 0.5 mm i.d.) helically coiled around it. The UV lamp and the tubing portion were placed inside a PVC cylinder fixed with aluminum foil to achieve the maximum light reflection. No cooling device was necessary since all the experiments were carried out at room temperature. The PTFE tubing of various lengths from 0.5 m to 2.5 m were tested and an optimized length of 2.0 m was selected for this study.

The water samples were filtered through a 13 mm membrane syringe filter (Xiboshi, pore size 0.45 μm, Tianjin Fuji Tech Co., Tianjin, China) and stored in amber glass bottles at 4 °C for further use. These samples were directly injected into chromatographic system without any pre-treatment.

The isocratic elution was carried out at a flow rate of 1.0 mL/min with the mobile phase containing 10 mmol/L NaOH–10% ACN (v/v, pH ~ 11) pumped through an anion-exchange IonPac® AS11column combined with an IonPac® AG11 guard column at room temperature. The injection volume was 20 μL. After the separation of thiacloprid the photoderivatization was performed in a UV photochemical reactor and fluorimetric detection was done at an excitation wavelength (λ_{ex}) of 236 nm and at an emission wavelength (λ_{em}) of 353 nm. The pesticide was exposed to UV-radiation for a short residence time (40 s) in the photochemical reactor. Retention time of the target analyte was 2.6 min. The change in peak shape of the target analyte was observed due to the geometry of our homemade photochemical reactor but the effect was insignificant.

3. Result and discussion

It was observed that thiacloprid has no native florescence in the aqueous solution. When alkaline aqueous solution was irradiated with UV-radiation, it became intensively fluorescent. In the present study, the attempt was made to identify the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) by using the on-line wavelength scanning function of the fluorescence detector. By conducting a flow injection analysis (FIA), it was found that basicity of the reaction medium and type of bases used to adjust the basicity had a critical effect on the on-line photochemically induced fluorescence. Various bases such as NaOH, KOH, Na_2CO_3, $NaHCO_3$ and Na_3PO_4 in the concentration range of 0.5–100 mmol/L were used. Since 10 mmol/L NaOH solution produced adequate photochemical fluorescence signals, it was selected as the reaction medium for the on-line photochemical reaction of thiacloprid. A small amount of ACN as organic modifier was mixed with 10 mmol/L NaOH to elute the pesticide on the IC column. It was observed that addition of ACN has no effect on relative fluorescence intensity (RFI) of thiacloprid. The thiacloprid molecule resembles the imidacloprid structure. The $-NO_2$ group in imidacloprid was converted to a hydroxyl group after the photochemical derivatisation [20]. Similarly, in the case of thiacloprid the –CN group was transformed to a hydroxyl group as a result of the photochemical reaction under UV radiation under basic conditions and formed a detectable, strongly fluorescent product. But it would be necessary to further study verify the photochemical product of thiacloprid.

Under the optimized experimental conditions typical chromatograms of a standard solution are shown in Fig. 2. It was found that without UV there was no signal and with UV there was a sharp peak due to photoactivation of the pesticide. The interference of foreign species was studied by injecting the standard solution of thiacloprid containing known amounts of selected interfering compounds (6-chloronicotinic acid, methomyl, phenoxim and triadimefon) into the chromatographic system. It was found that there was no interference from the tested foreign species for the separation on the IC column.

The performance of the proposed analytical method was evaluated through quantiation, based on peak areas, of standard solution directly injected in the IC-*hv*-FD system under the optimal experimental conditions mentioned above. The linear equation of thiacloprid in mobile phase was $y = 139988.4x - 13106.7$ with a linear range of 0.04–10.0 mg/L and a correlation coefficient (r) of 0.9998. The limit of quantification (LOQ, based on signal-to-noise ratio of 10, $S/N = 10$) was 33.1 μg/L and the limit of detection (LOD, $S/N = 3$) was 9.9 μg/L. The repeatability of the method was determined at a thiacloprid concentration level of 2.0.mg/L by

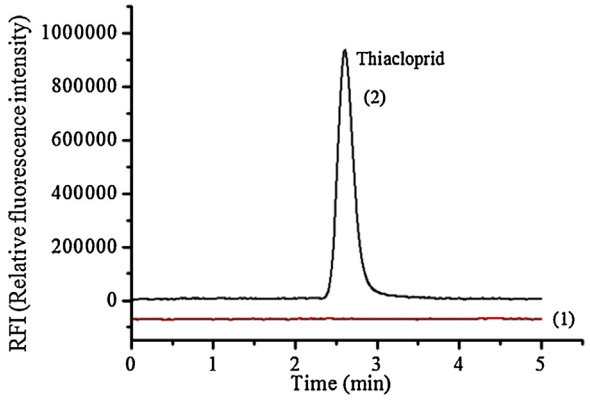

Fig. 2. Representative IC separation of thiacloprid (2.0 mg/L); (1) without UV and (2) with UV radiation.