

Determination of Dinotefuran and Thiamethoxam Residues in Pepper Fruits under Greenhouse Conditions using the QuEChERS Method and HPLC/DAD

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DETERMINATION of dinotefuran and thiamethoxam residues levels in pepper samples which were collected randomly at 0, 1, 3, 5, 7, 10, 15 and 21 days after treatment using quick, easy, cheap, effective, rugged, safe (QuEChERS) method and clean up step utilizing solid-phase extraction (SPE) followed by determination by high-performance liquid chromatography with diode-array detection (HPLC/DAD). Dinotefuran and thiamethoxam were recovered within 77-80% and 78-112%, respectively at the spike levels (0.01 - 1 mg/kg) in pepper samples with relative standard deviations (RSDs) lower than 3%. Good linearity was achieved for dinotefuran and thiamethoxam with an excellent correlation coefficient of $R^2 \geq 0.996$ and the matrix matched calibration also showed good linearity with determination coefficients $R^2 \geq 0.98$. The initial deposits of dinotefuran and thiamethoxam in pepper fruits were 6.59 and 1.38 mg/kg, respectively. The half-life period (RL_{50}) of tested pesticides on pepper fruits were 2 and 3.11 days for dinotefuran and thiamethoxam, respectively. According to maximum residue level (MRL) (0.01 mg/kg for dinotefuran and 0.7 mg/kg for thiamethoxam) the pre-harvest interval (PHI) was 11 and 4 days, respectively.

Keywords: Dissipation, Determination QuEChERS, Dinotefuran, Thiamethoxam, HPLC-DAD and Pepper.

Introduction

Neonicotinoid insecticides including imidacloprid, acetamiprid, thiacloprid, thiamethoxam, clothianidin, and dinotefuran are effective insecticides to control pest with novel modes of action [1].

Pesticides are widely applied on vegetables and fruits to guarantee their quality and to fulfill the consumer's requirements and for the trade. However, these compounds can be unsafe to humans, according to the levels of pesticides present. So, the European Union Council Directive 91/414/EEC controlled the maximum concentrations of these molecules [2]. On the other hand, MRLs for neonicotinoid insecticides

residues have been established by The United States EPA in the range 0.02–6 mg kg⁻¹ in different types of vegetables and fruits depending on the different pesticides and matrixes (<http://www.mrldatabase.com>).

The evaluation of pesticide residues in food matrices is a tremendous challenge mainly because the amounts of analytes are small compared to the huge quantities of interfering substances which strongly interact with analytes[3]. QuEChERS has been developed as a new sample preparation methodology between 2000 and 2002 for pesticide multiresidue analysis[4]. Generic extraction procedures, like QuEChERS method and ultra-high-performance liquid chromatography systems

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combined with polar embedded C18 phases, providing excellent peak shape and good resolution, enabled us to detect a wide spectrum of compounds which belong to different pesticides classes and chemical properties in each sample [4, 5].

Acetone, ethyl-acetate, methanol and acetonitrile-based sample extraction techniques are generally used for multi-class pesticides which are typically followed by a clean-up step [6]. Several methods have been reported for the analysis of neonicotinoids (thiamethoxam, imidacloprid, and acetamiprid), for example, HPLC coupled with ultraviolet detection (HPLC-UV), HPLC diode array detection (HPLC-DAD) or HPLC mass spectrometry (HPLC-MS) are used for the determination of imidacloprid in different environmental samples [7, 8]. HPLC-DAD is a technique with more widespread use and suitable for the separation and quantification of compounds with high molar absorptivity, such as neonicotinoids [9].

Greenhouses production of crops requires pesticides applications due to high liability of the crops to be infected with many pests, such as aphids, thrips and whiteflies, which cause economic injury to pepper through direct injury, virus transmission, leaf stunting, yellowing and curling on mature plants.

The objective of the present work was to determine the dissipation behavior and the residues of dinotefuran and thiamethoxam in pepper fruits under greenhouse conditions.

Materials and methods

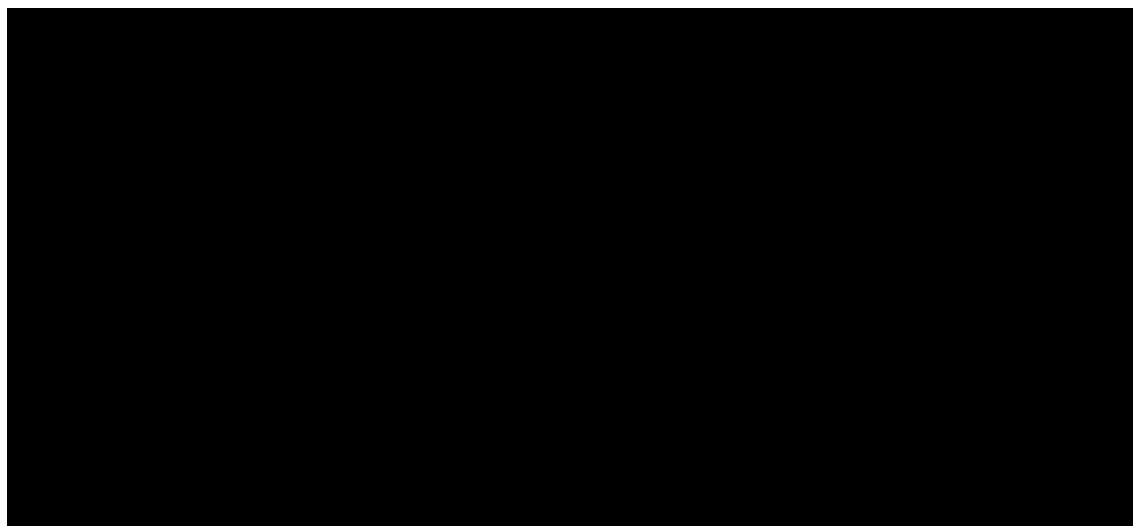
Materials

Chemicals and reagents

Certified reference standard of thiamethoxam and dinotefuran (figure 1) > 98% purity was obtained from Central Agricultural Pesticides Laboratory (CAPL). Acetonitrile of HPLC grade was purchased from Merck. Bulk primary secondary amine (PSA) sorbent (Bondesil-PSA, 40 μm) was bought from Subelco. Anhydrous magnesium sulfate and sodium chloride were purchased from Merck. Anhydrous magnesium sulfate and Sodium chloride were activated by heating at 250°C for 4 h in the oven before use and kept in desiccators. Pesticide technical formulations (Actara 25% WG), was supplied by Syngenta Agro, Egypt and (Oshin 20% SG), was supplied by Shoura Company, Egypt.

Apparatus

Agilent 1100 HPLC equipped with diode array detector (Agilent, Palo- Alto, CA USA) at UV wavelength 230 and 210 nm for thiamethoxam and dinotefuran. An ODS C18 HPLC column (4.6 mm \times 150 mm \times 5 μm) was used as the separation column. Mobile phase consisted of acetonitrile and water (90:10) and (60: 40) for thiamethoxam and dinotefuran, respectively with a flow rate of 0.8 ml/min. The retention time of thiamethoxam and dinotefuran under these conditions was 2.34 and 1.98 min, respectively.



Standard preparation

Stock solutions of thiamethoxam and dinotefuran were prepared by dissolving 10 mg of the analytes (of accurate weight) in 100 ml ethyl acetate and methanol, respectively to obtain solution concentration of 0.1 mg/ml. Working standard solutions of 10, 5, 2, 1, 0.5, 0.1 and 0.01 µg/ml of each were prepared by appropriately diluting the stock solutions with methanol. Stock solutions were stored at -20 ± 2 °C, and working standard solutions were stored in the dark at 4 °C when not in use.

Field experiment

Field experiment was carried out in experimental farm of Faculty of Agric. Cairo Univ. during 2016 season. Pepper plants were sprayed by dinotefuran (Actara 20% SG) at 125 g/100-liter water and thiamethoxam (Oshin 25% WG) at the recommended rate 20 g/100-liter water to determine the residues of these chemicals in pepper fruits. Random samples of the fruits were collected from the treated plants 0, 1, 3, 5, 7, 10, 15 and 21 days' post application for dinotefuran and thiamethoxam.

Sampling and storage:

Sampling was performed by randomly collecting 2 Kg of pepper from each untreated and treated areas (thiamethoxam and dinotefuran). The collected samples were representative of all plants in the area. First clean samples of pepper were collected from the control area, and then treatment of plants started on the previously mentioned dates, and sampling took place 2 h after application of the initial deposits, repeated 1, 3, 5, 7, 10, 15 and 21 days afterwards to study the dissipation of the pesticides. Field samples were transported in iceboxes to the laboratory.

Extraction and clean up.

The samples were extracted with modified QuEChERS method [10], 10 g of weighed chopped sample (blank or spiked) was shaken with 10 ml of acetonitrile in a 50-ml centrifuge tube then 4.00 g of anhydrous magnesium sulfate was added, and shaken for 1 minute. The tube was vortexed and centrifuged for 5 minutes at 4000 rpm. 6 mL of acetonitrile layer was transferred into a Polipropilene-single centrifuge tube which contains 150 mg PSA and 900 mg magnesium sulfate anhydrous. The sample was mixed vigorously by vortexing for 1 min and centrifuge extracted for 2 minutes at 6000 rpm.

Method validation.

The linearity of a method is a measure of

range within which detector response is directly proportional to the concentration of analyte in samples. Standard solutions in terms of micro-liters, at variable concentrations, were divided into individual amounts, with the interval 0.01, 0.1, 0.5, 1, 2, 5 and 10 mg/kg for injected solutions. The tests were repeated for three times at each concentration, proving favorable linear relationship of the pesticides. Correlation coefficients were 0.99 for dinotefuran and thiamethoxam.

Matrix-matched calibration (MMC) was used to compensate for the matrix effects. The matrix effects were defined as the influence of one or more co-extracted components from the sample on the measurement of thiamethoxam and dinotefuran concentration. The presence of these effects is demonstrated by comparing the response produced from the thiamethoxam and dinotefuran in a pure solvent solution with the samples were first extracted and then spiked with thiamethoxam and dinotefuran in the same solvent at the same concentration levels (10, 5, 2, 1, 0.5, 0.1 and 0.01 mg/kg).

Matrix effects (%ME) were calculated using the equation:

$$\text{ME \%} = \frac{(\text{M matrix} - \text{M solvent})}{\text{M solvent}} \times 100\%$$

where

ME: the matrix effect

M matrix: Slope of calibration curve in matrix.

M solvent: Slope of calibration curve in the pure solvent.

LOD means the validated lowest residue concentration which can be quantified by routine monitoring with validated control methods defined as a signal-to-noise ratio (S/N) of 3:1. LOQ is the lowest concentration of the analyte that has been validated with acceptable trueness (70-120%) and precision (RSD \leq 20%) by applying the complete analytical method defined as a signal-to-noise ratio (S/N) of 10:1. According to Dg-sanco, 2013 [11], the Limit of quantification should be \leq MRL.

The trueness was determined from the recovery assay results of samples spiked with all the analytes at the levels (0.01-1 mg/kg), five replicates per level used to check the recovery at acceptable mean recoveries are those within the range of 70-120%.

Trueness was calculated using the following equation:

$$\% R = (X/\mu) \times 100$$

%R: recovery percentage

X: experimental concentration of dinotefuran or thiamethoxam mg/kg

μ : calculated concentration of dinotefuran or thiamethoxam mg/kg

The precision is a measure of how close results are to another one (Repeatability (r)) was defined as standard deviation of measurement of dinotefuran or thiamethoxam obtained using the same method on the same samples in a single laboratory over a short period of time, during which differences in the materials and equipment used and analysts involved will not occur. The value of $\leq 20\%$ was used as the limit for RSD. Five replicates for each recovery levels (0.01 – 1 mg/kg) per day on three different days were used to check the precision.

$$\%RSD = (SD / M) \times 100$$

where

SD: standard deviation of the replicates.

M: the mean value of the recovery.

Statistical analysis.

The dissipation kinetics of thiamethoxam and dinotefuran residues in pepper was determined by plotting residue concentration against elapsed time after application and equations of best curve fit with maximum coefficients of determination (R^2) were determined. For dissipation of thiamethoxam and dinotefuran in pepper, exponential relationships were found to be applicable corresponding to the general first-order kinetics equation:

$$C_t = C_0 e^{-kt}$$

where C_t represents the concentration of the pesticide residue at the time of t , C_0 represents the initial deposits after application and k is the constant rate of pesticide dissipation per day. From this equation, the dissipation half-life periods ($t_{1/2} = \ln 2/k$), [12, 13, 14] of the studied insecticide were determined.

Results

Method Validation

The evaluations of calibration curve linearity of thiamethoxam and dinotefuran were done based on injections of standard solutions prepared in pure organic solvent methanol in series at (10, 5, 2, 1, 0.5, 0.1 and 0.01 mg/kg) for HPLC-DAD.

Standard calibration curve of thiamethoxam and dinotefuran was constructed by plotting analyte concentrations against peak areas. The correlation coefficient ($R^2 = 0.99$).

The pesticide residue analysis study, the injected sample contained large amounts of the unavoidably present co-extractives which are responsible for the matrix effects occurring on the injector. The matrix effect was investigated by comparing the slopes of calibration curves at (10, 5, 2, 1, 0.5, 0.1 and 0.01 mg/kg) of dinotefuran and thiamethoxam in pepper and in pure solvent. The % ME could be negative or positive and would be classified in three categories: no matrix effect (between -20% and 20%), medium matrix effect (between -50% and -20%) and strong matrix effect (below -50% or above 50%) [15, 16]. The results showed that the matrix effect was -17.75% for dinotefuran and 4.36% for thiamethoxam which indicated that no interfering endogenous peak appeared and did not significantly suppress or enhance the response of the instrument.

The lowest validated level of dinotefuran and thiamethoxam with acceptable precision and trueness LOQ was 0.01 mg/kg for HPLC analysis in pepper. According to Dg-sanco, 2013 [11], the LOQ values are acceptable where $LOQ \leq MRL$ (0.01 and 0.7 mg/kg for dinotefuran and thiamethoxam, respectively).

The trueness, bias or mean of recovery was carried out in 5 replicates at 3 fortification levels (1, 0.5, 0.01 mg/kg) by spiking 10 g of blank samples with standard solution. The obtained mean recoveries range from 77-80% and 78-112% for dinotefuran and thiamethoxam, respectively with relative standard deviation (%RSD) ranged from 2.08 to 2.51 and from 1.92 to 2.14. According to Dg-sanco, 2013 [11], the found mean recoveries were in the acceptable range (70-120%). So, the value showing that the method was sensitive and suitable for the determination of dinotefuran and thiamethoxam residue in pepper.

The repeatability precision (%RSD) involved repeat of recovery levels (1, 0.5, 0.01 mg/kg), five replicates for each level per day on three different days. The (%RSD) value ranged from 1.22 to 2.89 and 2.04 to 3.27 According to Dg-sanco, 2013 [11], the obtained (%RSD) value was within the acceptable range $\leq 20\%$.

Dissipation of insecticide thiamethoxam and dinotefuran in pepper.

Thiamethoxam

Dissipation of thiamethoxam in pepper fruits was studied during 21 days. The dissipation pattern of thiamethoxam in pepper at different

sampling intervals (0, 1, 3, 7, 10, 15 and 21 days) is presented in Table (1) and figure (2) The initial deposit of thiamethoxam in pepper fruits was 1.38 mg/kg two hours after application. The residue of thiamethoxam in pepper fruits decreased to 1.27 mg/kg with 7.97% loss after 24 hours of application. The dissipation continued for thiamethoxam to reach 0.72 mg/kg with 47.82% loss in the third day of application. The rapid dissipation was found in the seventh day after spraying, which thiamethoxam residue reached 0.083 mg/kg with 93.98% loss. The degradation continued to reach 0.061 mg/kg with 95.57% loss after 10 days after

application. The residues of thiamethoxam on pepper decreased to 0.034 mg/kg with 97.31 % loss and 0.01 mg/kg with 99.27% loss after 15 and 21 days of application, respectively. Based on the previous results, the calculated half-life period (RL_{50}) of thiamethoxam on pepper fruits was 3.13 days. The maximum residue limit (MRL) of thiamethoxam in pepper fruits is 0.7 mg/Kg according to Codex Alimentarius Commission for Pesticide Residues (CAC/PR). 2009 [17]. The results presented here in clearly show that pepper fruits can be consumed safely by human after 4 days from spraying with thiamethoxam.

TABLE 1. Dissipation of thiamethoxam residue in pepper fruits.

Time after application	Residues (mg/kg)±SD	% loss	% persistence
Initial	1.38±0.54	0.00	100
1 day	1.27±2.87	7.97	92.03
3 days	0.72±1.05	47.82	52.18
5 days	0.39±2.59	71.73	28.27
7 days	0.083±2.01	93.98	6.02
10 days	0.061±0.54	95.57	4.43
15 days	0.034±0.81	97.31	2.69
21 days	0.01±0.24	99.27	0.73
RL_{50} (days)		3.11	
MRL		0.7	
PHI (days)		4	

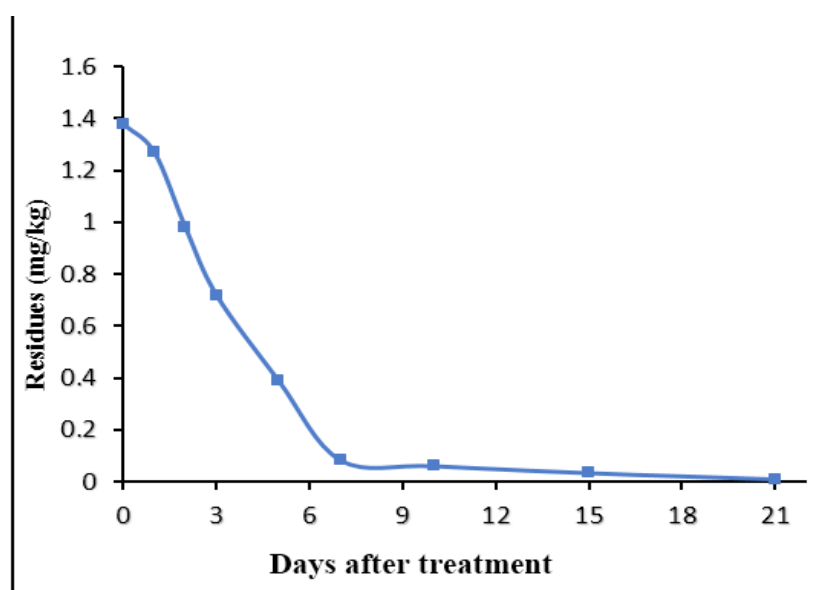


Fig. 2. Dissipation Curve of Thiamethoxam in Pepper Fruits.

dinotefuran

Data presented in Table (2) and figure (3) demonstrate the initial deposits as well as the residual behavior of dinotefuran in pepper fruits. The initial deposit of dinotefuran in pepper fruits was 6.59 mg/kg two hours after application. The residue of dinotefuran in pepper fruits within the first 24 hours after application decreased to 5.40 mg/kg with 18.06% loss. The amounts of dinotefuran residue decreased to 1.28 mg/kg with high percent loss (80.58%) in the third day of application. Data indicated that dissipation of dinotefuran residue was rapidly within the first

three days after spraying. Residues of dinotefuran in pepper fruits continued and reached to 0.09 and 0.01 mg/kg with 98.63 and 99.84% loss after 7 and 10 days of application, respectively. The residues became undetectable on 15th and 21th day after application. Based on the previous results, the calculated half-life period (RL_{50}) of dinotefuran in pepper fruits was 2 days. The maximum residue limit (MRL) of dinotefuran in pepper fruits is 0.01 mg/Kg according to Codex Alimentarius Commission for Pesticide Residues (CAC/PR). 2009 [17], so the pepper fruits can be consumed safely after 11 days of application.

TABLE 2. Dissipation of dinotefuran residue in pepper fruits.

Time after application	Residues (mg/kg)±SD	% loss	% persistence
Initial	6.59±1.25	0.00	100
1 day	5.40±0.95	18.06	81.94
3 days	1.28±1.01	80.58	19.42
5 days	0.67±1.38	89.83	10.17
7 days	0.09±2.09	98.63	1.37
10 days	0.01±0.22	99.84	0.15
15 days	ND	---	---
21 days	ND	---	---
RL_{50} (days)		2	
MRL		0.01	
PHI		11	

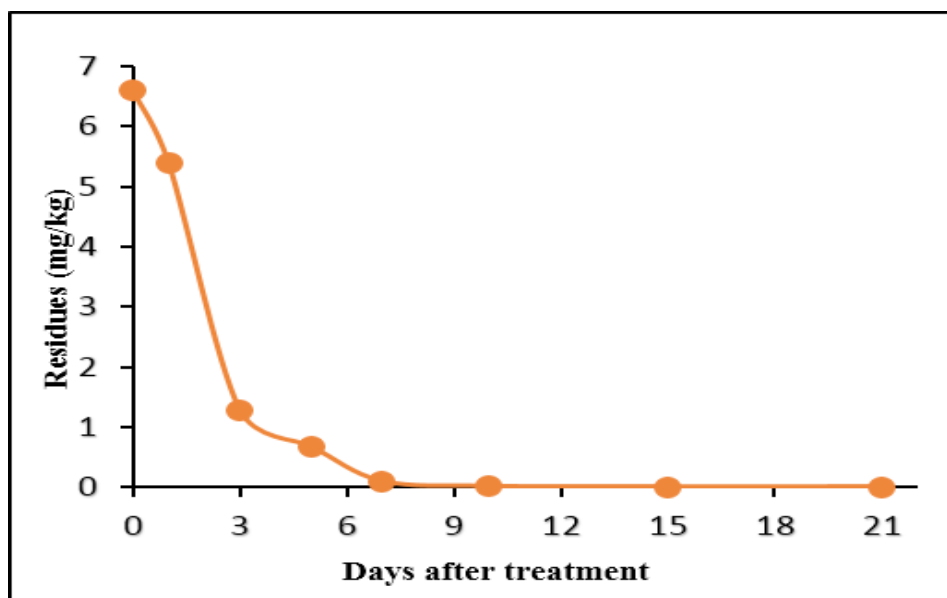


Fig. 3. Dissipation curve of dinotefuran in pepper fruits.

Discussion

The evaluations of calibration curve linearity of thiamethoxam and dinotefuran were done with HPLC-DAD. The correlation coefficient ($R^2 = 0.99$). The results showed that the matrix effect was -17.75% for dinotefuran and 4.36% for thiamethoxam which indicated that no interfering endogenous peak appeared and did not significantly suppress or enhance the response of the instrument.

The residual amount of thiamethoxam was rapidly decreased during the third day of spraying followed by gradually decreasing until the end of experimental period, the lowest dissipation rate per day found from the seventh to tenth day of application, while the highest value occurred in the first 24 hours of spraying. The pepper fruits could be used safely for human consumption after 4 days from spraying with thiamethoxam, because the residues below the MRL of thiamethoxam on pepper. Also, the initial deposit of thiamethoxam (Actara 25% WG) on pepper fruits was lower than the other tested pesticides. It may be due to that the rate of application for Actara 25% WG (20 g/100 L water).

The highest dissipation rate of dinotefuran per day was found in the first day, a quick decline of dinotefuran concentration mainly during the first three days was observed followed by gradually decrease until the 15th day after treatment. In the same concept, Galiotta, *et al* 2010 [18] reported that 16 days after application pepper by dinotefuran are necessary to meet the European MRL requirements and zero days for the USA requirements. On the other hand, Rahman *et al* 2013 [19] found a maximum of 0.32 mg kg⁻¹ of dinotefuran residue was detected in leek sample sprayed three times at 7-day intervals until 7 days prior to harvest.

The climatic conditions, dosage, the intervals between application and harvest effect on the dissipation of pesticide residues in crops, also the rapid dissipation of originally applied pesticide is dependent on a variety of environmental factors such as sunlight and temperature, however, high temperature is reported to be the major factor in reducing the pesticides from the plant surface, light plays an important role in the behavior of pesticide in the environment. Also, the decline of pesticides may be due to biological, chemical or physical processes, or if still in the field, due to dilution by the growth of the crop [20, 21].

Conclusion

In this work, an HPLC-DAD analytical method based on QuEChERS sample pretreatment procedures was used for the determination of dinotefuran and thiamethoxam residues in pepper fruits. The developed method is easy and compatible for residue analyses of dinotefuran and thiamethoxam, the mean recoveries ranged from 77–80% and 78–112% respectively, and repeatability of the method, expressed as the relative standard deviation, was lower than 3%. The calculated half-life period (RL_{50}) of tested pesticides on pepper fruits were 2 and 3.11 days for dinotefuran and thiamethoxam, respectively. According to maximum residue limit (MRL) the pre-harvest interval (PHI) of thiamethoxam and dinotefuran in pepper was 4 and 11 days after the treatment, respectively.

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تقدير متبقيات ميبيدي داينوتيفيوران و ثياميثوكسام في ثمار الفلفل باستخدام طريقة HPLC/DAD وجهاز QuEChERS

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تم تجميع عينات ثمار الفلفل عشوائيا من المناطق المعاملة بالجرعات الموصى بها لتحليل متبقيات المبيدات بها بعد صفر، ١، ٣، ٥، ٧، ١٠، ١٥، و ٢١ يوم من الرش بالتوازي مع عينات غير معاملة حيث تم تقدير متبقيات ميبيدي داينوتيفيوران و ثياميثوكسام في ثمار الفلفل باستخدام جهاز HPLC/DAD وكانت طريقة الاستخلاص المتبعة هي ما يسمى بطريقة QuEChERS حيث تعتبر طريقة سهلة وسريعة وفعالة ورخيصة في تقدير متبقيات المبيدات وكانت معدلات الإسترجاع للمركبين بهذه الطريقة تتراوح ما بين ٧٧-٨٠٪ و ٧٨-١١٢٪ لكلا من داينوتيفيوران و ثياميثوكسام على الترتيب. وكانت حدود التقدير لهذه الطريقة ٠,٠١ - ١ ملجم/كجم لكلا المبيدين في عينات الفلفل. كانت الكمية الأولية لمبيدي داينوتيفيوران و ثياميثوكسام في ثمار الفلفل ١,٣٨، ٦,٥٩، ١,٣٨ ملجم/كجم على الترتيب، وأوضحت الدراسة أن فترة نصف العمر للمبيد داينوتيفيوران هي ٢ يوم في حين بلغت ٣,١١ يوم لمبيد ثياميثوكسام وذلك بناء على قيمة (MRL) الخاصة بكلا المبيدين والتي تقدر بـ ٠,٠١ و ٠,٧ ملجم/كجم على الترتيب، وكانت قيمة (PHI) ١١ و ٤ يوم لكلا من داينوتيفيوران و ثياميثوكسام على الترتيب.