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In-coupled syringe assisted octanol–water partition microextraction coupled with high-performance liquid chromatography for simultaneous determination of neonicotinoid insecticide residues in honey

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ABSTRACT

A simple and fast method namely in-coupled syringe assisted octanol–water partition microextraction combined with high performance liquid chromatography (HPLC) has been developed for the extraction, preconcentration and determination of neonicotinoid insecticide residues (e.g. imidacloprid, acetamiprid, clothianidin, thiacloprid, thiamethoxam, dinotefuran, and nitenpyram) in honey. The experimental parameters affected the extraction efficiency, including kind and concentration of salt, kind of disperser solvent and its volume, kind of extraction solvent and its volume, shooting times and extraction time were investigated. The extraction process was carried out by rapid shooting of two syringes. Therefore, rapid dispersion and mass transfer processes was created between phases, and thus affects the extraction efficiency of the proposed method. The optimum extraction conditions were 10.00 mL of aqueous sample, 10% (w/v) Na_2SO_4, 1-octanol (100 μL) as an extraction solvent, shooting 4 times and extraction time 2 min. No disperser solvent and centrifugation step was necessary. Linearity was obtained within the range of 0.1–3000 ng mL^{-1}, with the correlation coefficients greater than 0.99. The high enrichment factor of the target analytes was 100 fold and low limit of detection (0.25–0.50 ng mL^{-1}) could be obtained. This proposed method has been successfully applied in the analysis of neonicotinoid residues in honey, and good recoveries in the range of 96.93–107.70% were obtained.

1. Introduction

Neonicotinoids are a relatively new generation of insecticides deriving from nicotine [1]. Neonicotinoid insecticides act as agonizts at the insect nicotinic acetylcholine receptors (nAChRs), which plays an important role in synaptic transmission in the central nervous system [2]. These compounds are among the most effective insecticides for the control of sucking insects such as aphids, whiteflies, leaf- and plant-hoppers, thrips, some micro-lepidoptera and a number of coleopteran insects [3]. These neonicotinoids include imidacloprid, acetamiprid, clothianidin, thiacloprid, thiamethoxam, dinotefuran, and nitenpyram. They are commonly used on rice, maize, sunflowers, rapeseed, potatoes, sugar beets, vegetables, and fruits crops [4]. The widespread use of neonicotinoid insecticides at various stages of agricultural cultivation and during postharvest storage could give rise to serious risks for human health. The amended European Union legislation has set the maximum residue limits (MRLs) for neonicotinoid insecticides in different agricultural products including vegetables and fruits. The MRLs ranged between 0.1 and 1 mg kg^{-1}[5]. Therefore, the evaluation and monitoring of trace levels of these compounds is crucial for proper assessment of human exposure to the insecticides through foods.

Several chromatographic methods have been widely employed for the separation and quantification of neonicotinoid residues in various samples, including gas chromatography with mass spectrometry [6,7], liquid chromatography (LC) with mass spectrometry (MS) [7,8], high performance liquid chromatography and diode array detector (HPLC–DAD) [9,10] and capillary electrophoresis with mass spectrometry (CE-MS) [11]. Although these are sensitive instrumental methods of analysis, another step before the analysis, known as

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sample preparation, is still required [12]. The effective performance of sample preparation provides not only sample clean-up, but also concentration of the target neonicotinoids and removal of interfering species.

One of the most common sample preparation methods is liquid–liquid extraction (LLE) [13,14]. It is a basic separation technique for a diverse range of water samples, but is a time-consuming and tedious process that requires large volumes of organic solvents [15]. To overcome the problems of LLE methods, liquid-phase microextraction (LPME) techniques have been developed. There are various LPME techniques that have been used, including single-drop microextraction (SDME), liquid-phase based liquid-phase microextraction (HF-LPME), dispersive liquid–liquid microextraction (DLLME) and solidification of floating organic drop microextraction (SFODME). A recent method is based on the principle of DLLME and SFODME, called DLLME–SFO [16]. DLLME is based on a ternary solvent system in which a mixture of extracting and dispersive solvent is rapidly injected into an aqueous sample containing the analytes of interest, which caused formation of a cloudy solution [17]. Then the emulsion was separated into two phases by centrifugation. However, one of the limitations of DLLME is related to the requirements of a high density, but hazardous, extraction solvent such as chlorobenzene, chloroform and carbon tetrachloride. The extractant is evaporated to dryness before analysis by HPLC, because these halogenated solvents are not compatible with the mobile phase of reverse-phase HPLC [18]. In the SFODME method, a droplet of an immiscible solvent with a low density such as toluene, hexane, and 1-octanol, is floated on the surface of an aqueous sample containing the analytes. Agitation is used to maximize contact area between the two solutions. After centrifugation, the extractant can be floated on the top of the solution. DLLME–SFO is simple, easy to operate, low cost, has high recovery and utilizes low consumption of toxic organic solvents.

To enhance the dispersion and to accelerate the formation of fine droplets of extraction solvent into an aqueous solution, various agitators were used for the extraction process, including ultrasound [19], vortex [10,12], centrifuge [20] and magnetic stirrer [21]. Very recently, in-syringe dispersive liquid–liquid microextraction (IS-DLLME) is of increasing interest [22]. This technique is a quick and easy method, which is probably the most attractive benefit. A glass syringe is used as an extraction, separation and preconcentration container. A 1-mL syringe is used to rapidly inject the solvent mixture of extraction solvent and dispersing solvent. The simultaneous enormous increase of the interaction surface with the sample enables efficient mass transfer of the analyte into the extraction solvent droplets. After the separation of two phases, the extractant containing the target analytes can be easily collected and transferred into the analytical instrument for analysis. No centrifugation step is necessary.

The present study is focused on the development of simple and efficient methods for preconcentration of neonicotinoids from honey employing in-coupled syringe assisted octanol–water partition microextraction combined with HPLC. A low-density solvent was used as an extraction solvent and the coupled syringe was used to increase dispersion of the extraction solvent into aqueous solution. Moreover, it is the first time that in-coupled syringe has been used in combination with octanol–water partition microextraction. The effect of various experimental parameters on the extraction performance of the target compounds, such as salt addition, type and volume of the extraction solvent, type of disperser solvent, shooting times and extraction time were investigated and optimized.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of at least analytical reagent grade. The analytical standards of neonicotinoid insecticides including acetamiprid, clotianidin, nitenpyram, imidacloprid, and thiamethoxam were obtained from Dr.Ehren-storfer GmbH (Germany), and dinotefuran and thiacloprid were obtained from Sigma-Aldrich (Germany). The stock solutions of each insecticide were prepared at 1000 mg L^{-1} by dissolving an appropriate amount in MeOH. The working solution was prepared in water. Deionized water obtained from RiOsTM Type I Simplicity 185 (Millipore Waters, USA) with the resistivity of 18.2 MΩ cm was used throughout the experiments. Methanol (MeOH), acetonitrile (ACN) and 1-octanol of HPLC grade and acetone were obtained from Merck (Germany). Ethanol was purchased from RCI Labscan Ltd. (Thailand). NaCl and anhydrous Na_2SO_4 were obtained from Ajax Finechem (New Zealand), CH_3COONa and KI were obtained from Carlo Erba (France).

2.2. Apparatus

The HPLC system was comprised of a Waters 600 multisolvent delivery system (USA), a Rheodyne injector with a sample loop of 20 μL, and a Waters 996 photodiode array detector. The Millennium software was used for data acquisition. The separation of neonicotinoids was carried out on an Atlantis dC18 (4.6 × 150 mm^2, 5.0 μm) column (Waters, USA) with isocratic elution using 25% acetonitrile in water. The injection volume was 20 μL. The detection of target analytes was set at a wavelength of 254 nm. Seven neonicotinoid insecticides were separated within 18 min with the elution order of dinotefuran, nitenpyran, thiamethoxam, clothianidin, imidacloprid, acetamiprid and thiacloprid.

2.3. In-coupled syringe assisted octanol–water partition microextraction

A 10-mL aliquot of standard solution of each neonicotinoid or honey sample was mixed with 10% (w/v) of Na_2SO_4 and then taken by syringe A. After that, 100 μL of 1-octanol was rapidly injected into the solution through the 1- mL syringe. In order to obtain the mass transfer and provide high extraction efficiency, the syringes A and B were assembled through their tips. The coupled-syringes system was then held horizontally and the content of syringe A was injected into syringe B and vice versa. In order to enhance the extraction efficiency, this cycle was repeated with pulling the plungers back and forth constantly (four cycles). When the last cycle was finished,

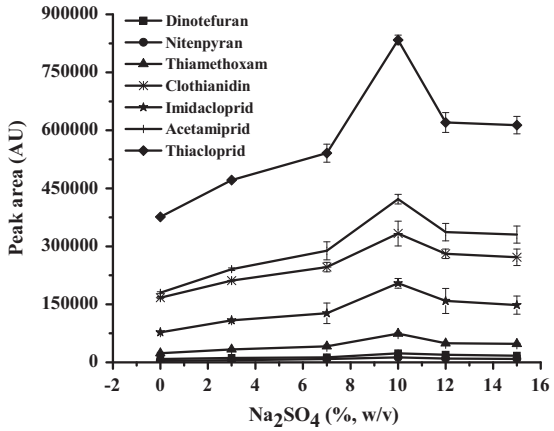

Fig. 1. Effect of salt concentration on the extraction recovery (50 ng mL^{-1} of each neonicotinoid).