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New method for the determination of carbamate and pyrethroid insecticides in water samples using on-line SPE fused core column chromatography



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ABSTRACT

A new HPLC column-switching method using large volume sample injection and fused-core columns for on-line solid phase extraction have been developed for the determination of the following carbamates and pyrethroids: aldicarb, carbaryl, pirimicarb, carbofuran, kadethrin, flumethrin, fenprothrin, fenoxycarb, tau-fluvalinate and fenvalerate, in surface water samples. Sudan I was used as internal standard. The proposed method was performed using 100 μl sample injection followed by an on-line solid phase extraction procedure and finally the compounds were identified and quantified by liquid chromatography with ultraviolet detection. The separation was carried out on C-18 reversed phase column based on fused-core particle technology. The influence of the injected sample volume, the variables affecting to SPE process and the conditions for the separation on an analytical column, were studied and optimized. The limits of detection ranged from 5.5 to 8.9 $\mu\text{g L}^{-1}$, and limits of quantification from 18.4 to 29.7 $\mu\text{g L}^{-1}$, while inter- and intra-day variability was under 15%. This new analytical procedure was satisfactorily applied for the determination of these organic pollutants in surface water samples located in Czech Republic. Concentration levels were found for some of these pollutants up to 26.11 $\mu\text{g L}^{-1}$ in the river Elbe and up to 34.53 $\mu\text{g L}^{-1}$ in the closed lakes samples.

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1. Introduction

In 2007, the world pesticide amount used was estimated in 2.36 billion kg. Approximately 40% of this production corresponds to herbicides, 17% insecticides, 10% fungicides and 33% others [1]. Nowadays, there is an increasing public concern for environmental safety and for this reason it is necessary to study the presence of organic pollutants in different environmental compartments [2,3]. The use of large quantities of insecticides and pesticides in agriculture activities is one of the main causes of pollution of surface and ground water [4] and for this reason legislation is constantly changing and becoming more strict. The Water Framework Directive (WFD) (Directive, 2000/60/EC – European Parliament and Council of the European Union, 2000), have established the environmental quality standards (EQS) for pesticides, their relevant metabolites, degradation and reaction products in 0.1 $\mu\text{g L}^{-1}$ for individual compounds and 0.5 $\mu\text{g L}^{-1}$ for the sum of pesticides in ground water [5].

N-methylcarbamates are derived from carbamic acid and are extensively used in agriculture as insecticides, herbicides and

fungicides [6]. Pyrethroids are synthetic insecticides based on the structure of the natural chemicals pyrethrins, which are produced by the flowers of pyrethrums and they are used as pesticides too. The use of carbamates is increasing due to they are less persistent in the environment than other pesticides such as pyrethroids, organophosphorous and organochlorine, however it is important to take into account that carbamates are highly biodegradable but more toxic than pyrethroids [7], and for example some carbamates such as carbofuran, are very toxic to the central nervous system and it is a strong endocrine disruptor affecting human and animal at low doses [8]. Ryan et al. determined the acute toxic effects of carbofuran on the levels of endocrine hormones in the serum of male Sprague-Dawley rats. When rats were exposed to an acute dose of carbofuran (1.5 mg kg^{-1}) showed the onset of cholinergic signs and when intensity was increased, toxic signs of maximal severity were observed within 30–60 min. The results suggest that an acute exposure to carbofuran may cause transient endocrine disruption [9]. Dana et al. evaluated in utero exposures to pesticides by measuring maternal and cord serum biomarkers in a New Jersey cohort of pregnant women and the birth outcomes of their neonates. Carbofuran was one of the pesticides most frequently detected in the serum samples. The results suggest that in utero exposures to certain pesticides may alter birth outcomes [10]. For this reason is

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necessary to develop new procedures where the sample treatment is simplified and an improved of the chromatographic techniques is carried out to detect these compounds in a low range of concentration.

In the present work the following compounds were analyzed: aldicarb, carbaryl, pirimicarb, carbofuran, kadethrin, flumethrin, fenprothrin, fenoxycarb, tau-fluvalinate and fenvalerate. These compounds were chosen for our study due to they are used in the Czech republic and due to their toxicity is necessary to develop sensitive analytical methods for their determination in the environment.

In the literature many articles describe the determination of pesticides in environmental matrices. Some methods are based on the use of gas chromatography (GC) [11–13]. For example Yang et al. [14] proposed a sensitive and selective gas chromatographic mass spectrometric method, based on derivatization with 9-xanthidrol for the simultaneous determination of five carbamate pesticides in surface water, and the limits of quantification (LOQ) were in the range of 0.007–0.028 $\mu\text{g L}^{-1}$, but in this study none of analytes were detected in samples. However the majority of methods published are based on the use of liquid chromatography (LC). Different detection techniques were used such as: (1) ultraviolet detection [15], for example 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. Recoveries between 60 and 90% were obtained and LODs were between 5 and 50 mg kg^{-1} [16] and an analytical method for the determination of polar pesticides in water using coupled column RPLC with UV detection and injecting 4 mL of sample was proposed. The limits of determination for pesticides such as bentazone and isoproturon were 0.1 pg L^{-1} [17]; (2) fluorescence detection [18], for example García de Llasera et al. studied the presence of pesticides in ground and surface waters from an agricultural zone in northwest Mexico. Trace determinations were made by liquid chromatography with post-column fluorescence detection. Level of contamination with methiocarb was 5.4 $\mu\text{g L}^{-1}$ in a ground water sample and for 3-hydroxycarbofuran was 18 $\mu\text{g L}^{-1}$ in a surface water sample [19]. Vassilakis et al. [20] evaluated the extraction of triazines, organochlorine, carbamates and acidic pesticides from surface and ground water from Greece, using gas chromatography with selected detection methods (electron-capture detection, nitrogen–phosphorus detection, mass spectrometry) and liquid chromatography–post-column derivatization fluorescence detection. Recoveries varied from 52 to 102%. The limit of detection for seventeen organochlorine compounds was better than 0.003 $\mu\text{g L}^{-1}$ and the limit of detection for other 15 analytes was better than 0.06 $\mu\text{g L}^{-1}$; (3) and mass spectrometry detection [20–23], such as Kampioti et al. [24] developed an automated method for the determination of twenty pesticides in natural and treated waters using on-line solid phase extraction and liquid chromatography mass spectrometry. Limits of detection between 0.004 and 2.8 ng L^{-1} were obtained. García-Ac et al. [25] developed an on-line solid phase extraction of large-volume injections coupled to liquid chromatography tandem mass spectrometry method for the simultaneous quantitation and confirmation of 14 selected trace organic contaminants in drinking and surface water. Extraction recoveries ranged from 60 to 109% and the method detection limits ranged from 0.6 to 6 ng L^{-1} . Although several methods have been published for determination of these compounds in the environment, due to the complexity of matrices and they are present in trace levels, sample pre-treatment like as soxhlet extraction, ultrasonic assisted extraction, microwave extraction, pressurized liquid extraction, super-critical fluid extraction, etc., is required, but these extraction techniques present several disadvantages due to they are tedious, time consuming

and consuming large amounts of organic solvent. On the other hand, sensitive detection is required and although the use of MS detectors allows to obtain good sensitivity, however it is expensive [26]. These reasons along with trends are focused on the application of green chemistry principles [27] have allowed the development of improved chromatographic techniques, e.g., column switching chromatography, on-line SPE and liquid chromatography and multidimensional chromatography [28–30]. A remarkable decrease in total analysis time can be achieved with the introduction of the on-line SPE step in which the loading of the sample into the cartridge, the clean-up of the matrix, the extraction of target analytes and their determination is automatically coupled in one chromatography system.

Today, the new approach in fast chromatography and high efficiency separations in conventional HPLC systems is using columns with fused-core particles technology. These columns are packed with porous shell silica particles consisting of 1.7 μm fused-core, 0.5 μm layer of porous silica coating and 2.7 μm total particle diameter. This column technology enables the shortening of the diffusion path for analytes, which allows rapid mass transfer and, thus, reduced axial dispersion and peak broadening. Fused-core column technology offers the following advantages: improvement of the efficiency of the separation process over fully porous particles, its efficiency of separation is comparable to totally porous sub-2 μm particle size columns but with lower backpressures and it allows to work with higher flow rates [31].

Notably, there is important to highlight that only a few papers concerning the on-line SPE–HPLC coupled with fused-core columns are described in the literature. For example, an analytical method based on an on-line solid phase extraction coupled to liquid chromatography with fluorescence detection has been developed to determine quinolones in tap water and human urine by Lara et al. [32]. A C-18 column containing core–shell particles (2.6 μm) was used to achieve peak efficiencies up to 200,000 plates/m and at a flow rate of 1.2 mL min^{-1} . The limits of detection were ranging between 7 and 110 ng L^{-1} . Gallart-Ayala et al. [33] proposed an on-line column-switching LC–MS/MS method to analyze bisphenol A and its chlorinated derivatives in water. Fast liquid chromatographic separation was performed on a C-18 reversed phase column based on fused-core particle technology (2.7 μm particle size) providing analysis times shorter than 3 min and high peak efficiencies, and Wode et al. [34] described a multiresidue method for the simultaneous quantification of 72 micropollutants in aqueous samples by ultra high performance liquid chromatography–high resolution mass spectrometry (UHPLC–HRMS). A sample volume of 1 mL was enriched by on-line SPE, separated on a 2.6 μm core–shell column and detected with high resolution mass spectrometer. Limits of quantification ranged between 0.01 and 0.06 $\mu\text{g L}^{-1}$ in drinking water, 0.03 and 0.38 $\mu\text{g L}^{-1}$ in diluted surface water, 0.06 and 0.38 $\mu\text{g L}^{-1}$ in diluted wastewater treatment plant effluent.

From this point of view, the idea of fused-core columns for on-line solid phase extraction of samples is highly innovative and not well described. Therefore, on-line coupling of fused-core sorbents to conventional HPLC instruments shows a novel and promising approach for future instrumental applications in column-switching systems.

The aim of this work is, for the first time presented and new method for the determination of carbamates and pyrethroids in surface water samples employing large volume sample injection and column-switching technique using an on-line sample preparation and separation in one step. Compounds with a wide range of physicochemical properties, pyrethroids and carbamates with very different $\log P$ values, were simultaneously extracted and separated. The influence of the injected sample volume, the variables affecting SPE process and the conditions for the

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