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SIMULTANEOUS DETERMINATION OF THIAMETHOXAM, ITS METABOLITE AND CHLORANTRANILIPROLE RESIDUES IN PADDY BY QuEChERS METHOD

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ABSTRACT

The study was conducted with an objective of analyzing residues of thiamethoxam, CGA322704 and chlorantraniliprole in paddy grain, straw and soil samples. Field trial of Virtako1.5% GR (thiamethoxam and chlorantraniliprole) on paddy was carried out following application 60 and 30 g a.i. ha^{-1}(once and twice at an interval of 15 days). A simple QuEChERS (Quick Easy Cheap Effective Rugged and Safe) methodology was standardized for the simultaneous extraction of residues in paddy grain, soil and straw followed by estimation and confirmation on HPLC (High Performance Liquid Chromatography). The limit of quantification for the instrument was established as 0.01 mg kg^{-1} and detection limit was thus worked out as 0.003 mg kg^{-1}. At harvest, residues observed in grain, soil and straw samples were below detection.

Keywords: Chlorantraniliprole, Grain, HPLC, *Oryza sativa*, Straw, Thiamethoxam ,

Rice (*Oryza sativa*) is an extensively consumed cereal food playing a pivotal role in attaining food and livelihood security (Izawa and Shimamoto, 1996). India produced over 122 million metric tons of rice in the year 2020-21, ranking second in the rice production and is the biggest exporter of rice in the world (*Anonymous, 2019*). The warm and humid environment during crop growth encourages growth and development of insect pests (Das, 2020) infesting almost at all growth stages and all plant parts causing a decline in the production (Pathak and Khan, 1994). According to Mondal *et al.* (2017) insect pests like hoppers, leaf folder, stem borer and *gundhi* bug decrease rice production by 27.9 per cent and the production can be increased by minimization of these losses. To sustain ever growing population with constraints of a limited cultivated land, implementation of effective pest management strategies with new chemistry molecules is very important (Popp, 2011).

Pesticide use has been established as a first line of defense strategy to combat the most damaging insect pests of Rice (*Oryza sativa* L.). Increased use of pesticides has helped to increase the rice yields. Recently, pesticide mixtures have been commercialized to achieve more efficient control of pests (Peng *et al.,* 2010). Besides, these offer and manage crop resistance. Pesticide mixtures imply a single spray solution combining two or more pesticides, thus simultaneous exposing each pesticide to the target pest population. Also, these are more useful in effectively controlling different life stages (eggs, larvae, nymphs and adults) as compared to single pesticides, besides offering reduction in cost of labor and reduction of total insecticide use (Das, 2014). The mixtures can probably improve the commercial status of already existing pesticides by widening the activity spectrum, delaying the resistance by reducing the selection pressure (Roush, 1993) and solving the problem of scarce development of newer pesticides. About 66 insecticide mixtures have been registered in CIB&RC for management of insect pests on various crops. Virtako® is one such popularly used insecticide mixture of the neonicotinoid and anthranilic diamide chemical groups, providing higher efficacy in the control of insects.

Virtako1.5 % GR, mixture of chlorantraniliprole (0.5%) and thiamethoxam (1.0%), has been recommended for management of leaf folder, leaf hopper and stem borers (CIB&RC, 2022). Chen *et al.* (2014) reported that Virtako1.5 % GR could be substituted in pest management programme of brown plant hopper and leaf folders. One application of Virtako1.5 % GR effectively controls insect pests in paddy fields after a single application, and the original population of natural enemies recovered within three weeks of application (Chen *et al.,* 2016).

Chlorantraniliprole ({3-bromo-N-[4-chloro-2-methyl-6-[(methylamino) carbonyl] phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxamide}, an anthranilic di amide is a ryanodine receptor insecticide. It offers an effective control of lepidopteran, dipteran, coleopteran, hemipteran and isopteran insect pests (Lahm *et al.,* 2007). It acts by causing discharge of internal calcium by opening calcium channels resulting in exhaustion of

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calcium, stoppage of feeding, sluggishness, paralysis of muscles and death. The systemic and trans-foliar activity, make it effective against chewing insects (Hanning, 2009)

Thiamethoxam [3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4ylidene (nitro) amine] belongs to the group of nitro substituted neonicotinoids (Fan *et al.,* 2019). Neonicotinoids act agonistically on the nicotinic acetylcholine receptors (nAChRs) on the post synaptic membrane of the central nervous system leading to excitability of neurons, immediately causing the insect's death (Moffat *et al.,* 2016). Being a systemic insecticide, it finds many applications against foliar feeding insects by means of seed treatment, soil by means of irrigation, and for direct foliar application (Maienfisch *et al.,* 2001). Kathikeyan *et al.* (2019) validated analytical methodology using QuEChERS technique for the estimation of neonicotinoids in rice grain and straw and obtained satisfactory results with recoveries between 75 to120 per cent.

Though these insecticides effectively keep major insect pests of rice at bay, their residues can persist and contaminate the edible portions of the plant. The mixtures can lead to increased persistence of pesticides until harvest and become a major health concern (Chen, 2016). To ensure the safety of food for the consumers, it is important to investigate the residues of these insecticides in grain and other parts which can be fed to animals and in turn incorporate themselves in food chains. Research studies have shown presence of pesticide residues in rice grains. Dong *et al.* (2011) detected chlorantraniliprole residues in rice and corn fields using High-performance liquid chromatography-tandem mass spectrometry.

Zhang *et al.* (2012) determined chlorantraniliprole residues in brown rice grain in China using LC-ESI-MS/MS and detected final residues lower than maximum residue limit of 0.02 mg kg $^{-1}$ fourteen days after an application @ 30 and 60 g active ingredient (a.i.) ha^{-1}).

The amount of the insecticide residues in the rice grains vary with the part being analyzed (hull, bran or polished grain) and chemical group of insecticides as different chemicals vary in their tendency to associate with different part of the grain. (Teló *et al.,* 2015). In Rice, scanty work has been done on determination of residues of insecticide mixture of thiamethoxam and chlorantraniliprole. The little work done has been carried out in different environmental conditions leading to variations in the presence of pesticides in rice grains. No study on degradation or residues of these insecticides in rice grain has been reported in north India. The study is important with respect to food safety concerns associated with residues of insecticides and were undertaken using good agricultural practices, at the application of the recommended doses aiming at generation of residue data under North Indian conditions. Thus, keeping in view the nutritional importance of rice and restricted knowledge on the residues of mixture of thiamethoxam and chlorantraniliprole, the supervised field trial on the residues of Virtako1.5 % GR in unpolished and polished rice, straw and soil was conducted at Entomological research farm and pesticide residue analysis laboratory, Punjab Agricultural University, Ludhiana.

MATERIALS AND METHODS

Reagents and chemical formulations

The analytical standard of Thiamethoxam (purity 98.9%), CGA 322704 (purity 98.0%) and Chlorantraniliprole (purity 98.0%) were supplied by Syngenta India Ltd, Pune, India. All the solvents used in the residue analysis were of laboratory grade. The solutions were stored at 4 ˚C before use.

Primary secondary amine (Bondesil-PSA 40 µm) sorbent and anhydrous $MgSO_4$ were procured from Agilent Technologies, India Pvt. Ltd., Bangalore, India were used in Dispersive solid phase extraction (DSPE). Sodium chloride and Sodium sulfate anhydrous were obtained from the Sisco Research Laboratories Pvt. Ltd., Maharashtra, India. The solvents and other chemicals were checked for their suitability by running reagent blanks prior to analysis.

Field trial

In the Kharif season, Basmati rice crop, variety Punjab Basmati 2 was raised at Punjab Agricultural University, Ludhiana, Punjab during *Kharif* season in 2019 accordance with the recommended package of practices (Anonymous, 2019). The trial included two treatments i.e. T_1-one time manual broadcast application of 60 g a.i.ha^{-1} and 30 g a.i. ha^{-1} at tillering stage, T_2 - Two times broadcast of 60 g a.i.ha^{-1} and 30 g a.i. ha^{-1} (first application at tillering stage and another at 15 days interval) and one untreated control as T_3 . The three treatments three replications for each were arranged in the randomized block design for proper statistical analysis with a plot size of 50 m^2 each. The average weather conditions are presented in the Table 1. Soil of the experimental area (pH-8) was constituted by 78.0 per cent sand, 10.2 silt, 11.8 per cent clay and 0.30 organic carbon.

Apparatus

High Performance Liquid Chromatograph equipped with photo diode array detector (PDA), a dual pump (LC-20AT) (Shimadzu Corp., Kyoto, Japan), CBM-20A system controllerand RP C_{18} column (Agilent

Table 1. Meteorological conditions at the trial location during experimental period

Weather parameters	11 August, 2019 to 2 November, 2019
Range of maximum temperature (°C)	26.0-36.4
Range of minimum temperature (°C)	14.2- 28.4
Morning relative humidity (%)	69-96
Evening relative humidity (%)	31-95
Total Rainfall (mm)	276.6

Technologies) of 250 mm length, 4.6 mm i.d. and 5 µm of particle size was used to estimate the residues of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole. Instrument control, data acquisition and processing were done with the Shimadzu LC solution software. Chlorantraniliprole was estimated using acetonitrile: water (30:70) as mobile phase in isocratic mode at a flow rate of 0.30 mL min^{-1} having RT of 21.93while for thiamethoxam and its metabolite CGA 322704 acetonitrile: water (60:40) with flow rate of 0.30 mL min^{-1} was used in isocratic mode having RT of 17.64 and 21.96 minutes. The residues were determined at wavelength of 254 nm.

Sampling

Brown rice (de-husked unpolished) 1 Kg, white polished rice (500 g), straw (250 gm) and soil (1 kg) were randomly collected from replicated plots at harvest time (63 days after second application) from all the three treatments. Rice samples were dehusked and polished to obtain brown and white rice samples. Samples were extracted immediately after sampling and analyzed.

Extraction and cleanup

Brown rice, white rice and soil

The samples for the determination of residues of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole were prepared following QuEChERS method. A 15 g sample was weighed into a centrifuge tube (50 mL) and then acetonitrile (30 mL) was added into it. In case of soil, distilled water (10 mL) was added in addition to acetonitrile. Upon homogenization for 3 minutes at 15000 rpm, Sodium chloride (@10 ± 0.1 g) was added for phase separation. It was then centrifuged at 2,500 rpm for 3 minutes and. 15 mL aliquot of acetonitrile layer was transferred to a test tube with 10 ± 0.1 g anhydrous sodium sulfate (Na_2SO_4). In Dispersive solid phase extraction (DSPE), 6 mL acetonitrile aliquot was taken in a test tube containing PSA sorbent (0.15 ± 0.01 g), and anhydrous $MgSO_4$ (0.90±0.01 g) and thoroughly vortexed. Four mL aliquot was taken in centrifuge tube for estimation of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole in soil. The aliquot was concentrated under vacuum using Low volume concentrator with nitrogen gas flow to 2 ml in case of brown rice and white rice for estimation of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole.

Straw

Acetonitrile (100 mL) was dispensed into straw sample (5 g) in a 200 mL beaker and was kept overnight. Next day the samples were filtered and then were concentrated using Rotovac (Heidolph) and the volume was made to 5 mL with acetonitrile.

Validation of the methodology

The instrumentation method used for the determination of residues of chlorantraniliprole, thiamethoxam and its metabolite CGA 322704 on HPLC was validated in terms of its selectivity, linearity, limit of detection and quantification and recovery studies as per the SANTE guidelines (2019).

Comparison of three control samples was made with that of three samples spiked at limit of quantification (0.01 µg mL^{-1}). No peak was found at the retention time of standard concerned in case of control samples. Hence the selectivity of the method was checked.

The calibration curves of chlorantraniliprole, thiamethoxam and its metabolite CGA 322704 were prepared to check the uniformity in the response of the analyte. The sensitivity of the detector for the analyte was calculated from limit of detection and limit of quantification values. LOD is the lowest concentration of pesticide that has a signal-to-noise ratio of 3:1 whereas LOQ is defined as that lowest concentration which can be quantified with suitable precision at which chromatographic peaks are obtained at signal-to-noise ratio of 10:1. In addition, sample load was also determined for estimation of LOQ and LOD. The LOQ was established on the basis of the response of standard working solution injected (in ng) as well as of the sample weight injected (in mg), provided baseline of the HPLC instrument remains stable and without baseline noise.

The recovery studies were done at three different levels of fortification with LOQ as the lowest level of fortification. The acceptability criterion is the recovery

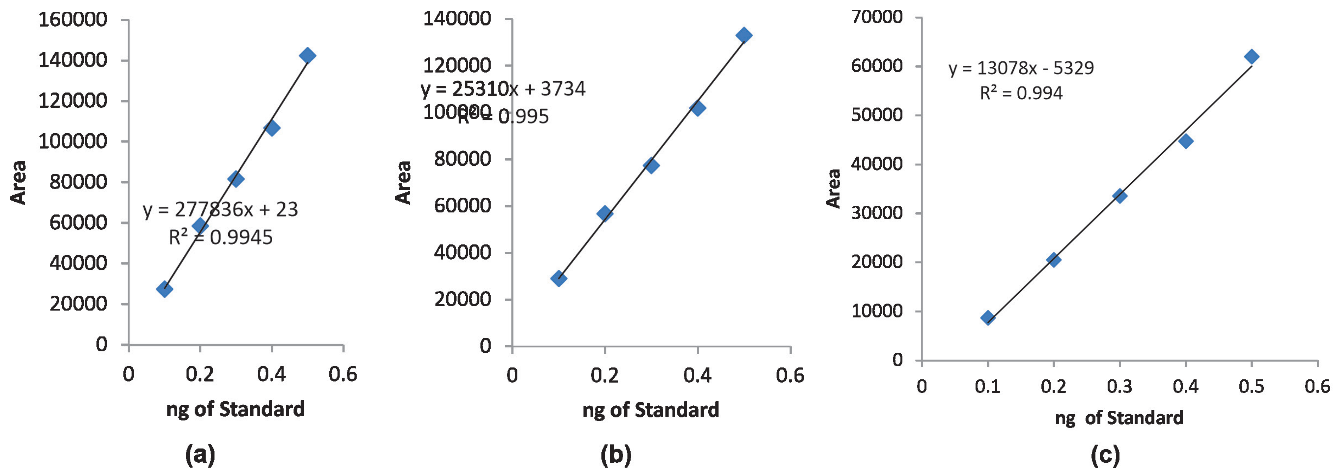

Fig. 1. Linearity equation of (a)Thiamethoxam, (b) its metabolite CGA 322704 and (c) chlorantraniliprole

range between 70-120 per cent. Brown rice, white rice (polished rice), straw and soil were spiked with chlorantraniliprole, thiamethoxam and its metabolite CGA 322704 at three levels of 0.01, 0.05 and 0.10 mg kg^{-1}having 3 replications each and analyzed as per the methodology described above. The recovery studies done at LOQ level of 0.01, 5 times of LOQ i.e. 0.05 and 10 times of LOQ i.e. 0.1 mg kg^{-1} were done, standard deviation and relative standard deviation was calculated to get the repeatability values (RSDr).

RESULTS AND DISCUSSION

Linearity

Five different concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 µg mL^{-1}), each of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole prepared in acetonitrile were injected to check the uniformity in the response of the analyte. The calibration curves with respect to various analytes produce a linear relationship between detector response (y) and analyte concentration (Fig. 1 a, b and c) with coefficient of determination (^{r2}) values above 0.990.

Limit of quantification and Limit of Detection

Residues of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole were estimated by comparison of peak height/peak area of the standard with that of the unknown or spiked samples run under identical working conditions of the HPLC.. The LOQ was established on the basis of the response of standard working solution injected (in ng) as well as of the sample weight injected (in mg), provided baseline of the HPLC instrument remains stable and without baseline noise. For LOD calculations, the signal to noise (S/N) ratio was 3 and for LOQ the S/N value was 10.The limit of detection (LOD) and limit of quantification (LOQ) were worked out to be 0.003 and 0.01 mg kg^{-1} for all the three pesticides.

Recovery studies

Per cent recovery was consistent and more than 80 % in all the cases (Table 2). Therefore no correction factor was applied on the results obtained. The repeatability (RSDr) for different analytes in paddy grain, straw and soil at 0.01mg kg^{-1} ranged from 1.43 to 3.01, 2.36 to 3.35 and 2.23 to 3.28 per cent for thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole, respectively. The results were found to be satisfactory for all the concentration levels investigated (Table 2). The overall results indicated good accuracy of the proposed HPLC method. QuEChERS method was validated in this laboratory for estimation of residues of another neonicotinoid, imidacloprid and its metabolites in cotton flower, nectariferous tissue, pollen and honey with 80.42 – 99.83 per cent having 0.01 µg g^{-1} LOQ (Brar *et al*., 2022)

Residues in paddy grains, straw and soil

During the field trial, residues of thiamethoxam, CGA 322704 and chlorantraniliprole on Brown rice (de-husked but unpolished), white rice (polished rice) and straw at harvest time were found to be below LOQ value of 0.01 mg kg^{-1}, following the application of thiamethoxam 1.0% w/w + Chlorantraniliprole 0.5% w/w GR @ 30 and 60 g a.i. ha^{-1}, after single and two sprays (Table 3). Soil samples collected at 68 days after application did not reveal the presence of thiamethoxam, CGA 322704 and chlorantraniliprole above LOQ of 0.01 mg kg^{-1}.

Residues of thiamthoxam and chlorantraniliprole has been estimated by many researchers in various crops. Wang and Zhang (2017) estimated dissipation kinetics and residue behavior of chlorantraniliprole in sugarcane and soil by using LC-MS/MS, following

Table 2. Per cent recovery and repeatability (% RSDr) for brown rice, white rice (polished rice), straw and soil spiked at four levels

Substrates	Level of fortification (mg kg^{-1})	Thiamethoxam		CGA 322704		Chlorantraniliprole	
		Mean*±S D	%RSD r	Mean*±S D	%RSD r	Mean*±S D	%RSD r
Brown rice (dehusked)	0.01	94.86±2.19	2.30	96.80±2.36	2.44	98.59±3.23	3.28
	0.05	92.55±4.40	4.75	93.51±2.79	2.98	93.71±3.41	3.64
	0.10	85.67±3.61	4.21	89.15±1.88	2.10	89.42±2.22	2.49
White Rice	0.01	98.54±1.41	1.43	99.68±3.34	3.35	95.18±3.13	3.28
	0.05	96.83±6.07	6.27	92.42±3.42	3.70	89.08±2.33	2.60
	0.10	89.42±2.03	2.26	90.64±3.06	3.37	92.54±1.79	1.93
Straw	0.01	99.19±2.35	2.37	96.18±3.17	3.30	91.58±2.09	2.29
	0.05	94.62±5.14	5.43	89.69±4.09	4.56	95.11±3.44	3.61
	0.10	89.52±2.09	2.34	85.36±0.94	1.10	92.24±2.14	2.32
Soil	0.01	91.25±2.75	3.01	96.87±2.28	2.36	97.60±2.17	2.23
	0.05	96.82±5.38	5.55	95.53±1.08	1.13	91.69±2.81	3.06
	0.10	87.56±2.07	2.37	92.31±4.44	4.81	88.72±1.43	1.61

*Mean of three replications

application @ 112.5 and 168.75 g a.i ha^{-1} and observed final residual concentrations in soil (after two years) to be lower than 0.01 mg kg^{-1} (lower than MRL (0.05 mg kg^{-1}) in China) corroborating the results in the present study. Similar results were obtained by Dong *et al.* (2011) where average levels of chlorantraniliprole residues in corn grains were less than 0.01 mg kg^{-1} at harvest after application @ 30 g a.i. ha^{-1}. Heena *et al.* (2021) found that chlorantraniliprole residues were not detected on 25th day after foliar spray of Coragen 18.5 SC at an application rate of 37 and 74 g a.i. ha^{-1}, in baby corn samples using HPLC, while residues in maize grains and soil at harvest were found to be below quantification limit.

Min He *et al.* (2016) observed the dissipation and residual levels of chlorantraniliprole by ultra-high-performance liquid chromatography–tandem mass spectrometry in maize straw, maize, and soil to be lower than 0.01 mg kg^{-1} in maize, between 0.01 and 0.31 mg kg^{-1} in maize straw, and between 0.03 and 1.91 mg kg^{-1} in soil following spray of a 40% wettable powder (20% chlorantraniliprole + 20% thiamethoxam) applied @ 118 g a.i.ha^{-1}. Chlorantraniliprole residues on brown rice (application @ 150 mL a.i. hm^{-2}) were observed to be lesser than MRL (0.02 mg kg $^{-1}$) after 14 d Pre-Harvest Interval (PHI) while these were 0.002–0.020 mg kg^{-1} and 0.005–0.049 mg kg^{-1} in rice straw and soil samples, respectively (Zhang *et al.,* 2012).

Telo *et al.* (2017) analyzed rice grains and rice hull samples for pesticide residues and thiamethoxam was not detected following application @ 28.2 g a.i.ha^{-1} at the R_2 growth stage. According to Ge *et al.* (2017) more than 89% of the initial amount of thiamethoxam dissipated within 90 days after planting rice seedlings in the soil treated with thiamethoxam @ 1 mg /kg soil and 10 mg /kg soil whereas in present study, residues

Table 3. Residues of thiamethoxam, CGA 322704 and chlorantraniliprole (mg kg^{-1}) in brown rice (de-husked but unpolished), white rice (polished rice), straw and soil at harvest time after the application of Thiamethoxam @ 60 g a.i. ha^{-1}[T_1] and 2 x 60 g a.i. ha^{-1} Chlorantraniliprole @ 30 and 2 X 30 g a.i. ha^{-1}[T_2]

Substrate	Residues of thiamethoxam, CGA 322704 and chlorantraniliprole (mg kg^{-1}) after application of					
	T_1			T_2		
	Thiamethoxam	CGA 322704	Chlorantraniliprole	Thiamethoxam	CGA 322704	Chlorantraniliprole
Brown rice	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
White rice	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Straw	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Soil	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

All values are mean of three replications, Limit of Quantification (LOQ) = 0.01 mg kg^{-1}

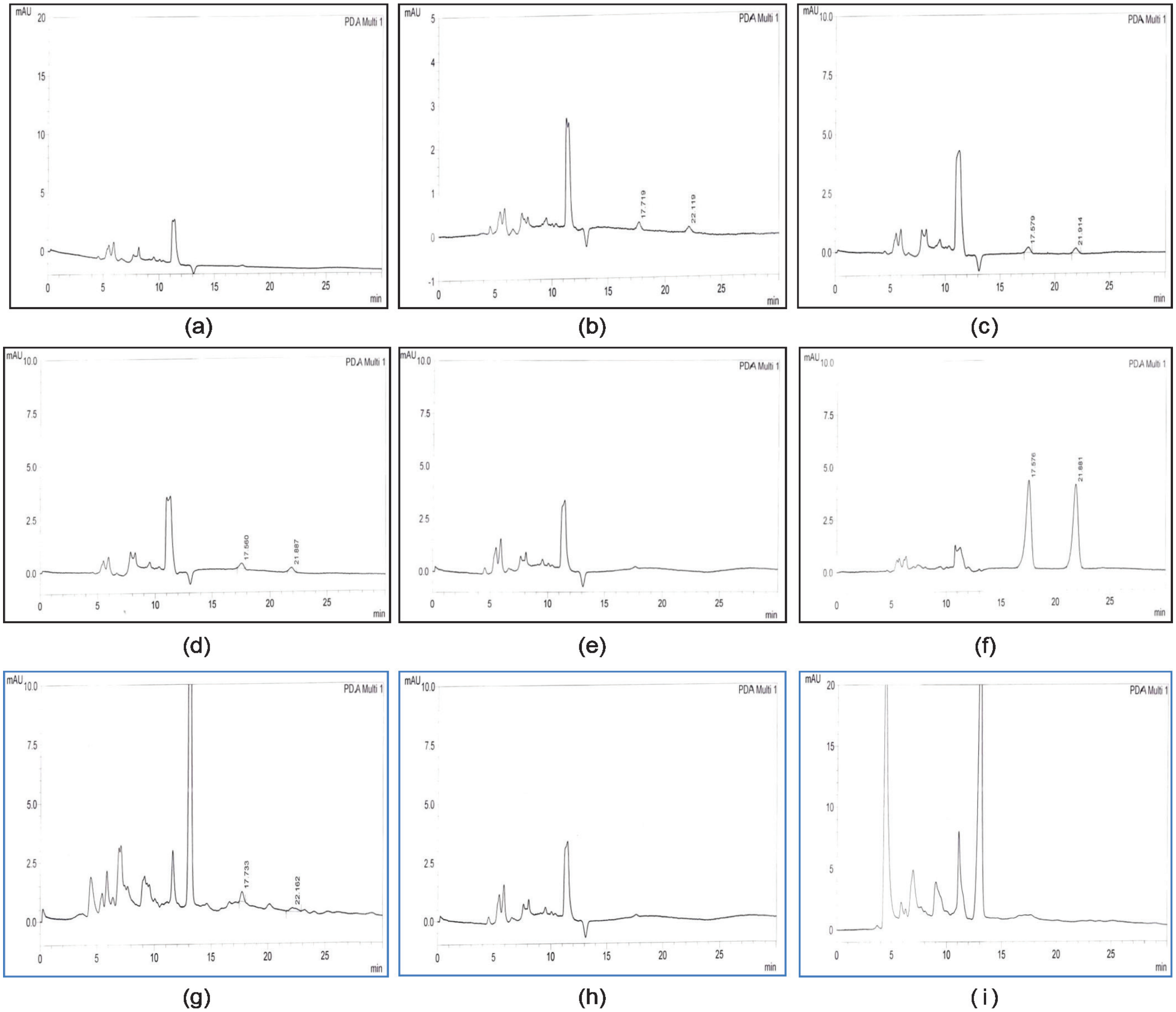

Fig. 2. HPLC chromatograms of a) 20 ng standard of thiamethoxam and chlorantraniliprole b) brown rice control sample c) white rice control sample d) straw control sample e) soil control sample f) white rice sample spiked at 0.01 ppm g) brown rice spiked at 0.01 level h) soil spiked at 0.01 j) straw spiked at 0.01 ppm

were not detected after 63 days of application. The residual concentrations of the thiamethoxam in maize and its straw were lesser than 0.01 while in soil ranging between 0.01–0.03 mg kg^{-1}, following spray of a 40% wettable powder of 20% chlorantraniliprole and 20% thiamethoxam @ 118 g a.i.ha^{-1} and after a 14- day pre harvest wait, the residues on maize were lesser than the MRL (0.02 mg kg^{-1}) (Min He *et al.,* 2016). Pareja *et al.*(2012) studied the rice cropping season for occurrence of pesticides and found that residues were below LOQ of 5 µg kg^{-1} in both brown and white rice. Barik *et al.* (2010) studied persistence of thiamethoxam (12.6%) (formulation Alika 247 ZC) in grain and straw of paddy and soil and found no detectable residues at harvest following the application of insecticide @ 33 and 66 g a.i. ha^{-1}.

All the substrates i.e. brown rice, white rice, straw and soil collected at harvest time did not reveal the presence of detectable residues of thiamethoxam, its metabolite CGA 322704 and chlorantraniliprole after the application of one and two sprays of thiamethoxam 1.0% w/w + Chlorantraniliprole 0.5% w/w GR @ 30 and 60 g a.i. ha^{-1}.

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Authors' contribution

Conceptualization of research work and designing of experiments(PKB, NS, KM,); Execution of experiments and data collection(NS, SS, RK); Data analysis and interpretation of results (NSS, SK, RK); Preparation of manuscript(NS, PKB, SS, RK).

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