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Analytical Methods

Development of a simple extraction and oxidation procedure for the residue analysis of imidacloprid and its metabolites in lettuce using gas chromatography

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ABSTRACT

Simple extraction and optimised oxidation procedures were developed for the determination of the total residues of imidacloprid and its metabolites (containing the 6-chloropicolyl moiety) in lettuce using a gas chromatography-micro electron capture detector (GC-μECD). Samples were extracted with acetonitrile, and the extract was then evaporated. The remaining residues were dissolved in water and oxidised with potassium permanganate to yield 6-chloronicotinic acid (6-CAN). The acid residues were further dissolved in *n*-hexane:acetone (8:2, v/v) and then silylated with MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide) to 6-chloronicotinic acid trimethylsilyl ester. Calibration curves were linear over the concentration ranges (0.025–5 μg mL^{-1}) with a determination coefficient (r^2) of 0.991. The limits of detection and quantification were 0.015 and 0.05 mg kg^{-1}, respectively. Recoveries at two fortification levels ranged between 72.8% and 108.3% with relative standard deviation (RSD) lower than 8%. The method was effective, and sensitive enough to determine the total residues of imidacloprid and its metabolites in field-incurred lettuce samples. The identity of the analyte was confirmed using gas chromatography–tandem mass spectrometry (GC–MS/MS).

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1. Introduction

The world's population is estimated to grow to 9.22 billion by 2075 (UN, 2004). Along with this rapid population growth, worldwide demand for food will increase, and potentially the need for pesticide use. Although humans are exposed to small amounts of pesticide residues after being metabolised by plants or decomposed by environmental agents, long-term exposure to pesticide residues could result in chronic diseases, such as cancer (Carrozza, Li, Wang, Horel, & Cooper, 2009). It is therefore necessary to predict the residual amounts of pesticides during cultivation periods, in order to prevent the distribution of contaminated agricultural products to consumers.

The neonicotinoids are amongst the most effective insecticides used to control a variety of insect pests (Elbert, Haas, Springer, Thielert, & Nauen, 2008; Gupta, Sharma, & Shanker, 2008; Hem, Abd El-Aty, Park, & Shim, 2012). Among them, imidacloprid is being extensively used in agricultural crops to control sucking insects such as aphids, leafhoppers, psyllids, thrips, whiteflies, and beetles. Imidacloprid is a relatively non-volatile, polar ($\log K_{ow}$ = 0.57, Tomlin, 2000) systemic insecticide with low toxicity for warm-blooded animals, and good plant compatibility (Schmuck, Nauen, & Ebbinghaus-Kintscher, 2003). It is an agonist for the nicotinic acetylcholine receptor (nAChR), leading to paralysis and death of insects (Buckingham, Lapied, Le Corrone, Crolleau, & Sattelle, 1997; Suchail, Guez, & Belzunces, 2001; Thrap, Johnson, & Onsager, 2000).

Many studies have demonstrated the action of imidacloprid in soil, water, and its metabolism in plants, and animals (Rouchaud, Gustin, & Wauters, 1996; Schulz-Jander & Casida, 2002). A total of 40 metabolites have been identified, among which 16 (containing the 6-chloropicolyl moiety) were found in plants (FAO, 2002), some of which are potentially toxic (Schmuck et al., 2003). According to Codex regulations (Codex Alimentarius, 2011), imidacloprid residues have been defined as the sum of imidacloprid and its metabolites containing the 6-chloropicolyl moiety. However, in the Republic of Korea, the residues of imidacloprid are limited to

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the parent compound (RDA, 2012). National policy is being changed to meet Codex regulations and various others. Thus, a simple and effective analytical method is needed to estimate the residue levels of the parent compound and perhaps its metabolites.

A method for the determination of pesticide residues in edible plants such as leafy vegetables is necessary since potential human exposure is expected to be greatest from vegetables that are consumed raw. Leafy vegetables form an important component of the human diet, and are typically low in calories and fat, but high in protein, dietary fibre, iron, calcium and phytochemicals. Lettuce was identified as one of the agricultural crops produced in the Republic of Korea that have high amounts of pesticide residue (KFDA, 2004). This is because the surface area of the leaves is large and rough, the deposit ratio is high, growth duration is short, and degradation time longer than the cultivation period (KFDA, 2004). The determination of trace-level pesticide residues in plants presents greater challenges due to pigments and fatty or waxy materials, which may cause matrix interference. Therefore, a prerequisite for analysis in plant samples is an effective sample preparation that eliminates potential interference, while ensuring maximum recovery.

The accumulation of pesticides in agricultural products is of great concern because plants act as intermediates in the transport of contaminants from soil, water, and air to humans and fauna. This situation has led to regulations setting maximum residue limits (MRLs) of pesticides in different agricultural commodities (Barriada-Pereira, Serôdio, González-Castro, & Nogueira, 2010). Efficient sample preparation and convenient instrumentation are important issues for trace-level analysis because of the complex nature of food matrices and the low concentrations of contaminants present. Recently, QuEChERS (quick, easy, cheap, effective, rugged, and safe), has become an attractive alternative to classical sample preparation methods. The method is based on a single-step acetonitrile extraction and salting out by liquid–liquid partitioning from the water in the sample with $MgSO_4$, followed by a dispersive-SPE clean up (Anastassiades, Lehotay, Štajnbaher, & Schenck, 2003). QuEChERS still relies on rapid liquid chromatography–mass spectrometry (LC/MS) and gas chromatography–mass spectrometry (GC/MS) analytical methods to achieve wide analytical scope, good quantification, high precision, low detection limits, adequate robustness, acceptable sample throughput, and the degree of selectivity needed to make analyte identifications (Lehotay, Koesukwiwat, van der Kamp, Mol, & Leepipatpiboon, 2011). These approaches, generally, require a clean-up step to reduce interference, improve detection limits and avoid peaks overlapping (Barriada-Pereira et al., 2010).

Existing imidacloprid analytical methods are primarily based on LLE and HPLC-UVD analysis (Ferandaz-Alba, Valverde, Agiiera, Contreras, & Chiron, 1996; Ishii et al., 1994; Khay, Abd El-Aty, Cho, et al., 2008; Liu et al., 2005; Rossi, Sabatini, Cenciarini, Ghini, & Girotti, 2005). Imidacloprid and its metabolites have been analysed individually using liquid chromatography–tandem mass spectrometry (LC–MS/MS), high performance liquid chromatography with fluorescence detector (HPLC-FLD), HPLC with electro chemical detector (HPLC-ECD), or HPLC with diode-array detection (HPLC-DAD) (Frenich, González, Vidal, Vázquez, & Sánchez, 2000; García, Galera, Valverde, Galanti, & Girotti 2007; Rancan, Sabatini, Achilli, & Galletti, 2006). Electrospray ionization (ESI) is susceptible to matrix components, which may result in signal suppression or isobaric interference, and therefore decrease the assay sensitivity. To reduce matrix effects, an additional step involving SPE cartridge clean up is needed. Placke and Weber (1993) and Lodevico and Li (2002) developed analytical methods for the determination of imidacloprid and its metabolites in plant materials and coffee. The method was developed based on liquid–liquid extraction (LLE) and oxidation procedures to yield 6-chloronicotinic acid. Imidacloprid and its metabolites (containing 6-chloropicolyl moiety) were analysed as 6-chloronicotinic acid trimethylsilyl ester using GC/MS. The GC method was ruled out from analysis because imidacloprid has low volatility (Navalón, González-Casado, El-Khattabi, Luis Cilchez, & Fernández-Alba, 1997).

The steps in the development of environmental methods involve the ability to extract the analyte(s) of interest with some degree of precision and accuracy from an environmental matrix, and the ability to accurately identify and measure the analytes at low (environmentally relevant) concentrations (Jones-Lepp, Sanchez, Moy, & Kazemi, 2010). The present study focuses on the development of simple extraction and effective oxidation procedures for the chromatographic determination of the total residues of imidacloprid and its metabolites (containing the 6-chloropicolyl moiety) in lettuce using QuEChERS (with no clean up) and GC-μECD. The method was applied to residue analysis of field-incurred samples. The identity of the analytes were confirmed using gas chromatography–tandem mass spectrometry (GC–MS/MS).

2. Experimentaland gas chromatography

2.1. Chemicals and reagents

Imidacloprid (99%) and its metabolites (6-chloronicotinic acid (97.5%) and urea-imidacloprid (99%)) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Other metabolites, 5-hydroxy-imidacloprid (96.7%) and olefin–imidacloprid (97.7%) were donated from Bayer CropScience (Seoul, Republic of Korea) (Fig. 1). Acetonitrile (ACN), ethyl acetate (EtOAc), *n*-hexane, and acetone were purchased from Burdick and Jackson (Ulsan, Republic of Korea). MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide), sodium bisulphite, and potassium permanganate were purchased from Sigma–Aldrich (Missouri, USA). Anhydrous magnesium sulphate, sodium acetate, and sodium sulphate were supplied by Junsei Chemical Co. Ltd. (Kyoto, Japan). Acetic acid, sulphuric acid, and sodium hydroxide were purchased from Daejung Chemicals & Materials (Siheung, Republic of Korea) and Duksan Pure Chemicals Co. Ltd. (Ansan, Republic of Korea).

2.2. Standard solution preparation

Standard solutions of imidacloprid were prepared in ACN at 100 $\mu g\ mL^{-1}$, and its metabolites (6-chloronicotinic acid, 5-hydroxy-imidacloprid, olefin-imidacloprid, and urea-imidacloprid) were prepared in EtOAc at 100 $\mu g\ mL^{-1}$. All standards solutions were stored at −40 °C. Stock solutions were diluted with an appropriate amount of EtOAc to create working solutions, which were used to spike samples. Calibration standards (0.025–5 $\mu g\ mL^{-1}$) were prepared by the diluting the 6-chloronicotinic acid stock using 2% acetone in *n*-hexane. All metabolites were converted to 6-chloronicotinic acid when oxidised.

2.3. Greenhouse experimental

Experimental trials were conducted in a greenhouse located at Chonnam National University, Gwangju, Republic of Korea. Commercial imidacloprid (WP, Conido®, 8% active ingredient, Dongbu HiTek, Seoul, Republic of Korea) was sprayed on to lettuce twice at an interval of 7 days, as recommended by the manufacturer. Following the second application, samples were collected after 1, 3, 5, 7, 10, and 14 days after application. An untreated plot was used as a control (blank). Samples were collected and transferred to the laboratory in sealed bags, chopped, mixed with other samples from the same plot, packed in plastic bags, and stored at −20 °C pending analysis.

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