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Determination of Chlorantraniliprole Residue in Soil by Gas Chromatography-Mass Spectrometry

Paramasivam, M.

ICAR-Krishi Vigyan Kendra, Tamil Nadu Agricultural University, Virinjipuram, Tamil Nadu (632 104) India

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Corresponding Author

Paramasivam, M.

✉: sivam25@gmail.com

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Abstract

Gas chromatography-mass spectrometry method was developed and validated for the quantification of anthranilic diamide insecticide chlorantraniliprole residues in soil. The soil samples were extracted with acetonitrile and dispersive solid phase extraction clean up. The average recoveries of chlorantraniliprole were in the range of 94.10-96.82% with reproducibility and repeatability was ranged between 0.17 to 1.90 and 0.97 to 1.22%, respectively. The limit of quantification of the analytical method was 0.01 µg g^{-1} and the matrix effect was less than 1%.

Introduction

Chlorantraniliprole, the first member of the new class of chemistry group belongs to anthranilic diamides. It has been used to control a wide range of pests belonging to the order of Lepidoptera, Coleoptera, Diptera and Isoptera species in food crops with the residual action on larvae and some adults through ingestion and contact routs of the entry (Bentley *et al.,* 2010). Chlorantraniliprole holds great promise in pest management as it exhibits outstanding insecticidal properties by activating a novel target, the ryanodine receptors channels leading to internal calcium store depletion that impairs regulation of muscle contraction and exposed insects lead to lethargy, paralysis and eventually to death (Bentley *et al.,* 2010). Chlorantraniliprole 18.5% SC (Suspension Concentrate) is recommended as a foliar spray for reducing the incidence of pests in vegetables (cabbage, chilli, okra, tomato, brinjal and bitter gourds), pulses (bengal gram, black gram and pigeon pea), rice, sugarcane and cotton (CIBRC, 2020). Chlorantraniliprole is new insecticide registered in India against eggplant shoot and fruit borer due to its low mammalian toxicity and wide spectrum of activity.

The dissipation of chlorantraniliprole has already been studied in corn, rice, okra and tomato crop ecosystems at varied levels of field doses under different edaphoclimatic conditions by adopting unique analytical methods (Dong *et al.,* 2011; Zhang *et al.,* 2012; Paramasivam and Bhuvaneswari, 2022; Paramasivam, 2020; Malhat *et al.,* 2012). However, information on the analysis of chlorantraniliprole residue in soil is few among the published research work. Pesticide effects are not limited to direct effects on human and animal (Salama *et al., 2022*); they also affect the properties of soil earthworms and arthropods. Increasing worldwide need for higher agricultural productivity can only be reached by an extensive use of pesticides. Soil is considered the most main agricultural resource, which has high ability to retain pesticides by direct application or spillage or rain wash. Hence, the present study was carried out to determination of chlorantraniliprole residue in soil by employing gas chromatography-mass spectrometry method.

Materials and Methods

Chemical and Reagents

Chlorantraniliprole (98.3%) was purchased from Sigma Aldrich, Bangalore, India. The HPLC grade Lichrosolv of

Acetonitrile (≥ 99.8%), acetone (≥ 99.8%) and hexane (≥ 95%), analytical grade NaCl (≥ 99%) and anhydrous MgSO$_4$ (≥ 99.5%) were obtained from M/s Merck Life Science Private Ltd., Mumbai, India. Primary secondary amine (40 μm particle size) was purchased from Agilent Technologies, Palo Alto, CA, USA.

Preparation of Standard Solutions

The chlorantraniliprole (400 μg mL^{-1}) standard solution was prepared with a mixture of solvents (acetone: hexane, 1:1, v/v) by dissolving the known amount (10.18 mg) of chlorantraniliprole in 25 ml volume. The intermediate standard of 40 μg mL^{-1} was obtained from the 400 μg mL^{-1}, from which the calibration and matrix-match solutions of 0.003, 0.01, 0.05, 0.1, 0.5 and 1.0 μg mL^{-1} were prepared and stored at -20 °C.

GC-MS Determination

Chlorantraniliprole residue was detected and quantified using gas chromatography (Shimadzu 2010 GC) mass spectrometry (Shimadzu GC-MS QP 2010 plus). The capillary (DB-1MS) column (30 m × 0.25 mm × 0.25 μm) was used to separate the chlorantraniliprole from the soil. The temperatures of injector, interface and ion source were set at 250, 280 and 250 °C, respectively. The helium was used as carrier gas at a constant flow rate of 0.98 mL min^{-1}. The column oven program was started at 60 °C (1 min), increased at the rate of 20 °C min^{-1} at 200 °C, followed by 2 °C min^{-1} to 220 °C and finally, increased at the rate of 20 °C min^{-1} to 280 °C min^{-1} (5 min). The mass spectrometry was operated in an EI mode at 70 eV. The acquisition of the data was done in the total ion chromatogram with the 60-600 m/z mass range. The ions of chlorantraniliprole pesticide were selected, as per characteristic features of the mass spectrum obtained in the full-scan mode and by comparison with the NIST library spectral data bank. GCMS solution 2.5 software of Shimadzu Corporation, Japan was used to analyze the output chromatograms.

Method Validation

The method assay was performed with the validation parameters of linearity, limit of quantification (LOQ), specificity, recovery, repeatability (RSDr), reproducibility (RSDwr), matrix effect and retention time as per SANTE guidelines (SANTE, 2017). Linearity of the instrument was performed from six levels of concentration of chlorantraniliprole ranging from 0.003-1.0 μg mL^{-1}. The limit of quantification (LOQ) was evaluated by lowest spiking of chlorantraniliprole. The specificity was done as the response in reagent blank and a blank control sample of soil. The recovery study was carried out on soil (blank) sample by spiking the standard solutions of chlorantraniliprole at 0.01, 0.05 and 0.1 μg g^{-1} concentrations levels and replicated thrice. The repeatability of the analytical method was evaluated as relative standard deviation (RSDr) at fortified concentrations of 0.01, 0.05 and 0.1 μg g^{-1}. The reproducibility of the method was performed from ongoing method validation as within-laboratory reproducibility (RSDwr). The matrix effect was assessed in terms of response of signal enhancement or suppression by considering the response of both solvent and matrix-matched solutions. The acceptable retention time of chlorantraniliprole in the GC-MS chromatogram was examined from the calibration standard and matrix match standard solutions.

Experiment

To estimate the residue of chlorantraniliprole in soil, one (1 kg) of soil sample was collected at the experiment field of Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India. The soil samples were collected randomly from the plow layer (up to 15 cm depth) and samples were brought to the pesticide toxicology laboratory for further processes. The soil moisture content were removed under shade dry, ground and passed through 2 mm sieve. The field soil was sandy loam, pH (8.46), EC (0.29 ds m^{-1}), CEC (5.7 cmol (p+) kg^{-1}) and organic carbon (1.32%).

Extraction and Cleanup

A well-homogenized soil sample (10 g) were taken in a centrifuge tube (50 mL) was added with acetonitrile (20 mL). After vortexing the sample for about minute, the reagents of anhydrous MgSO$_4$ (4 g) and NaCl (1 g) were added to the contents, vortexed for a min and centrifuged at 6000 rpm for 10 min. The upper aliquot (6 mL) was taken to a centrifuge tube (15 mL) for dispersive-solid phase extraction cleanup and PSA (100 mg) and anhydrous MgSO$_4$ (600 mg) was added. Subsequently, the tubes were vortexed for about one minute and centrifuged for 10 min at 3000 rpm. The solvents (4 mL) were evaporated using a low volume evaporator and the residues were redissolved in mixed solvents of acetone and hexane (1 mL). The solutions were filtered using membrane syringe filter (0.2 μm) and analysed using GC-MS.

Results and Discussion

GC-MS Method Validation

The chlorantraniliprole residues in soil were detected, confirmed and quantified using the GC-MS method and the peak was eluted at 21.059±0.1 min. The selected ion monitoring (SIM) mode was used to determine the residues of chlorantraniliprole and considering the quantifier of 278 m/z and two qualifier ions of 280 and 243 m/z) were selected from the mass spectrum obtained in full scan mode. The linear equations (correlation coefficients) of chlorantraniliprole, both for solvent and soil matrix-matched standards were y = 309488x - 2213.5 (R^2 = 0.9994) and y = 311291x + 126.27 (R^2 = 0.9993), respectively, showed excellent linearity (Figure 1). The chlorantraniliprole residue was quantified (LOQ) at 0.01 μg g^{-1}. The reagent blank and samples blank were injected into the GC-MS for evaluating any interference that occurs at particular retention of chlorantraniliprole eluted and it was found that there is no peak was eluted. This indicates these are specific to particular samples and up to 30% of the response from blank samples was allowed as per SANTE guidelines (SANTE, 2017).

Matrix effects (ME) are known to occur frequently in any chromatographic methods and matrix match calibration standards were commonly used to nullify the matrix effects. The ME was assessed at the initial method validation stage
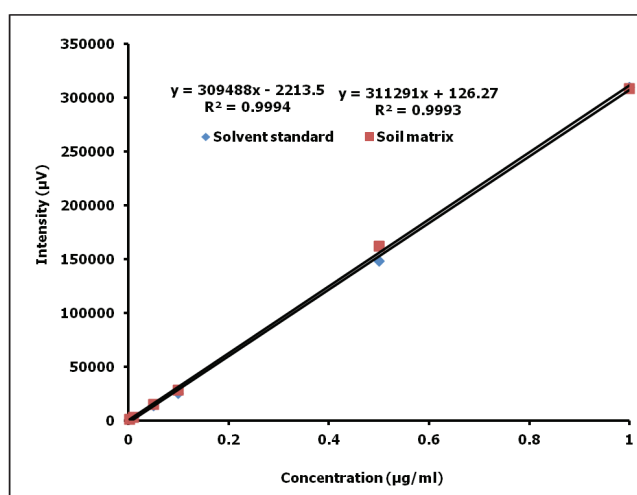
Figure 1: Linearity of chlorantraniliprole in GC-MS

using the extracts of blank (without chlorantraniliprole) matrix of soil for matrix match calibration. The calculated ME was less than 1% which was below the maximum threshold limit of 20% signal suppression or enhancement of SANTE guidelines (SANTE, 2017).

The recovery of chlorantraniliprole from soil was in the range of 94.10-95.69% at 0.01, 0.05 and 0.1 $\mu g\ g^{-1}$ levels of spiking and the corresponding RSDs were in the range of 0.16 to 1.79% (Table 1). The intra-laboratory comparison was performed as repeatability (RSDwr) and it was found in the range of 0.97 to 1.22%. The calculated ion ratio and retention time of target analyte was within the required limit of ± 30% and ± 0.1 min, respectively at all studied levels. Thus, the analytical procedure used to estimate the concentration of chlorantraniliprole in soil complied with SANTE guidelines (SANTE, 2017).

Table 1: Recovery of chlorantraniliprole in soil at different concentrations (n=3)

Spiked concentration ($\mu g\ g^{-1}$)	Recovered concentration ($\mu g\ g^{-1}$)	Recovery (%) ± SD	Reproducibility (RSDwr %)	Repeatability (RSDwr %)
0.01	0.009	94.10 ± 1.79	1.90	1.22
0.05	0.048	96.82 ± 1.01	1.04	0.97
0.10	0.096	95.69 ± 0.16	0.17	0.98

SD - standard deviation

Conclusion

To conclude, the sensitive GC-MS method was optimized to determine the chlorantraniliprole residue in soil with the limit of quantification of 0.01 $\mu g\ g^{-1}$.

Acknowledgment

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