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A preconcentration method for analysis of neonicotinoids in honey samples by ionic liquid-based cold-induced aggregation microextraction

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ABSTRACT

A preconcentration approach based on ionic liquid-based cold-induced aggregation microextraction for determination of neonicotinoid insecticide residues in honey samples before high-performance liquid chromatographic analysis has been developed. Room temperature ionic liquid [C_4MIM][PF_6] (extraction solvent) and SDS (emulsifier) was used for extraction of the target analytes. The parameters affecting the extraction efficiency were optimized. The optimum microextraction conditions were 200 μL room temperature ionic liquids [C_4MIM][PF_6] containing 0.05 mol L^{-1} SDS, 0.75 g sodium carbonate, vortex agitation speed of 1800 rpm for 30 s and centrifugation at 3500 rpm for 10 min. Under optimum conditions, the high enrichment factors of 200 could be obtained, leading to low limit of detection (0.01 μg L^{-1} for all analytes) with the relative standard deviations lower than 2.68% and 5.38% for retention time and peak area, respectively. Good recoveries for the spiked target neonicotinoids at three different concentrations of honey samples were obtained in 86–100% and relative standard deviations were lower than 8.1%. The results demonstrated that the proposed method can be used as an alternative powerful method for the simultaneous determination of the studied insecticides in real honey samples.

1. Introduction

Neonicotinoid insecticides, as one of the fastest growing new generation of insecticides in modern crop protection, have contributed to a significant reduction of toxicity for the environment [1,2]. These insecticides are active against numerous sucking and biting pests and insects, including whiteflies, aphides, beetles and some lepidoptera species as well [2]. The widespread use of neonicotinoid insecticides at various stages of agricultural cultivation and during postharvest storage could give rise to serious risks for the health and safety of the consumers [3]. They act as agonists at the insect nicotinic acetylcholine receptors (nAChRs), which plays an important role in synaptic transmission in the central nervous system [4]. Therefore, most nations and organizations, such as the European Union (EU) have been established standard/regulations for the maximum residue limits (MRL) in various products. The MRLs of some neonicotinoid pesticides in agricultural products ranged between 0.1 and 1 mg kg^{-1} (acetamiprid, imidacloprid, and thiacloprid, 0.05 mg kg^{-1}; thiamethoxam and clothianidin, 0.01 mg kg^{-1}, respectively) [5]. Thus, a simple and selective method for monitoring of neonicotinoid residues at low concentration levels is required to secure food quality and to protect hazard for consumer.

Analysis for the residues is often carried out in some steps for pretreatment mainly including sample preparation, matrix removal and preconcentration of the target analytes. In spite of clean-up of extracts may result in the partial loss of some compounds as well as increased labor and cost demands, but inadequate clean-up can lead to adverse effects related to the quality of the generated data [6]. Traditionally, conventional extraction and clean-up methods such as liquid–liquid extraction (LLE) [7,8] and solid phase extraction (SPE) [1,9,10] have been adopted. However, these techniques are tedious, time consuming, and require large volume of both samples and toxic organic solvent [11]. To solve these limitation, novel sample preparation methods, such as stir bar sorptive extraction (SBSE) [12], solid-phase

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microextraction (SPME) [13], ultrasound-assisted emulsification microextraction (USAEME) [14], salting-out assisted liquid–liquid extraction [15] and dispersive liquid–liquid microextraction (DLLME) [16,17], have been investigated.

Room-temperature ionic liquids (RTILs) are being recently used as replacement extraction solvents for preconcentration of the target analytes. They have some unique properties including: (1) negligible vapour pressure, (2) good thermal stability, (3) good extractability for various organic compounds and metal ions as a neutral or charged complexes, (4) additionally tunable viscosity and miscibility with water and organic solvents [18]. Therefore, the application of RTILs for preconcentration method has been reported for different groups of analytes such as liquid-liquid extraction [19], ionic liquids-ultrasound based extraction [20], vortex-assisted ionic liquid dispersive liquid–liquid microextraction [21], ionic-liquid based vortex assisted liquid-liquid microextraction [22].

The first development of new HLLME based on ILs termed cold induced aggregation microextraction (CIAME) was reported in 2008 by Baghdadi and Shemirani [23]. In this method, two types of ILs (extraction solvents) including, 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Hmim][Tf_2N] were added in a sample solution containing Triton X-114 (anti-sticking agent). Then, the solution was cooled in the ice bath and a cloudy solution was formed. The resulting emulsion was completely separated by centrifugation, and then the fine droplets of extraction phase were settled to the bottom of centrifuge tube. CIAME is a simple, fast and effective preconcentration method for determination of metal ions from water samples. It can be were successfully applied for analysis of sample solutions containing high concentration of salt and water miscible organic solvents. Furthermore, this technique is much safer in comparison with the organic solvent extraction. CIAME was developed for the determination of mercury [23], phthalate esters [24], and cobalt [22]. However, a method using CIAME for extraction of neonicotinoid insecticides has not been found.

In this work, we aim to extend and develop ionic liquid-based cold-induced aggregation microextraction followed the analysis by HPLC with photodiode array detection for the preconcentration and simultaneous determination of neonicotinoid insecticide residues. The effective parameters (e.g., kind of surfactant and its concentration, kind of extraction solvent and its volume, salting-out effect, vortex agitation and centrifugation time) affecting the extraction performance of the target insecticides were investigated and optimized. The developed method was then applied for the insecticides determination in honey samples.

2. Experimental

2.1. Chemicals and reagents

The analytical standards of neonicotinoid insecticides including clothianidin, and imidacloprid were obtained from Dr. Ehrenstorfer GmbH (Germany), and dinotefuran and thiacloprid were purchased from Sigma-Aldrich (Germany). All standard neonicotinoid insecticides were of analytical standard grade. The stock solutions of each insecticide (1000 mg L^{-1}) were prepared by dissolving an appropriate amount in methanol. Working standard solutions were prepared by diluting the stock standard solution with water. Deionized water obtained from RiOs™ Type I Simplicity 185 (Millipore Waters, USA) with the resistivity of 18.2 MΩ.cm was used throughout the experiments. Methanol and acetonitrile of HPLC grade and acetone were obtained from Merck (Germany). Other reagent used were of analytical grade. Sodium chloride (NaCl) anhydrous sodium sulfate (anh. Na_2SO_4) and sodium carbonate (Na_2CO_3) were obtained from Ajax Finechem (New Zealand), Sodium acetate (CH_3COONa) was obtained from Carlo Erba (France). 1-buthyl-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] RTIL, sodium dodecyl sulfate (SDS) and Triton X-100 were provided by Merck (Germany). Cetyltrimethyl ammonium bromide (Calbiochem, Germany) was also used.

2.2. Instrumentation

Neonicotinoid insecticides were analyzed with a Waters 1525 Binary LC system (Waters USA) using a LiChrospher® 100 RP-18 endcapped (4.6 × 150 mm, 5.0 μm) column (Merck, Germany). Manual injection were conducted with a Rheodyne injector equipped with a sample loop of 20 μL. Separations were carried out using isocratic elution of 25% (*v/v*) acetonitrile in water. A flow rate of 1 mL min^{-1} was used. All of studied insecticides were detected at 254 nm using a photo-diode array detector (PDA). The Empower 3 software was used for data acquisition. Four neonicotinoid insecticides were separated within 12 min with the elution order of clothianidin (t_R=5.20 min), imidacloprid (t_R=6.20 min), acetamiprid (t_R=7.20 min) and thiacloprid (t_R=12.17 min).

2.3. Ionic liquid-based cold-induced aggregation microextraction procedure

A 10-mL of sample or standard solution was mixed with 0.75 g of Na_2CO_3 before subsequently transferring to a 10-mL screw cap test tube. After that, 200 μL of RTIL containing SDS 0.05 mol L^{-1} was added into the sample solution before vortexing the tube for 30 s. And then centrifuged at 3500 rpm for 10 min to complete the phase separation and the reconstituted solution was observed at the bottom of the solution. The target analytes in aqueous sample were extracted into the fine droplets of ionic liquid settled to the bottom of the tube. The aqueous phase was removed by using a 10 mL syringe. Then, 50 μL of acetonitrile (the minimum amount necessary to completely dissolve the RTIL phase) was added to decrease viscosity and 20 μL was directly injected into HPLC.

2.4. Honey samples analysis

Honey samples were randomly purchased from various province (Chiang Mai, Lampang, Khon Kaen and Chiang Rai) in Thailand. 8-mL of sample was pipetted into 10-mL volumetric flask and diluted to the marker. Then it was filtered through a Whatman (no. 42) filter paper to remove particulate matter and passed through 0.45 μm nylon membrane filter before extraction and preconcentration by ionic liquid-based cold-induced aggregation microextraction procedure. For the accuracy evaluation, the studied honey samples were spiked with the standard neonicotinoid insecticides at the different concentration levels of 50, 100 and 500 μg L^{-1} prior to extraction and preconcentration.

3. Results and discussion

3.1. Optimization of ionic liquid-based cold-induced aggregation microextraction procedure

To obtain the maximum extraction efficiency of the proposed method, the parameters were investigated including surfactant and its concentration, extraction solvent and its volume, salting-out effect, vortex agitation and centrifugation time. In this study, these parameters were evaluated by one parameter at a time while the other remaining factors were kept constant. The optimization was carried out on the aqueous solution (10.00 mL) containing