

Ultra high performance liquid chromatography technique to determine imidacloprid residue in rice using QuEChERS method

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Abstract

Imidacloprid residue analysis in paddy samples was conducted using the simplified and validated QuEChERS preparation method. Samples were extracted with acetonitrile (ACN) and salts anhydrous magnesium sulphate (MgSO₄) and sodium chloride (NaCl) while cleaning was by treating with primary secondary amine (PSA). Imidacloprid residue was quantified with Ultra High Performance Liquid Chromatography (UHPLC) using short and narrow C18 column to reduce analysis duration and solvent consumption. The pumps were programmed to mix acetonitrile and water at a ratio of 2:8 to form the mobile phase, with a flow rate of 0.1 mL/min and 10 µl injection volumes. Imidacloprid was detected at 270 nm using UV detector. The method was validated in term of linearity, range, limit of detection (LOD), limit of quantification (LOQ), precision (repeatability and intermediate precision), and accuracy (recovery). The LOD was 0.001 mg/L whereas LOQ was 0.003 mg/L. The validated method provides good analytical results wherein the linearity r² was 0.9996, recoveries 80–120% and RSDs <20%. This method can be implemented in routine laboratories as it yields a higher sample throughput and reduced solvent consumption compared to the traditional Luke method approach.

Keywords

Imidacloprid
QuEChERS
UHPLC-UV
Rice

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Introduction

Pesticide residues in food are unnecessary and a preventable contamination. The residue uptake through diet has raised public concern nowadays (Kumar and Dikshit, 2001; Sahoo *et al.*, 2012). Periodic residue monitoring is being performed in food products mainly for the regularly consumed food to avoid any significant risk to human health. Maximum Residue Level (MRL) presents a set of legally permitted maximum level for pesticide residue in food items. Rice (*Oryza sativa* L.) is one of the most important staple food for the world's population, ranking third after wheat and maize in terms of production and consumption (Akinbile *et al.*, 2011). About half of the total world's rice productions are from China (194.3 million tonnes) and India (148.3 million tonnes) (Laborte *et al.*, 2012). Malaysia is at the 25th place with a total production of 2.4 million tonnes per season.

The extensive use of pesticides in agriculture field is mainly due to pest problems. Brown planthopper (BPH, *Nilaparvata lugens*) is considered as one of the major paddy cultivation pests species in Southeast Asia (Wen *et al.*, 2009). Imidacloprid, a novel class

neonicotinoid insecticide has been used since the mid-1990s in many East Asian countries and Indochina to control this species (Matsumura *et al.*, 2008). In addition, imidacloprid is also widely used by farmers as an early plant growth enhancer and foliar spray besides for soil treatment and seed dressing in paddy cultivation. Imidacloprid is a colourless and odorless crystal with a molecular formula of C₉H₁₀ClN₅O₂ and a molecular weight of 255.7 g/mol. The insecticide is a non-volatile compound due to lower vapour pressure of 1.0 x 10⁻⁷ mm Hg (Fossen, 2006). Various types of the respective pesticides applied in agricultural processes have become an unavoidable part of the environment, and it's presence at a trace level in the final products could be a potential health hazards for human upon consumption.

Analysis of pesticides residue often begins with some sample preparation steps which mainly involve solvent extraction and clean-up before analyzed using instruments (Lehotay *et al.*, 2010) and numerous methods have been developed to determine the concentration of pesticides residue in food matrices. However, presently QuEChERS (quick, easy, cheap, effective, rugged, and safe) method is being widely employed in the analysis of multi -pesticides residues

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in food matrices as compared to the traditional Luke extraction procedure that is more complicated and tedious. The latter method combined an initial salting out liquid-liquid extraction and a dispersive solid phase extractions (d-SPE) for cleanup. The initial extraction uses acetonitrile followed by anhydrous magnesium sulfate (MgSO_4) along with some buffering salts that induces partitioning, to salt out water from samples. At cleanup stage, primary secondary amine (PSA) and anhydrous MgSO_4 are employed to remove organic acids from the sample matrix, and reduce excessive water in the extract respectively.

Gas chromatography (GC) and high performance liquid chromatography (HPLC) coupled with different types of detectors are commonly used by researchers as analytical equipment for pesticide residue analysis (Kruve *et al.*, 2007). However, HPLC is more preferable compared to GC due to low volatility and thermally unstable nature of imidacloprid besides being a highly polar molecule. To date, liquid chromatography system combined with mass spectrometry (LC-MS) has become a trend in term of specificity and sensitivity to analyzing pesticide residue. Yet, HPLC with conventional UV detection or diode array detection (DAD) is still commonly used in most research laboratories as a routine method. This is because LC-MS is an expensive instrument as compared to the conventional HPLC-UV and DAD method (Obana *et al.*, 2003; Baig *et al.*, 2012; Zhao *et al.*, 2012; Bilehal *et al.*, 2014; Akoijam *et al.*, 2014).

An improved version of HPLC, the Ultra High Performance Liquid Chromatography (UHPLC) provides many advantages ranged from analysis time as well as chromatographic resolution to speed and sensitivity of analysis. Cost of analysis including solvent consumption and analysis time are the main concern for analytical laboratories. Fast analysis also indicates reduced solvent consumption. UHPLC uses fine particles ($<2.0 \mu\text{m}$) column as stationary phase compared to the traditional ($5 \mu\text{m}$) columns enabling a much faster analysis with reduced solvent consumption (Bilehal *et al.*, 2014). A number of studies also found that UHPLC is more sensitive than the conventional HPLC system (Jerkovich *et al.*, 2005; Churchwell *et al.*, 2005; Leandro *et al.*, 2006; Desai and Thaker, 2012; Bilehal *et al.*, 2014). The QuEChERS method, on the other hand, effectively covers a very wide analyte scope, including highly polar pesticides as well as highly acidic and basic ones. Additional advantages of the method includes high sample throughput and low amounts of solvent, glassware, and bench space required. The method was primarily designed for low-fat commodities, but

commodities with intermediate or high fat contents can also be analyzed when certain aspects are taken into account (Lehotay *et al.*, 2005; Paya *et al.*, 2007; Wilkowska *et al.*, 2011).

Thus, the objective of this paper is to report a simple, relatively fast and efficient QuEChERS method using UHPLC-UV technique to analyze imidacloprid residue in rice samples. It aids the screening purposes, conducted mainly to ensure that the residue in food products does not exceed the national MRL. In this procedure, original QuEChERS method was optimized according to UHPLC-UV condition for analysis and the method was validated based on linearity and range, limit of detection (LOD) and quantification (LOQ), precision (repeatability and intermediate precision), and accuracy (recovery).

Materials and Methods

Chemicals and standards

HPLC grade acetonitrile (ACN) was purchased from Friendemann Schmidt Chemical (Australia) and water was purified using Elga /UK Pure Water System Model: Purelab S and BP MK1 (resistivity $18.2 \text{ M}\Omega \text{ cm}$) water purification system. Imidacloprid analytical standard (purity $> 99\%$) was procured from Fluka Sigma-Aldrich (Malaysia) for analytical purposes. The stock standard solution was prepared at 1 mg/mL in acetonitrile and stored in the darkness at -20°C . Intermediate working standards for imidacloprid were prepared at 1, 5, and 10 ppm used to establish the analytical curve. The salts anhydrous magnesium sulphate (MgSO_4) and sodium chloride (NaCl) and primary secondary amine (PSA) included in roQ QuEChERS kit were purchased from Phenomenex for extraction and cleanup. Ceramic homogenizer was purchased from Agilent to break salt agglomerates, promoting consistent sample extraction and increasing product recovery during extraction and dispersion.

Extraction procedure

The extraction and clean up of imidacloprid residue in paddy sample in this study was done using QuEChERS method followed by EN 15662, an original non-buffered method, introduced by Anastassiades *et al.* (2003). This method was specifically developed for pesticides screening in cereal grains such as corn, oats, rice and wheat. The extraction procedure involved homogenization of the representative subsample and grounding with Waring blender through cryogenic milling technique. Then, 5 g of the comminuted homogenous and frozen sample were weighed using a calibrated balancing scale and

mixed with 10 mL each of ultrapure water and ACN in a 50 mL screw cap centrifuge tube. After that, 4 g of anhydrous magnesium sulphate (MgSO_4) and 1 g of NaCl from roQ QuEChERS extraction kit were added into the centrifuge tube that was successively closed and shaken vigorously by hand for 1 minute. The tube was then centrifuged for 5 minutes at 4000 rpm to separate solid materials from the liquid layers. Clean-up and removal of excessive residual water was done by a rapid dispersive solid-phase extraction (d-SPE) procedure in which 1 mL of supernatant from the extraction process was pipette into 2 mL screw cap tube containing 150 mg of MgSO_4 and 25 mg of PSA. The tube was closed and shaken vigorously by hand for 30 seconds followed by 5 minutes centrifugation at 4000 rpm to separate solid materials from the liquid layer. The d-SPE with PSA will effectively removes polar matrix components. The supernatant was then filtered through a 0.22 μm Thermo-filter and transferred into 2.0 mL amber vials prior to the UHPLC-UV analysis.

UHPLC-UV analysis

UHPLC system (Perkin Elmer Flexar FX-15 system, USA) is equipped with a binary pump, an auto sampler, a thermostatted column oven and a UV-detector. Chromera™ software was used for instrument control, data acquisition and processing. The chromatographic separation was carried out using reverse phase column C18 Brownlee HRes, measuring 30 mm in length, 2.1 mm inner diameter, and 1.9 μm particle size from Perkin Elmer (USA) as a stationary phase. ACN and water were used as mobile phase. The mobile phase was filtered through 0.45 μm nylon Whatman filter paper before injected into UHPLC system. The pumps were programmed to mix and thrust the mobile phase at a ratio of 2:8 acetonitrile to water with a flow rate of 0.1 mL/min and 10 μl of injection volume. The total run time for each analysis was programmed to be 1.5 minutes. Mobile phase was allowed to flow for 5 minutes at 0.1 mL/min after each run to remove traces of analyte that may cause contamination in the subsequent analysis. Imidacloprid was detected at 270 nm using UV detector. The retention time of imidacloprid under these conditions was 0.435 minutes.

Method validation

Method validation is a process that verifies if an analytical procedure matches the laboratory and instrument condition for the intended analysis. To ensure data credibility in the quantitative residue analyses, sample preparation was thoroughly validated considering parameters like recovery,

precision (relative standard deviation), determination coefficient (R^2), linearity, limit of detection (LOD) and limit of quantification (LOQ). In the present study, method was validated following the established European Union guidelines on quality control procedures for pesticide analysis (EU, 2007)

Linearity

The quantification of imidacloprid was based on six-point calibration curve with concentration ranging from 0.1 to 2 mg/L. The calibration standards were dissolved in the 100% ACN. Three replicates were made for each concentration against which the detector's responses were plotted. Regression equation with slope, y-intercept and coefficient of correlation (R^2) were evaluated for imidacloprid.

Recovery

Recovery describes the efficiency of separating analyte from the sample (Kruve *et al.*, 2008). In this present study, the extraction recovery was tested using certified organic paddy sample as a reference matrix. The organic paddy samples obtained from Kahang organic rice eco farm (KOREF) Johor, was free from pesticides. Experiments were performed by spiking the reference matrix with imidacloprid standard at two different concentrations (0.05 and 0.10 mg kg^{-1}).

Precision

Method precision was demonstrated via inter-day and intra-day variation studies. In intra-day studies, imidacloprid standard at known concentrations was injected five repeated times and the results were expressed as % RSD of the measurement. For inter-day variation, five repeated injections of standards were done for five consecutive days and the response factor of imidacloprid peak and percentage RSD were calculated.

Limit of Detection (LOD) and Limit of Quantification (LOQ)

The LOD and LOQ were determined by signal-to-noise (S/N) approach. The noise and signal were measured experimentally on chromatogram. LOD and LOQ were determined at S/N ratio of 3 and 10, respectively.

Results and Discussions

A typical chromatogram from the analysis is shown in Figure 1 that illustrates the retention time for imidacloprid. The residue was detected in rice sample at 0.43 minutes.

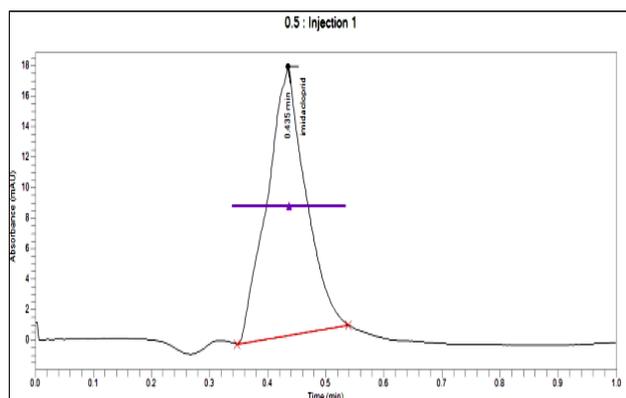


Figure 1. Chromatogram of a standard solution of imidacloprid (0.5 ppm)

UHPLC-UV analysis

While analyzing pesticides residue in cereal matrices, for instances wheat, oats and rice, co-extracted organic matters might produce interfering peaks on liquid chromatograms (Schwedler *et al.*, 2000; Koesukwiat *et al.*, 2010). However, this can be overcome by prior analytical method validation. In the present study, QuEChERS sample preparation procedure for UHPLC-UV analysis was validated to determine imidacloprid residue in paddy grains. In QuEChERS procedure, the extracts were purified by liquid-liquid partitioning followed by d-SPE for further purification. The cleanup procedure described, effectively removes the potentially interfering co-extractives from samples. Separation of imidacloprid was conducted on a Brownlee HRes C18 column using isocratic acetonitrile and water mixture as mobile phase. The signal for imidacloprid was monitored at 270 nm. Previous studies showed similar instruments conditions and the peak of analyte was completely resolved (Ishii *et al.*, 1994; Xie *et al.*, 2009; Wang *et al.*, 2012; Ying and Kookana, 2012; Akoijam *et al.*, 2014).

Linearity

Figure 2 shows the 5-point calibration curve for imidacloprid. The calibration curve was constructed by plotting concentration of imidacloprid standard versus peak area. Linear equation for the calibration curve was obtained for concentration ranging from 0.1-2 ppm. The linear equation ($Y = 356314.0725x + 39983.2015$) and R^2 (0.9996) were obtained which R^2 value was > 0.999 indicating a good linearity and a precise linear relation exist between the injected imidacloprid amount and the corresponding peak area. This is supported by Al-Rimawi (2014) which stated that R^2 was required to be at least 0.990 and typically exceeded 0.995 for accurate quantification. Moreover, R^2 values > 0.99 explains that peak height has a similar trend

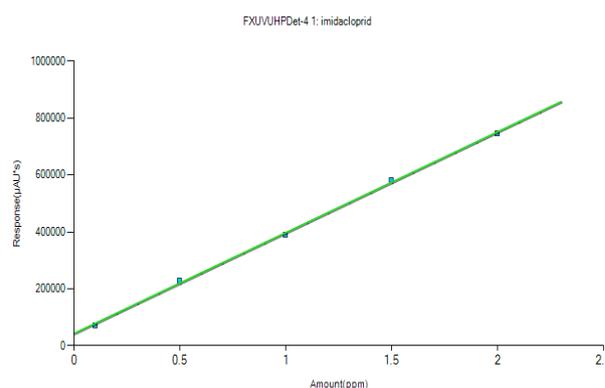


Figure 2. Calibration curve of imidacloprid

to relevant peak areas and therefore can be used for quantification purpose (Iqbal *et al.*, 2012).

Recovery and precision

Recovery is a measure of exactness of an analytical method, measured as the percentage of analyte recovered after spiking samples in a blank (Rimawi, 2014). Recovery also describes the efficiency of separating analyte from sample (Kruve *et al.*, 2008). Table 1 shows that the recoveries of imidacloprid from two spiked levels, 0.05 mg/kg and 0.1 mg/kg in paddy samples ranged from 92.2% to 96.1% with RSD between 2.5% to 4.5%. These results indicate that the current method has a good recovery rate. SANCO (2007) supports this by saying that mean recoveries for a sample should be in the range from 70-120% with a $RSD \leq 20\%$.

Precision is a measure of method repeatability under normal operation and is generally expressed as the relative standard deviations (RSD) of total samples (Rimawi, 2014). In this study, precision was evaluated based on RSD of intra- and inter-day tests. The intra-day precision was performed by analyzing rice sample spiked at two different spike concentrations, 0.05 and 0.1 ppm for five times in a day. The inter-day precision on the other hand was performed over 5 days by analyzing rice sample spiked at two different concentrations, 0.05 and 0.1 ppm (Chen and Li, 2012). Based on the result in Table 2, mean RSDs of intra- and inter-day tests ranged from 2.33% to 6.57%.

Limit of detection (LOD) and limit of quantification (LOQ)

Lowest concentration of analyte detectable and quantifiable with a stated degree of reliability is one of the many important parameters of any analytical method. Limit of detection is the lowest amount of analyte in a sample that can be detected but not necessarily quantified. Meanwhile, limit of

Table 1. Recoveries of imidacloprid from two spiked levels in rice sample

Spike concentration (mg/kg)	Recoveries (mean ± RSD)%	Intraday (%RSD)	Interday (%RSD)
0.05	96.08±2.47	2.33	6.57
0.1	92.24±4.54	6.45	5.14

quantification is defined as the lowest concentration which can be reproducibly quantified above baseline level. LOD determined on the basis of signal to noise ratio of 3:1 while LOQ was determined on the basis of signal to noise ratio of 10:1 (Sahoo *et al.*, 2012; Gao *et al.*, 2014). The LOD and LOQ of this method were 0.001 mg/L and 0.003 mg/L, respectively.

Applicability of the method

The developed method was applied to determine the imidacloprid residue in selected paddy and rice samples. Result of the analysis showed that most of the rice samples showed detectable imidacloprid residues with the concentration range from (0.564-0.792 mg/kg).

Conclusions

As a conclusion, the validated analytical method is applicable to verify the MRL compliance of imidacloprid residue in rice. The result of validation parameters conclude that the usage of UHPLC-UV in detecting imidacloprid residue in rice samples were acceptable. Moreover, this study also has led to the development of a relatively straightforward and reliable method for determination of imidacloprid residue rice samples.

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