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Determination of neonicotinoid insecticide residues in sugarcane juice using LCMSMS

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ABSTRACT

A simple, sensitive and inexpensive LC–MS/MS method was developed and validated for for the simultaneous detection and quantification of (five) neonicotinoid insecticides in sugarcane juice. The juice samples were extracted with acetonitrile and subsequent cleanup was done by dispersive solid-phase extraction (QuEChERS method). The quantification was carried out by liquid chromatography–tandem mass spectrometry with electrospray ionization source (LC-ESI-MS/MS). After the optimization of the extraction parameters, the method was validated by evaluating linearity, limits of detection and quantification, precision (repeatability) and accuracy (recovery). Validation was based on analyses at three fortification levels that showed satisfactory recoveries (62.06–129.93%) and high precision (RSDs between 2.52% and 14.57%). Detection levels for all the five analytes ranged from 0.0007 to 0.002 μg g^{-1} and quantification level ranged from 0.002 to 0.005 μg g^{-1}, respectively.

1. Introduction

The sugarcane (*Saccharum officinarum* L.) is an important cash crop in India and is the main source of white sugar and jaggery (NABARD, 2010). India has the largest area under sugarcane cultivation and is the second largest producer next only to Brazil. Sugarcane is infested by more than 280 insects of which nearly two dozen cause heavy losses to the quality and quantity of the crop (DSD, 2013). Farmers depend on pesticides to a large extent for their management. Indiscriminate use of pesticide is an important factor that leads to health and environmental problems. Though biological control is successful in sugarcane with respect to borer pests, sucking pests like wooly aphids, whitefly, scale insects and mealy bugs are controlled only by application of systemic insecticides. Neonicotinoids are one such group widely used on this crop. Raw cane is used for consumption. Fresh sugarcane juice, extracted from pressed cane with a mix of lemon juice and ice is a well-liked drink all over India. Since sugarcane products such as juice and syrup, may contain residues of pesticides (Mussen & Oliver, 2012; Zuin et al., 2006), it becomes imperative to develop methods to determine pesticide residues in these products. Sugarcane juice is a complex medium that is rich in carbohydrates, proteins, minerals and vitamins. So a selective sample preparation technique is required to eliminate the co-extractives during analysis.

The neonicotinoids are one of the new major classes of insecticides, derived synthetically from nicotinoids. In India, five neonicotinoids viz., imidacloprid, acetamiprid, thiacloprid, thiamethoxam and clothianidin are widely used (Kapoor et al., 2013; Pradnya & Pandurang, 2014) (Fig. 1). Neonicotinoid insecticides act as agonists at the insect nicotinic acetylcholine receptor. They are active against many sucking and biting pest insects, including aphids, whiteflies, some lepidopteran and coleopteran species (Larsen, Nuessly, & Cherry, 2016; Ramasubramanian, 2013; Santos, Borem, & Caldas, 2015; Timmeren, Wise, & Isaacs, 2012).

Analysis for pesticide residues is often carried out following different steps including solvent extraction, cleanup, concentration and final determination. Cleanup of extracts may result in the limited loss of some compounds but inadequate clean-up could compromise the quality of data obtained. The most commonly followed technique is liquid-liquid extraction. But the disadvantage with liquid-liquid partitioning is that it requires a large quantity of sample and solvents. In case of solid phase extraction, besides requiring a large volume of the solvents, the purification process is cumbersome. Due to the shortcomings of above stated methods, dispersive solid phase extraction (DSPE) was developed for the extraction of pesticides from fruits and vegetables (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003). This method consists of an acetonitrile extraction/partitioning and a dispersive solid phase clean up. The main advantages of these method are that it is less expensive and increases the recovery for pesticides with wide ranging polarities (Mojtaba, Najmeh, & Mahnaz, 2016; Yang et al., 2011).

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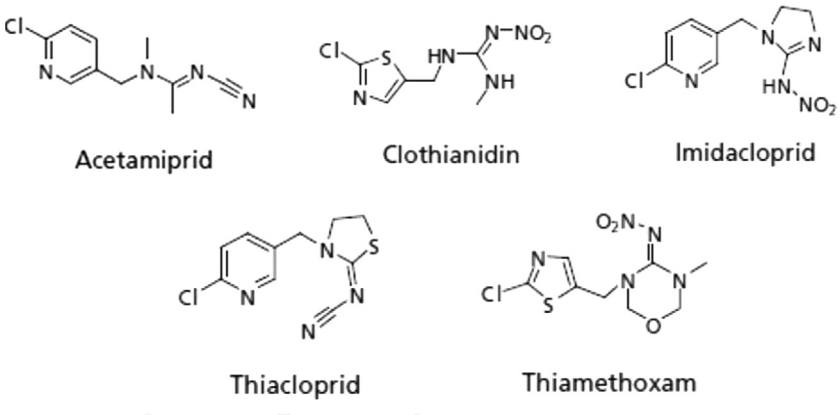

Fig. 1. Chemical structures of neonicotinoid insecticides.

Pesticide residue analyses in sugarcane are reported to be done by liquid-liquid extraction (LLE), matrix solid-phase dispersion (MSPD), solid-phase microextraction (SPME) using solvents such as ethyl acetate, methanol and acetonitrile, following which different clean up procedures are adopted. Subsequently, the samples are subjected to liquid or gas chromatography analysis, coupled with mass detectors. Fumes, Andrade, Neto, and Lancas (2016); Furlani, Marcilio, Leme, and Tfouni (2011) and Aysal, Ambrus, Lehotay, and Cannavan (2007), followed QuEChERS method for preparation of sugarcane juice samples and detected pesticide residues using GC-ECD and GC–MS.

The residues of neonicotinoid insecticides in different matrices are mainly determined by liquid chromatography techniques (Galeano et al., 2013; Karmakar, Singh, & Kulshrestha, 2012; Maicon, Tomasini, Cardoso, Caldas, & Primel, 2012; Ramasubramanian, Paramasivam, & Jayanthi, 2012; Fernandez, Otero, & Gandara, 2015). Gas chromatography is not suitable for analysis of neonicotinoid residues, as neonicotinoids are characterized by low volatility and high polarity.

Many studies have been conducted on neonicotinoid residues in fruits and vegetables. However, the studies on neonicotinoid residues in sugarcane is limited. This report summarises effective sample treatment procedures based on dispersive solid phase extraction (DSPE) and a validated method for residue determination of five neonicotinoid insecticides in sugarcane.

2. Materials and method

2.1. Apparatus

A Waters Alliance 2695 Separations unit equipped with an autosampler, quaternary solvent delivery pump and waters analytical column C18, 5 µm (4.8 × 250 mm), was used for chromatographic separation. Mass spectrometry was achieved in Acquity Tandem Quadrapole Detector with an ESI interface. In remote control mode, the Waters software Masslynx version 4.1 was used for instrument operation, analysis and data acquisition.

2.2. Reagents and standards

Acetonitrile and Formic acid of MS grade were purchased from Sigma Aldrich. Magnesium sulfate and anhydrous sodium chloride (analytical-reagent grade), purchased from Merck India Ltd., were heated at 650 °C for 4 h before use and kept in desiccators. Primary secondary amine (PSA) was obtained from M/s. Agilent Technologies. Distilled water purified at 18.2 MΩ with a lab scale Q3 Merck Millipore unit was used during the whole analysis. The certified reference materials of all the selected five neonicotinoid pesticides *viz.*, acetamiprid, imidacloprid, thiacloprid, thiamethoxam and clothianidin were purchased from Sigma Aldrich and were > 90% (w/w) pure.

2.2.1. Preparation of standard solutions

2.2.1.1. Primary stock solution. Stock solutions (1000 µg ml^{-1}) of acetamiprid, imidacloprid, thiacloprid, thiamethoxam and clothianidin were prepared by dissolving the technical grade material in acetonitrile (v/v) separately. These were labeled and stored in a refrigerator at −20 °C.

2.2.1.2. Intermediate stock solution. An intermediate stock solution of 100 µg ml^{-1} for each insecticide was prepared by transferring one ml of stock solution to a 20 ml graduated test tube and diluting to 10 ml with MS grade acetonitrile. An intermediate stock solution of 10 µg ml^{-1} was prepared from this by mixing appropriate quantities of each pesticide stock solution and diluted accordingly.

2.2.1.3. Working standards. Working standard solutions of individual pesticides (0.005–1 µg ml^{-1}) were prepared by diluting intermediate stock solution. These working standards were used to find out the retention time of these compounds and for quantitation of residues in samples. All the stock and working standard solutions were stored in a refrigerator at −20 °C until further use.

2.3. Sugarcane samples

The cane procured from non-treated fields from Tamil Nadu in India was used for juice extraction. The extracted juice was stored in glass bottles and analysed following the procedure described below and those samples showing the absence of target analytes were only used in the recovery study.

2.4. Sample extraction and clean-up

2.4.1. Sample extraction

Sugarcane juice extracted from the canes was filtered. Then, a representative sample of 10 g of the juice was accurately weighed into a 50 mL centrifuge tube. The samples were spiked at levels of 0.005, 0.01, 0.025, 0.05 and 0.1 µg g^{-1} and replicated sevenfold. To this, 20 mL acetonitrile was added and vortexed for 20 min. About four grams of anhydrous $MgSO_4$ and one gram of NaCl were subsequently added and vortexed. Further, the contents were centrifuged at 6000 rpm for 10 min.

2.4.2. Sample clean-up

After centrifuging, six ml of supernatant aliquot was transferred into a 15 ml centrifuge tube containing 200 mg Primary Secondary Amine (PSA) and 600 mg anhydrous $MgSO_4$. The mixture was vortexed for one minute and then centrifuged for 10 min at 3000 rpm. The upper extract was filtered through a 0.2 µm syringe filter. Of this, 4 ml was transferred into a turbovap tube and concentrated to dryness under a gentle stream of nitrogen in a turbovap LV at 40 °C. The final volume was