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Method Validation and Application of Liquid Chromatography- Mass Spectrometry/Mass Spectrometry for Determination of Neonicotinoid Pesticide Residues in Tomato

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Abstract

A method employing dispersive solid phase extraction and quantification of five neonicotinoid insecticides by liquid chromatography-tandem mass spectrometry/mass spectrometry (LC-MS/MS) was optimized in tomato matrix. QuEChERS method was followed for residue extraction using acetonitrile as the extraction solvent. The validated method showed a linear range, from 0.025 to 0.5 µg mL^{-1} and detection and quantitation limits (LOD and LOQ) of 0.0015 to 0.008 µg g^{-1} and from 0.005 to 0.025 µg g^{-1}, respectively. Validation was based on analysis at five fortification levels and showed satisfactory recoveries (60.00% to 99.14%) and high precision (RSDs between 2.05% to 17.44%). The method is easy, with low consumption of reagents, is characterized by reliability, sensitivity and therefore is suitable for the monitoring the levels of neonicotinoid residues in tomato. Moreover, the developed method was successfully applied to quantify neonicotinoid residues in market samples of tomato.

Keywords: Neonicotinoid insecticides; Multi-residue analysis; Tomato; LC/MS/MS

Introduction

India is one of the largest producer of tomato in the world. Tomato is a major vegetable consumed all over India. The fruits are great source of vitamin C, potassium, folate and vitamin K and are the major dietary source of the antioxidant lycopene. Tomato crop is ravaged by severe pest and disease problems. To combat pests, farmers frequently apply various insecticides. Pesticides use in tomato production to reduce the food loss which result from occurrence of resistant pests is inevitable [1]. Neonicotinoid pesticides like imidacloprid and thiamethoxam are used for the management of sucking pests and mainly vector transmitted viral diseases in tomato [2-5].

The neonicotinoids are synthetic derivatives of nicotinoids introduced as an alternative to the organophosphates, N-methyl-carbamates and pyrethroid insecticides. The ease of applicability of these pesticides as foliar sprays to plants, soil drench, seed treatment and seedling dip has popularized its use among farmers [6-8]. The five neonicotinoids viz., imidacloprid, acetamiprid, thiacloprid, thiamethoxam and clothianidin are predominantly used in India for the management of sucking pests in vegetables, protected cultivation crops, cotton and fruit crops [9-12]. These systemic insecticides are not susceptible to ultraviolet light degradation, wash off or ozonisation. Pesticide residues on vegetables constitute a possible risk to consumers and have been a human health concern. In most countries, fresh vegetables and fruits produce sold at local markets is usually not analyzed for pesticide residues unlike export products are, which raises concerns about the perceived safety levels of local food supplies. Keeping in view the importance of residues of these neonicotinoid insecticides in vegetables, the present study was undertaken to develop a method for determination of residues in tomato as representative vegetable matrix and detection of residues in market tomato samples that are ready for consumption.

In vegetable matrix, pesticide residues are extracted by various methods involving liquid-liquid extraction [13], solid-phase dispersion [14], ultrasonic solvent extraction [15] and by QuEChERS method [16,17]. Solvents like methanol [14], acetone [18] and acetonitrile [19] are used for extraction by different researchers. Residues of volatile and thermally stable pesticides in vegetables were determined by GC-MS [19,20]. Neonicotinoid insecticides are characterized by low volatility and high polarity and their residues are amenable for determination by HPLC and LC/MS/MS [14,21-24].

This report summarizes effective sample treatment procedures based on dispersive solid phase extraction (DSPE) and a validated method establishing a multi-residue determination of five neonicotinoid insecticides in tomato. Also, this study aims to demonstrate the presence of neonicotinoids, if any, in tomato fruits that people commonly consume.

Materials and Methods

Apparatus

Liquid chromatography was performed in a Waters make Alliance 2695 Separations Module fitted with an autosampler, a membrane degasser and a quaternary pump. Mass spectrometry was performed in a Acquity TQD with an ESI interface. The LC separation was carried out in an XTerra analytical column C18, 5 µm (4.8 × 250 mm) (Waters, Milford, MA, USA). Analytical instrument control, data acquisition and treatment were performed by software Mass lynx version 4.1, 2005 (Waters, Milford, MA, USA).

Reagents and standards

Standards for of all 5 pesticides (acetamiprid, imidacloprid, thiacloprid, thiamethoxam and clothianidin) were purchased from Sigma Aldrich, Bangalore and were of purity >90% (w/w). LC-MS-grade acetonitrile and formic acid were purchased from Merck India Ltd. Water used for the experiments was purified by MilliQ ultra (Q3 Merck Millipore unit). Magnesium sulfate, anhydrous sodium chloride (analytical-reagent grade from Merck), were heated at 650°C for 4 h and kept in desiccators. Primary secondary amine (PSA) was obtained from Agilent Technologies.

Preparation of standard solutions

Stock standard solution of the five neonicotinoid insecticides were prepared by dissolving the technical grade material in acetonitrile (v/v) separately. The working standard solutions (0.05 to 1 mg L^{-1}) were prepared by dilution of the corresponding stock solution with acetonitrile. The obtained solutions were stored in a refrigerator -20°C until further use.

Sample preparation, extraction and clean up

The country tomato samples taken from untreated fields from Tamil Nadu was used for analysis. Tomato fruit samples were ground to a pulp using a high-speed blender. The pulp was stored in glass bottles and analyzed following the procedure described below.

A representative sample of 10 g of the fruit pulp was accurately weighed into a 50 mL centrifuge tube and mixed with 10 mL acetonitrile. The mixture was vortexed for 20 minutes. About four grams of anhydrous $MgSO_4$ and one gram of NaCl were subsequently added and again shaken well by vortexer, then centrifuged at 6000 rpm for 10 minutes. 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 Magnesium sulphate ($MgSO_4$). The mixture was vortexed for one minute and then centrifuged for 10 minutes at 3000 rpm. A 1-mL aliquot of the supernatant was transferred into a turbovap tube and dried under a stream of nitrogen in a turbovap LV at 40°C. The dried extract was then redissolved in 1 mL of acetonitrile and transferred into a 1.5 mL glass auto sampler vial for Liquid Chromatography Mass Spectrometry-Mass Spectrometry (LCMSMS) analysis.

Optimization of instrument conditions

Liquid chromatography was performed in a Waters Alliance 2695 Separations Module fitted with an autosampler, a membrane degasser and a quaternary pump. XTerra analytical column C18, 5 µm (4.8 × 250 mm) (Waters, Milford, MA, USA) was used for chromatographic separation. Analytical instrument control, data acquisition and treatment were performed by software Masslynx version 4.1, 2005 (Waters, Milford, MA, USA). The mobile phase was Acetonitrile: Water acidified with 0.1% formic acid (50:50, v/v). Aliquots of 10 µL were injected to the LC-MS/MS system using C18 column at a mobile phase flow rate of 0.5 mL min^{-1} and a run time of 10.0 min. The mobile phases were degassed for 15 min in a sonicator before use.

After separation by reversed-phase liquid chromatography using C18 column the five neonicotinoid insecticides were detected by Acquity triple Quadrupole mass spectrometry. Ionization of the pesticides was studied by using ESI interface in the positive (PI) ionization mode. The interface conditions were optimized for maximum intensity of the precursor ions as follows: capillary voltage 3.5 kV; desolvation (drying gas) and cone gas flows were set at 1100 and 50 L h^{-1}, respectively; collision gas flow was 0.18 mL min^{-1}; source block and desolvation temperatures were 150 and 500°C, respectively. Nitrogen was used as desolvation and cone gas, and the collision gas was Argon. Tuning was done by infusing dilute solution of standards @ 20 µL/min and the voltages on the lenses were optimized in Tune Master (Mass Lynx software). The chromatograms were recorded in full scan mode with positive ESI interface. Pesticides were identified according to their retention times, target and qualifier ions in their MRM mode.

Method performance

The method was validated by the following parameters: specificity, linearity, limits of detection and quantification, recovery, precision and accuracy. All the analyses were carried out using the same blank sample of tomato fruit.

Specificity: The specificity of the analytical method for neonicotinoids detection was confirmed by obtaining positive results from tomato fruit sample containing the analytes barring control samples.

Linearity studies: To study linearity, solvent matched standards calibration curves were created by injecting the pesticide mix in the concentration levels 0.025, 0.05, 0.1, 0.25 and 0.5 µg mL^{-1} in LC-ESI-MS/MS with three replicate injections per concentration. A sample volume of 10 µL was injected by an autosampler. The first calibration level was lower than, the MRLs established by the Codex Alimentarius Commission for the five neonicotinoid insecticides.

Detection and quantification limits: The LOD were calculated from the standard deviation associated with the measurement of the pesticide taken during recovery and students t value. For this purpose, 7 independent analyses of a tomato fruit sample spiked with pesticides at a level of 0.025 µg g^{-1} were performed. The one-sided t-distribution was determined using the mean value and standard deviation of replicate injections, and was multiplied versus the determined standard deviation. For seven samples (with five degrees of freedom) the t value for a 99% confidence interval is 3.14. The limits of quantification (LOQs) were calculated by considering a value of 3.3 times the LOD.

Accuracy and precision: Accuracy and precision of the method was determined from the measurements during recovery study carried out by samples spiked at levels of 0.025, 0.05, 0.1, 0.25 and 0.5 µg g^{-1} following seven replications. Repeatability of the method was evaluated through the relative standard deviation (RSD, %).

Market sample analysis: Country tomato varieties with more market preference were purchased from different markets in Tamil Nadu and were analyzed following the developed method.

Results and Discussion

All the five pesticides under study were optimized in the positive electrospray ionization (ESI+) mode. The mass spectrometer was operated in scan and MRM (multiple reaction monitoring) modes. The optimization of the precursor ion, product ions, cone voltage and collision energy were performed via direct injection of the individual pesticide standard solution (1 µg mL^{-1}) into the mass spectrometer using a syringe pump at flow rate 10 µL min^{-1}. All the five pesticides tested showed a good fragmentation. The collision energy was modulated from 5 to 80 of instrumental maximum to obtain the better

fragmentation pattern. The most intense transition was used for quantitation, while the other was employed for confirmation. The optimized parameters are presented in Table 1.

Pesticide	Retention Time (min)	Ion Monitoring (m/z)			Cone (V)	Collision (V)
		Parent ion	Quantifier ion	Qualifier ion		
Acetamiprid	6.73	223.16	126.115		26	16
		223.16		56.222	26	22
Thiacloprid	7.74	253.096	126.126		30	36
		253.096		90.23	30	20
Imidacloprid	6.65	256.132	209.146		24	19
		256.132		175.205	24	16
Thiamethoxam	5.61	292.168	211.109		24	23
		292.168		132.104	24	13
Clothianidin	6.30	250.10	169.110		16	16
		250.10		132.110	12	12

Table 1: MRM transitions for ions of neonicotinoids in LC-MS/MS.

LC-MS/MS methods based on triple quadrupole analyzers are frequently used in environmental samples because of the high sensitivity achieved using Multiple Reaction Monitoring (MRM) acquisition mode. As a compromise between sensitivity, acceptable chromatographic peak shape, and confirmation purposes, two MRM transitions are monitored in this study.

The liquid chromatographic method developed in our laboratory was based on the results of preliminary studies carried out on matrix-fortified standards. When methanol+water was used, a poor response was obtained. Hence, a mobile phase consisting of acetonitrile+water was tried in different ratio. The mobile phase with a binary gradient of 0.5% HCOOH in water and 0.5% HCOOH in acetonitrile (50:50) gave good response. Formic acid proved to be efficient for ionizing the pesticides under investigation and all the five pesticides formed $[M+H]^+$ parent ions. Under the standardized chromatographic conditions, the neonicotinoid compounds were eluted in less than 10 minutes and identifiable on the basis of signals, and good sensitivities were obtained. Each analyte showed a typical mass spectrum profile similar to that identified by direct infusion in the MS. In the MRM mode, only the ions of interest were observed with the mass analyzer which increased the consistency of the results. Detection of pesticides even at low concentration of 0.025 μg g^{-1} in the matrix was achieved with the triple quadrupole detector coupled with chromatography (Figure 1).

Linear relationships among the ratios of the peak area signals and the corresponding concentrations (0.025-0.5 μg mL^{-1}) were observed. The linear ranges, regression coefficients (r^2) are summarized in Table 2. It can be seen that all the regression coefficients are higher than 0.997.

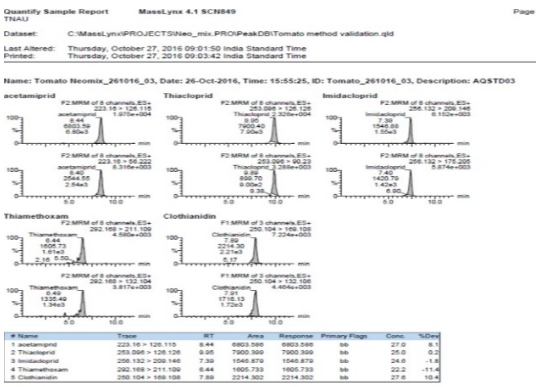

Figure 1: Chromatogram of neonicotinoid spiked (0.025 μg g^{-1}) tomato fruit sample.

Pesticides	Linear range (μg /mL)	Variation coefficient
Acetamiprid	0.025-0.5	0.998929
Thiacloprid	0.025-0.5	0.998988
Imidacloprid	0.025-0.5	0.997442
Thiamethoxam	0.025-0.5	0.997611
Clothianidin	0.025-0.5	0.998166

Table 2: Mixed standard solutions, linear range, variation coefficient and linear equation of five neonicotinoid residues.

Compound name	Mean	SD	LOD (μg g^{-1})	LOQ (μg g^{-1})
Acetamiprid	0.019	0.0015	0.004	0.01
Thiacloprid	0.02	0.0007	0.002	0.007
Imidacloprid	0.016	0.0004	0.0015	0.005
Thiamethoxam	0.024	0.0028	0.008	0.025
Clothianidin	0.02	0.0019	0.006	0.02

Table 3: LOD and LOQ for five neonicotinoid insecticides.

Pesticide	Codex Alimentarius MRL (mg kg^{-1})
Acetamiprid	0.2 (fruiting vegetables)
Thiacloprid	0.5
Imidacloprid	0.5
Thiamethoxam	0.7 (fruiting vegetables)
Clothianidin	0.05 (fruiting vegetables)

Table 4: MRL (mg/kg) for tested neonicotinoids in tomato.

With LC-MS/MS, lower limits of detection and quantitation could be achieved (LOD ≤ 0.008 μg g^{-1} and LOQ ≤ 0.025 μg g^{-1}) (Table 3).

Even at such low concentration levels the recoveries and the precision of the method. All the five pesticides were successfully detected at or below their Codex Alimentarius Commission Maximum Residue Level (MRL) in the spiked tomato samples (Table 4).

Table 5 presents recovery data and repeatability (RSD) for the five pesticides analyzed in 5 different spiking levels. The recoveries ranged from 60.00% to 99.14%. Precision was studied as intra-day precision.

Pesticide	Spiked level (µg g^{-1})									
	0.025		0.05		0.1		0.25		0.5	
	Recovery%	RSD	Recovery%	RSD	Recovery%	RSD	Recovery%	RSD	Recovery%	RSD
Acetamiprid	77.44	7.62	73.8	7.14	83.19	3.53	79.90	4.52	84.53	2.05
Thiacloprid	79.02	3.30	75.20	4.54	86.16	2.84	82.97	3.50	86.13	2.25
Imidacloprid	63.57	2.71	60.00	7.39	67.39	7.17	63.53	5.21	68.91	3.59
Thiamethoxam	99.14	11.30	88.83	10.89	80.68	14.64	82.83	17.44	76.68	4.72
Clothianidin	78.75	9.87	74.40	8.18	90.10	4.17	85.56	5.81	91.74	2.21

Table 5: Average recovery (%) and RSDs of five neonicotinoid pesticides in tomato fruit.

The intraday precision was evaluated by assaying seven fortified tomato samples for each level on the same day at the five concentration levels of the recovery studies. The precision was expressed as the Relative standard deviation (RSD) values. RSDs of intra-day ranged from 2.05% to 17.44% showing good repeatability. Except for imidacloprid, the other four pesticides showed recovery more than 70%. Though in case of imidacloprid, recoveries were lower than 70 per cent, the RSD values were less than 20 per cent and hence are acceptable. In terms of repeatability, all pesticides gave satisfactory RSD <20% [25]. A robustness study was performed by varying the laboratory personnel and the results were compared (Table 6). The within laboratory reproducibility was ≤ 20% indicating that the method was robust.

For the analysis of the pesticide with thermo labile and high volatile nature, this LC-MS/MS method has an advantage over GC. Country tomato being a fruit with high water content, 10 mL of acetonitrile proved sufficient for extraction. Using 100 mg Primary Secondary Amine (PSA), 600 mg anhydrous Magnesium sulphate ($MgSO_4$) and 10 mg graphitized carbon black (GCB) better recoveries were observed. In the final step, only one ml of the sample extract was finally concentrated, reconstituted to 1 mL with acetonitrile and filtered through a 0.2 µm syringe filter.

Compounds	Recovery of neonicotinoids fortified @ 0.025 µg g^{-1}									
	Analyst 1					Analyst 2				
	R1	R2	R3	Mean	RSD%	R1	R2	R3	Mean	%RSD
Acetamiprid	70.57	73.89	81.68	75.38	7.57	82.71	70.46	77.94	77.04	8.02
Thiacloprid	75.49	79.55	76.00	77.01	2.87	82.13	80.81	81.22	81.39	0.83
Imidacloprid	61.84	65.72	61.11	62.89	3.94	64.26	64.10	62.73	63.70	1.32
Thiamethoxam	80.90	111.49	92.00	94.80	16.34	103.63	107.32	107.4	106.12	2.03
Clothianidin	86.24	85.80	82.51	84.85	2.40	84.77	69.73	73.1	75.87	10.40

Table 6: Robustness study of the developed method.

In the market samples analyzed, out of 30 samples, 2 samples contained neonicotinoid residues. Of this, one sample was found contaminated with imidacloprid (0.047 µg g^{-1}) and another sample with acetamiprid (0.168 µg g^{-1}) but all below the respective MRL levels. Neonicotinoid insecticides are used for the management of sucking pests in tomato [26,27]. A study [28] revealed that portions of thiacloprid and clothianidin residues and radiolabeled neonicotinoids penetrate into and beyond the outer flesh regions of apples 24 h after topical application. The residues of thiamethoxam and acetamiprid were reported in cherry leaves and the fruit 14 days after field application [29]. Though systemic nature of these pesticides is advantageous in pest management, translocation of neonicotinoids into plant tissues after foliar application may potentially be subject to human consumption and subsequently dietary intake.

Conclusion

The use of modern techniques and the use of high quality equipment enables the determination of even trace level analytes. Existing techniques are being improved and new ones developed so

that different classes of pesticides can be reliably determined in a quick, simple, cheap and environmentally friendly manner. The SPE extraction procedure is very simple and inexpensive method for determination of neonicotinoid residues in tomato. The mobile phase, acetonitrile and water showed good separation and resolution and the analysis time required for the chromatographic determination of the five neonicotinoids is very short (around 8 min for a chromatographic run).

Since five levels of matrix spiked samples were included, and seven replications were run, the average recovery and precision data reflected not only the repeatability of the method over multiple injections of matrix samples, but also the response linearity from low to high concentrations. Acceptable validation parameters such as linearity, recovery, precision and LOQ were also established. Therefore, the projected residue analysis procedure could be useful for determining the neonicotinoid residues in tomato samples. The findings of neonicotinoid insecticides in real samples though below the MRL level, demonstrate the importance of including this analyte group in routine analysis. As tomato is considered poor man's apple in India and also consumed raw, the results of this study are important for taking measures that will reduce residues in tomato fruits.

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