Talanta 142 (2015) 124–130

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

An on-line SPE–HPLC method for effective sample preconcentration and determination of fenoxycarb and cis, trans-permethrin in surface waters

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ARTICLE INFO

Article history:
Received 16 February 2015
Received in revised form
16 April 2015
Accepted 21 April 2015
Available online 29 April 2015

Keywords:
On-line SPE
Chromatography
Fused-core columns
Fenoxycarb
Permethrin
Surface water

ABSTRACT

A new on-line SPE–HPLC method using fused-core columns for on-line solid phase extraction and large volume sample injection for increasing the sensitivity of detection was developed for the determination of insecticides fenoxycarb and *cis-*, *trans*-permethrin in surface waters. The separation was carried out on fused-core column Phenyl–Hexyl (100 × 4.6 mm), particle size 2.7 μm with mobile phase acetonitrile: water in gradient mode at flow rate 1.0 mL min^{-1}, column temperature 45 °C. Large volume sample injection (1500 μL) to the extraction dimension using short precolumn Ascentis Express RP C-18 (5 × 4.6 mm); fused-core particle size 2.7 μm allowed effective sample preconcentration and efficient ballast sample matrix removal. The washing mobile phase consisting of a mixture of acetonitrile:water; 30:70, (v/v) was pumped at flow rate of 0.5 mL min^{-1} through the extraction precolumn to the waste. Time of the valve switch for transferring the preconcentrated sample zone from the extraction to the separation column was set at 3rd min. Elution of preconcentrated insecticides from the extraction precolumn and separation on the analytical column was performed in gradient mode. Linear gradient elution started from 40% of acetonitrile at time of valve switch from SPE column (3rd min) to 95% of acetonitrile at 7th min. Synthetic dye sudan I was chosen as an internal standard. UV detection at wavelength 225 nm was used and the method reached the limits of detection (LOD) at ng mL^{-1} levels for both insecticides. The method showing on-line sample pretreatment and preconcentration with highly sensitive determination of insecticides was applied for monitoring of fenoxycarb and both permethrin isomers in different surface water samples in Czech Republic. The time of whole analysis including on-line extraction, interferences removal, chromatography separation and system equilibration was less than 8 min.

1. Introduction

Nowadays many organic pesticides are widely used in different industries and agricultural areas being one of the main causes of pollution of surface and groundwater [1]. The use of large quantities of the insecticides and pesticides in agriculture activities is one of the main causes of the pollution of surface and groundwater [2]. The Water Framework Directive (2000/60/EC) established a maximum allowed concentration of 0.1 g L^{-1} for each individual pesticide and 0.5 g L^{-1} for the sum of pesticides [3]. Therefore, it is necessary to study the distribution of these compounds and the monitoring of trace levels in different environmental matrices because these compounds can produce negative health effects and show negative influence on ecosystems and fauna [4,5]. In this sense, it is necessary to develop reliable, sensitive and efficient techniques for the analysis of trace concentrations of organic pollutants in environmental samples.

Fenoxycarb and permethrin are widely used insecticides that are applied mainly in agricultural and veterinary areas in Czech Republic [6]. Fenoxycarb [ethyl 2-(4-phenoxyphenoxy) ethylcarbamate] is a carbamate insect growth regulator used to control a wide variety of insect pests. Compared to other carbamates, fenoxycarb is one of the least toxic in this chemical class. Permethrin [3-phenoxybenzyl (±) cis/trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylate], is a pyrethroid insecticide, which is widely used throughout the world as a wide-spectrum insecticide.

The use of carbamates is increasing due to they are less persistent in the environment than other pesticides such as pyrethroids. However it is important to take into account that carbamates are highly biodegradable but more toxic than pyrethroids [7]. Environmental toxicity of carbamates and their effect on aquatic organism were widely studied and reviewed [8,9]. Pyrethroids are highly toxic

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http://dx.doi.org/10.1016/j.talanta.2015.04.066
0039-9140/

to aquatic organisms. The recently published data showed when pyrethroid insecticides were taken together there was a higher incidence of morphological defects, greater inhibition in proneural gene expression and more oxidative stress, compared to the single chemical at the corresponding doses [10,11].

Up to now, analysis of carbamate and pyrethroid insecticides has been accomplished by different analytical methods [12–16]. In the literature many articles describe the determination of pesticides using gas chromatography (GC) [17–19]. The majority of published methods are based on the use of liquid chromatography. For example, our research group has recently proposed a new HPLC column-switching method for on-line solid phase extraction and determination of carbamates and pyrethroids in water samples from Czech Republic. The total time of the one analysis run including sample extraction and chromatographic separation was less than 28 min [20]. Gil-García et al. developed an analytical method based on liquid chromatography–mass spectrometry to determine trace levels of pyrethroids in ground and sea water samples. Solid-phase extraction (SPE) using C18 cartridges was applied for preconcentration of pesticide trace levels ($ng\,L^{-1}$) in both ground and sea water samples [21]. Hogendoorn et al. proposed both a screening method for the determination of acidic pesticides in four types of soils, based on the use of microwave assisted solvent extraction and coupled-column reversed-phase liquid chromatography (LC–LC) with UV detection at 228 nm [22]. The advantages and disadvantages of the different instrumental techniques for insecticides determination were widely reviewed [23].

Due to the complexity of environmental matrices and very low levels of insecticides in surface waters, there is a need to find modern, fast, cheap and effective preconcentration techniques which are effective to remove interfering matrix components and to increase the sensitivity of detection. Although several techniques have been published for extraction of the pesticides in the environmental analysis [18,20,21], their off-line implementation is tedious and time consuming.

Therefore the aim of this work is to present a new analytical methodology using modern fused-core chromatography sorbents for on-line solid phase extraction of the insecticides from surface water samples. The approach can show fast extraction and chromatography separation in one step and one chromatography system [24–27].

This paper presents a new approach for easy sample preparation and determination of insecticides in surface water samples employing modern fused-core particle columns coupled to both dimensions of the column switching on-line SPE system. The developed on-line SPE–HPLC method was validated and successfully applied for the sensitive determination of fenoxycarb and both permethrin isomers in river and lake water samples.

2. Materials and methods

2.1. Chemicals

Standards of fenoxycarb (purity ≥ 99%), permethrin (purity ≥ 98%) and sudan I (purity ≥ 95%) were purchased from Sigma-Aldrich (Prague, Czech Republic) and all tested organic solvents were of analytical grade quality and were provided by Sigma-Aldrich (Prague, Czech Republic). The ultra-pure water was purified through a Milli-Q (Millipore, Bedford, MA, USA). Polytetrafluoroethylene (PTFE) filters (pore size 0.45 μm, and 25 mm in diameter) were supplied by Trading New Technologies S.A (USA).

2.2. Instrumentation and software

Analysis was performed using a Shimadzu Prominence system (Shimadzu Corporation, Kyoto, Japan), the high-performance liquid chromatography system equipped with solvent delivery systems LC-20AD, with a SIL-20AC autosampler, DGU-AS online degasser, SPD-M20A DAD detector, CTO-20AC column oven with FCV-12AH high pressure six-port switching valve and CBM-20A communication module. The system control, data acquisition and data evaluation were performed by Shimadzu "LC Lab-Solution" software (Shimadzu Corporation, Kyoto, Japan).

2.3. Preparation of stock solutions and samples

Individual stock standard solutions of fenoxycarb and permethrin were prepared by dissolving of substance in acetonitrile in concentration 60 $mg\,L^{-1}$ and 240 $mg\,L^{-1}$, respectively. Standard stock solutions were stored at 4 °C in the dark, remaining stable for at least six months. Working standard solutions were prepared by appropriate dilution in 30% acetonitrile in water. The calibration standard solutions were prepared in the concentration range of 3–540 $ng\,mL^{-1}$, using eight calibration points. Prior to injection into the HPLC system the solutions were filtered through a 0.45 μm PTFE filter.

2.4. Sample collection and preparation

Surface water samples (river Elbe, river Orlice and small lakes) were collected from water sources close to the city Hradec Králové and Městec Králové. All samples (5 river samples from Hradec Králové and 7 lake samples from Hradec Králové and Městec Králové, (sample volume 250 mL)) were kept in amber glass bottles and stored refrigerated in the dark at 4 °C until analysis. The surface water samples were filtered through a 0.45 μm PTFE filter to glass vials before analysis. A volume of 1500 μL filtered sample solutions were injected directly into the on-line SPE–HPLC column switching system.

2.5. HPLC column switching analysis

A simple column-switching HPLC system was used for the simultaneous preconcentration and determination of the analytes (Fig. 1). The chromatographic separation of insecticides (fenoxycarb and cis- and trans-permethrin) was performed on Supelco Ascentis Express fused-core column Phenyl–Hexyl (100 × 4.6 mm), particle size 2.7 μm with mobile phase acetonitrile:water in gradient mode at flow rate 1.0 $mL\,min^{-1}$, column temperature 45 °C, and UV detection at wavelength 225 nm. Linear gradient elution started from 40% of acetonitrile at time of valve switch from SPE column (3rd min) to 95% of acetonitrile at 7th min. Equilibration of analytical column back to initial conditions was carried out in the time of following sample extraction. On-line pretreatment and effective preconcentration of environmental water samples was performed by direct injection of 1500 μL of sample onto extraction guard column Ascentis Express RP C-18 (5 × 4.6 mm), fused-core particle size 2.7 μm, where the enrichment of insecticides and wash-out the sample matrix was performed. The washing mobile phase consisted of a mixture of acetonitrile:water; 30:70, (v/v) was pumped at flow rate of 0.5 $mL\,min^{-1}$ to the waste. Time of valve switch for transfer the preconcentrated sample zone from the extraction to the separation dimension was set at 3rd min. Synthetic dye sudan I was chosen as an internal standard.

3. Results and discussion

3.1. On-line SPE sample preconcentration—the choice of extraction precolumn

The aim of this step was to find the suitable sorbent and to preconcentrate the pesticides on the extraction precolumn with a