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Capillary electrophoresis–mass spectrometry as a new approach to analyze neonicotinoid insecticides

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ABSTRACT

This paper represents the first report of a capillary electrophoresis (CE) method compatible with mass spectrometry (MS) detection for simultaneously analyzing seven neonicotinoid insecticides (acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid and thiamethoxam). Different variables affecting CE separation (buffer concentration, pH, applied voltage and injection time) and MS detection (electrospray parameters) were studied. Low limits of detection (LOD) and quantification (LOQ) were achieved for all analytes, ranging from 1.0 to 2.3 μg/L, and from 3.5 to 7.2 μg/L, respectively. In addition, the proposed method showed itself to be linear in the range from LOQ to 1000 μg/L and to be precise, as the relative standard deviations of the migration times were lower than 4% in all cases. Finally, the proposed CE–MS method was applied to assess the efficacy of a beeswax cleaning treatment with oxalic acid to remove residues of three of the most commonly used neonicotinoids (clothianidin, imidacloprid and thiamethoxam), use of which has recently been restricted by the European Union.

1. Introduction

Neonicotinoids (imidacloprid, acetamiprid, clothianidin, thiacloprid, thiamethoxam, dinotefuran and nitenpyram, see structures in Table 1) are a class of insecticides deriving from the nicotine moiety. Their use has increased considerably since the early 1990s, representing one of the fastest growing types of insecticides, employed extensively for the control of agricultural pests by spraying and also widely used in seed dressings and soil additions [1]. However, concerns regarding the side effects on health and the environment of synthetic chemical pesticides such as neonicotinoids continue to increase, since the parent compounds and their metabolites can be transferred to the environment and the food chain, with potential adverse consequences for biodiversity. Therefore, it is necessary to monitor and analyze neonicotinoid residues.

The separation and analysis of neonicotinoid insecticides has been accomplished mainly by chromatographic techniques such as gas chromatography (GC) [2–4] or liquid chromatography (LC) with UV/diode array [5–8], fluorescence [9], electrochemical [10] or mass spectrometry (MS) [1,11–18] detectors; coupled LC–MS has been the most common method. However, in the last few years certain capillary electrophoresis (CE) approaches have also been proposed to analyze this group of insecticides [19–26]. All of these CE publications were based on the micellar electrokinetic chromatographic mode (MEKC) using UV [19–25] or indirect laser-induced fluorescence (LIF) [26] detection (see Table 2). It must be pointed out that previous sample treatments such as solid phase extraction (SPE) [20,21,24,25] or dispersive liquid–liquid microextraction (DLLME) [22,24] have been employed in most of these articles in order to improve the limits of detection (LODs) when UV-absorbance detectors were used in CE applications. However, it should be highlighted that, to our knowledge, no specific CE method with mass spectrometry (MS) detection for analyzing neonicotinoids has yet been reported. This coupling combines the advantages of CE techniques (high separation efficiency, speed of analysis and low consumption of sample and reagents) with the high sensitivity, selectivity and capacity for identifying unknown compounds that is offered by MS detection. In addition, previous derivatization (LIF) or sample treatments (UV to improve sensitivity) are not strictly required for the detection of these compounds when MS detectors are used. Thus, due to the keen interest in developing methodologies enabling the analysis of these insecticides at trace levels, the aim of this study has been to present a CE methodology compatible with MS detection for the simultaneous analysis of seven neonicotinoids.

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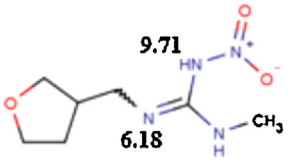
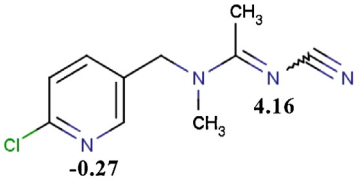
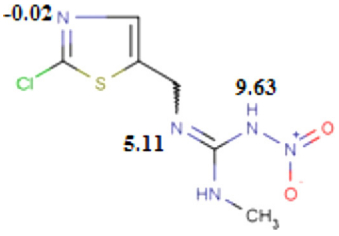
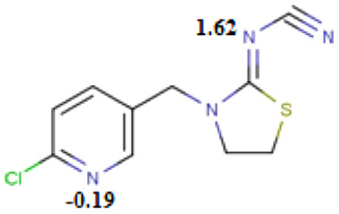
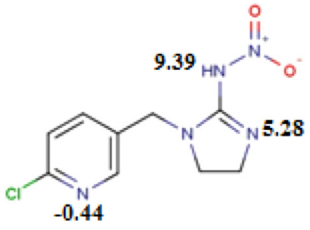
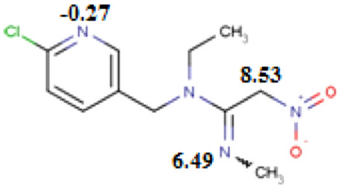
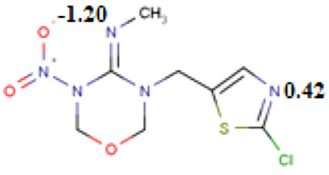
Table 1
Structures, pKa values and estimated charge of the studied neonicotinoids.

Neonicotinoid	pKa	Estimated charge	
		Acid medium (pH 1.0–6.0)	Basic medium (pH 8.0–14.0)
Dinotefuran		Positive (NH—C(—NH)=NH^+)	Negative (NH—C(—N^-)=N)
Acetamiprid		Positive (CH_3—C(—NH)=NH^+)	Neutral
Clothianidin		Positive (NH—C(—NH)=NH^+)	Negative (NH—C(—N^-)=N)
Thiacloprid		Neutral	Neutral
Imidacloprid		Positive (N—C(—NH)=NH^+)	Negative (N—C(—N^-)=N)
Nitenpyram		Positive (CH_2—C(—N)=NH^+)	Negative (CH^-—C(—NH)=N)
Thiamethoxam		Neutral	Neutral

In addition, the applicability of the method was demonstrated by the analysis of neonicotinoids in beeswax samples. The choice of beeswax as matrix is due to [1,18]: (i) beeswax could be considered a contaminant reservoir, and the pesticides present in wax could directly affect the bee colony or be transmitted to other bee products; (ii) there are concerns regarding potential adverse effects caused by such insecticides on non-target organisms, particularly pollinators; (iii) it is a complex matrix. The European Union has recently adopted a proposal (Regulation (EU) 485/2013) [27] to restrict the use of three of these (clothianidin, imidacloprid and thiamethoxam) which have been recognized as representing severe risks for honeybees due to their connection with colony collapse disorder, for example, when bees have been exposed to dust, pollen and/or nectar of several crops treated with these neonicotinoids