Food Science and Human Wellness 8 (2019) 362–367

Contents lists available at ScienceDirect

Food Science and Human Wellness

journal homepage: www.elsevier.com/locate/fshw

Development and validation of an analytical method for detecting chlorantraniliprole residues in fresh tea leaves

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ARTICLE INFO

Article history:
Received 14 October 2019
Received in revised form 7 November 2019
Accepted 7 November 2019
Available online 8 November 2019

Keywords:
Multiwalled carbon nanotubes
Fresh tea leaves
Chlorantraniliprole
Dispersive solid-phase extraction
Gas chromatography

ABSTRACT

An efficient method using multiwalled carbon nanotubes (MWCNTs) as dispersive solid-phase extraction sorbent was established for determining chlorantraniliprole residues in fresh tea leaves, which are known to be a troublesome matrix containing abundant pigments, via gas chromatography with an electron capture detector. Acetonitrile was used as the extraction solvent, with sodium chloride enhancing the analyte partition in the organic phase. The optimal mixture of MWCNTs and primary secondary amine (PSA) was based on the distribution of the target analyte recovery and on the clean-up efficiency; while matrix-matched calibration was recommended to combat the matrix effect. Mean recoveries of 95.2%–108.8% were obtained with intraday and interday precisions of less than 7.9% and 10.3%, respectively. Good linearity was observed for concentrations of 0.02–1.0 mg/kg with a correlation coefficient of 0.9984. The limits of detection and quantification were 0.005 mg/kg and 0.02 mg/kg, respectively. The method was employed to investigate the dissipation dynamics of chlorantraniliprole in fresh tea leaves with real field samples. Consequently, the dissipation rates of chlorantraniliprole in fresh tea leaves followed pseudo-first-order kinetics with a half-life of 1.9 d, and the average chlorantraniliprole residue content was below 0.02 mg/kg with a harvest withholding period of 14 d.

1. Introduction

Chlorantraniliprole is a new anthranilic diamide insecticide, which is efficacious for the control of lepidopteran insect pests and some species in the orders Coleoptera, Diptera and Hemiptera [1]. The structural formula is shown in Fig. 1. The compound is a potent and selective activator of insect ryanodine receptors, which are critical for muscle contraction [2]. Through efficient activation of the ryanodine receptors in insects, chlorantraniliprole can induce the out-of-control release and extensive loss of endogenous calcium ions, leading to regulation weakness, numbness and paralysis of the muscle until death [3]. Pending target crops for this insecticide include rice, corn, soybeans, vegetables, fruits and others. Because of its low toxicity to humans, animals and aquatic organisms (fish and shrimp) [4,5], this pesticide can meet the requirements of modern environmental protection. In 2009, chlorantraniliprole was listed as an alternative pesticide for methamidophos and other highly toxic pesticides by the Ministry of Agriculture of China [6], indicating its broad application prospects. Because of growing concerns over food safety problems caused by pesticide residues, developed countries and international organizations, including the United States, Japan and the European Union [7–9], have strictly limited the allowed level of chlorantraniliprole residues on various crops through the establishment of a maximum residue limit (MRL) for fruits, vegetables, cereals, beans, milk and other food and agricultural products. In China, the temporary maximum residue limit (TMRL) for chlorantraniliprole in cereals, fruits, vegetables and other agricultural products has been specified as 0.02–20.0 mg/kg [10].

Fresh tea leaves, raw materials for producing tea products, are known to be a troublesome matrix as they contain complex components, including alkaloids, pigments, polyphenols, etc. The analysis of pesticide residues in tea leaves is usually difficult owing to matrix interferences and complicated extraction procedures. Numerous extraction and cleanup methods have been published

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Peer review under responsibility of KeAi Communications Co., Ltd.

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https://doi.org/10.1016/j.fshw.2019.11.001

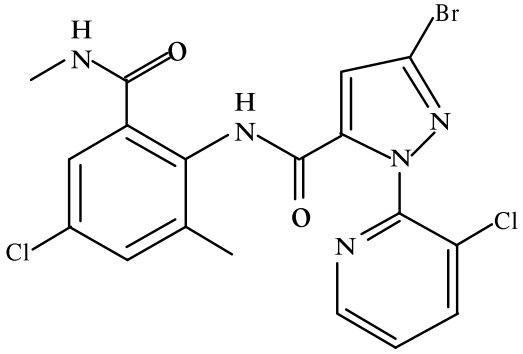

Fig. 1. Structural formula of chlorantraniliprole.

on determining chlorantraniliprole residues in food samples using high-speed homogenization [11], mechanical oscillation extraction [12], sonication extraction [13], liquid-liquid extraction [14] and solid-phase [15] and dispersive solid-phase extractions (SPEs) [16], as well as identification and quantification by gas chromatography (GC) [17,18], high-performance liquid chromatography (HPLC) [19,20], HPLC-tandem mass spectrometry [21,22] and enzyme-linked immunosorbent assay [23]. Among the above pretreatment methods, dispersive SPE exhibits the advantages of accuracy, rapidness, simple operation and low cost and is thus favored by most analysts. This approach has become an important sample pretreatment method and is widely employed for determining pesticide residues in samples of fruits, vegetables, grains, soil and water [24–28], yielding good results. During the process of dispersive SPE, a material with suitable absorbability, such as primary secondary amine (PSA), octadecylsilane (C_{18}), or graphitized carbon black (GCB), is directly added to the sample extract, and the resulting mixture is shaken to achieve rapid purification through the interaction between the sorbent and the interfering substances in the sample matrix [29]. In this case, the sorbent is a key factor that determines the selectivity and sensitivity. Conventional sorbent materials, such as PSA, GCB and C_{18}, often present various disadvantages, including a low recycling rate, poor selectivity and high cost. Multiwalled carbon nanotubes (MWCNTs) are nanosized hollow tubes formed from curved graphite-like planes composed of six-membered rings of carbon and have unique physical and chemical properties, such as high mechanical strength, strong acid and alkali resistance and good heat resistance. Compared with PSA, GCB and C_{18}, MWCNTs possess a large specific surface area, a strong adsorption capability, a low cost and can effectively remove both pigments and hydrophobic substances. As new high-performance sorbent material, MWCNTs have been widely applied to detect organic and inorganic pollutants in food and agricultural products, including pesticides and veterinary medicines [30,31], heavy metals [32], antibiotics [33], mycotoxins [34], polycyclic aromatic hydrocarbons [35] and polychlorinated biphenyls [36]. However, the use of MWCNTs as an adsorbent and purification agent for analyzing chlorantraniliprole residues in sample matrices such as fresh tea leaves has not been studied.

The aim of this study was to develop a simple and effective method based on MWCNTs as dispersive SPE material and the GC method with an electron capture detector (ECD) for the analysis of chlorantraniliprole residues in fresh tea leaves. The parameters affecting both the extraction and cleanup steps, including the variety and volume of extraction solvent, extraction time and type and amount of sorbent were optimized. This work represents the first detection of chlorantraniliprole residue in fresh tea leaves with an easy and reliable method. The proposed method was utilized for analyzing field samples and investigating the dissipation dynamics of chlorantraniliprole in fresh tea leaves.

2. Materials and methods

2.1. Instruments

Chromatographic separation was undertaken with a 7890A GC equipped with a ^{63}Ni ECD (Agilent, USA). A KQ-500DE ultrasonic cleaner was provided from Kunshan Ultrasonic Instrument Co., Ltd. A TG16-WS high-speed centrifuge was provided from Hunan Xiangyi Experimental Equipment Co., Ltd. A HSC-24B nitrogen blowing instrument was bought from Tianjin Heng Ao Technology Development Co., Ltd.

2.2. Chemicals and reagents

The chlorantraniliprole (200 g/L) suspending agent was purchased from DuPont Agricultural Chemicals Ltd. (Shanghai, China). A standard solution of chlorantraniliprole (100 mg/L) was provided from the Environmental Monitoring and Research Institute of the Ministry of Agriculture (Tianjin, China). MWCNTs, with an outer diameter of 10–20 nm, and PSA, with a particle size of 40–60 μm, were purchased from Bonna-Agela Technologies, Inc. (Tianjin, China). n-Hexane was of HPLC grade and bought from Oceanpak Alexative Chemical, Ltd. (Goteborg, Sweden). All other chemical reagents involved in this study were of analytical grade or better and provided by Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.3. Preparation of standard solutions

A 1-mL chlorantraniliprole standard solution with a mass concentration of 100 mg/L (in methanol) was transferred to a 5-mL volumetric flask and slowly blown to near dryness using a nitrogen evaporator, then diluted to the mark with acetone/*n*-Hexane (1:1, *V/V*) to obtain a standard solution with a concentration of 20 mg/L and stored at 4 °C. The prepared standard solution was gradually diluted with acetone/ *n*-Hexane (1:1, *V/V*) to obtain working standard solutions with concentrations of 1.0, 0.5, 0.2, 0.1, 0.05 mg/L and 0.02 mg/L.

The blank sample was treated by the developed method, and the extract was then dried through nitrogen evaporation. After 1 mL of the working standard solutions with different concentrations was added, the resulting mixture was shaken and filtered through a 0.22-μm organic membrane to obtain matrix-matched standard solutions of the corresponding concentrations.

2.4. Sample preparation

Fresh tea leaf samples were crushed and mixed evenly, and 5.0 g of samples was accurately weighed and placed in a 50-mL centrifuge tube. Subsequently, 10 mL of acetonitrile and 1 g of sodium chloride were added to the tube, which was vortex-mixed for 1 min followed by sonication extraction for 15 min at 500 W and 40 kHz. Then, 4 g of anhydrous magnesium sulfate was added to the sample tube, which was vortex-mixed for 2 min and centrifuged at 7000 r/min for 4 min. Afterwards, an aliquot of 4 mL was transferred from the supernatant to a new clean 10-mL centrifuge tube containing 70 mg of MWCNTs, 150 mg of PSA and 300 mg of anhydrous magnesium sulfate as dispersive SPE adsorbents. Centrifugation was then carried out as described above. Subsequently, 2 mL of the supernatant was transferred to another clean tube and concentrated to near dryness under nitrogen at 70 °C. The resulting residue was dissolved in 1 mL of acetone/*n*-Hexane (1:1, *V/V*), filtrated through a 0.2-μm membrane, and then subjected to GC analysis.

2.5. Chromatographic conditions

The separation was carried out using an Agilent HP-5 (5% phenyl methyl siloxane) fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). Ultrahigh purity nitrogen gas (99.999%) was used as the carrier gas at a flow rate of 1.0 mL/min. The injector and detector temperatures were set at 240 °C and 300 °C, respectively. The oven temperature was programmed from an initial value of 80 °C (held for 1 min), ramped to 180 °C at a rate of 30 °C/min (held for 5 min) and ramped to 260 °C at a rate of 20 °C/min (held for 18 min). The injection volume was 1 μL for the splitless mode.

2.6. Matrix effect

To evaluate the matrix effect in the present work, a series of matrix-matched standards and corresponding solvent standards with different concentrations (0.02, 0.05, 0.1, 0.2, 0.5, 1.0 mg/kg and 20.0 mg/kg) were prepared to compare the GC signals obtained through three parallel tests. The difference between two response signals divided by the response signal of the solvent standard represented the matrix effect, which was determined by the following equation: matrix effect/% = (response of the matrix-matched standard/response of the solvent standard with the same concentration - 1) × 100. A signal enhancement would occur when the percentage of the matrix effect was positive. When the value was negative, it would be indicative of signal suppression [37].

2.7. Method validation

The validation of the developed method was carried out using the following parameters: linearity, accuracy, precision, limit of detection (LOD) and limit of quantification (LOQ). Linearity was studied by analyzing matrix-matched standards in triplicate with concentrations of 0.02, 0.05, 0.1, 0.2, 0.5 mg/kg and 1.0 mg/kg. The chromatograms were recorded, and the calibration curve was constructed by plotting the integrated chromatographic peak area versus the corresponding concentration value. Accuracy and precision were assessed by performing recovery experiments, analyzing spiked blank samples at spiked concentration levels of 0.02, 0.05, 0.2, 1.0 mg/kg and 20.0 mg/kg. The spiking of a sample was achieved by adding the appropriate volume of the pesticide standard solution in acetone/*n*-Hexane (1:1, *V/V*) to 5 g of homogenized fresh tea leaf sample before extraction with acetonitrile. Based on the SANCO/825/00 guideline [38], recoveries were considered satisfactory in the ranges of 70%–110% at 0.2, 1.0 mg/kg and 20.0 mg/kg spiked concentrations and of 70%–120% at 0.02 mg/kg and 0.05 mg/kg. The precision of the method was evaluated by measuring the intraday and interday relative standard deviations (RSDs). The intraday precision was obtained within one day by analyzing six replicates fresh tea leaf samples spiked with chlorantraniliprole at five concentrations of 0.02, 0.05, 0.2, 1.0 mg/kg and 20.0 mg/kg. The interday precision was determined once a day for five successive days by analyzing replicate fresh tea leaf samples spiked with the above concentrations. RSD values below 10% at a 20.0 mg/kg spiked concentration, below 15% at 0.2 mg/kg and 1.0 mg/kg and below 20% at 0.02 mg/kg and 0.05 mg/kg were considered satisfactory. The LOD was viewed as the concentration producing a signal-to-noise ratio (R_{SN}) of 3:1, and the LOQ was defined on a R_{SN} of 10:1. Both LOD and LOQ values were estimated by analyzing the spiked samples at the lowest concentration.

2.8. Dissipation study

The developed method was applied in a field trial of chlorantraniliprole dissipation. The field experiment was performed on September 2015 in an evenly growing Biluochun tea garden in East Dongting Mountain, Suzhou City, China with an experimental design according to NY/T 788–2004 "Guideline on Pesticide Residue Trials" issued by the Ministry of Agriculture of China [39]. The field was divided into 30 m^2 sections for the control, as well as for the dissipation rate measurement, and three parallel cells were used for each treatment.

When the tea plants of variety Chawan 3 showed new sprouts, the tea in the experimental area was sprayed once with a suspension of 200 g/L chlorantraniliprole diluted with 1125 L water per hm^2 to obtain the recommended dose of 15 g a.i/hm^2. Fresh tea leaf samples were randomly collected from shoots with two to three leaves at 10–15 sites on days 0 (2 h after spraying), 1, 3, 5, 7, 10, 14, 17 and 21 from 11 September to 1 October, 2015. All samples were placed into polyethylene bags and transported to the laboratory, and the subsamples were then kept deep-frozen (−20 °C) until analysis.

The dissipation of chlorantraniliprole residues with time was described mathematically by the pseudo-first-order rate equation, which can be calculated as $C_t = C_0 e^{-kt}$, where C_t is the concentration (mg/kg) at time t (d) after application and C_0 is the initial concentration (mg/kg) [40]. The dissipation half-life ($t_{1/2}$) was determined from the equation $t_{1/2} = 0.693/k$, which was obtained from the above equation, where k is the first-order rate constant (/d).

3. Results and discussion

3.1. Optimization of extraction and cleanup

3.1.1. Extraction solvent

The blank sample of fresh tea leaves spiked with the standard at a concentration of 0.02 mg/kg was used to investigate the extraction efficiency. The results showed that the extraction efficiency and repeatability for the target pesticide with acetonitrile, ethyl acetate and acetone solvents were satisfactory, with recovery rates of 99.5%, 97.8% and 104.3% and standard deviations of 4.3%, 4.1% and 7.1%, respectively. Due to the good selectivity of acetonitrile, pesticide extraction with this solvent resulted in fewer interfering impurities, such as wax and fatty acid, which enhanced the purification. Additionally, the salting-out effect of acetonitrile was better than that of ethyl acetate and acetone, and the improved effect of acetonitrile aided the separation of the extract. As a result, acetonitrile was selected as the extraction solvent, and the assessment of the pesticide extraction efficiency with acetonitrile volumes of 10, 15 and 20 mL revealed that 10 mL of acetonitrile could fully extract the target pesticide.

3.1.2. Extraction time

The sonication technique is a common tool used to extract pesticides from food matrices, accelerating the pesticide dissolution from the sample matrix due to mechanical vibration and cavitation effects, thus, improving the extraction efficiency. The blank sample of fresh tea leaves spiked with a concentration of 0.02 mg/kg was sonicated, and the extraction efficiency obtained for different sonication times (i.e., 5, 10, 15, 20, 25 min and 30 min) was determined. As shown in Fig. 2, the recovery rate of the target pesticide showed a gradual improvement with the increase in sonication time. A sonication time of 15 min resulted in a recovery rate of 94%, with good parallelism, and the recovery rate did not show any marked changes with further increases in the sonication time. Therefore, an ultrasonication time of 15 min was selected.

3.1.3. Type and amount of adsorbent

Fresh tea leaves contain many alkaloids, organic acids, polyphenols and pigments, which can be extracted with the analyte during the extraction process. These matrix coextracts may have a deleterious effect on the instruments, for example, causing a large

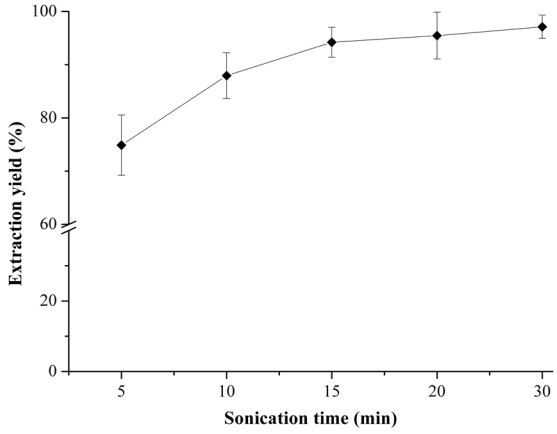

Fig. 2. Selection of the sonication duration.

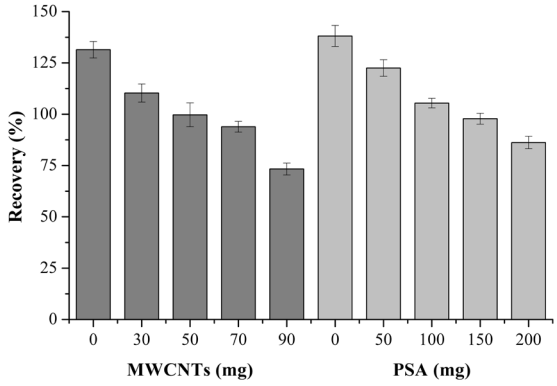

Fig. 3. Effect of the amounts of MWCNTs and PSA on the spike recovery of chlorantraniliprole.

matrix effect, contaminating the instrument system and shortening equipment operating life. To reduce the influence of the matrix on the analysis results and on the instrument, the impurities were removed by dispersive SPE, and PSA and MWCNTs were tested as the dispersive scavenger. PSA presents a strong ion-exchange capacity and can effectively remove tea catechins, polyphenols, fatty acids, some organic acids and sugars from samples through hydrogen bond interactions with the interfering compounds [41–43], but its ability to purify pigments is limited. This preliminary experiments showed that after purification with different amounts of PSA, the color of the sample solution remained green and showed little change. MWCNTs exhibit a nanoscale hollow tubular structure and a large specific surface area, which gives them the ability to strongly adsorb and remove pigments [44]. Additionally, MWCNTs are stable, durable and inexpensive. Thus, a mixture of PSA and MWCNTs was used as the sorbent for the dispersive SPE process.

The amount of sorbent is a key factor that influences the cleanup performance and the recovery rate. The use of a too-small an amount would result in a weak purification, whereas a too-large amount would exert a satisfactory purification but a recovery rate that is lower than that required for determination. In this work, 4 mL of supernatant from the centrifuged sample (with a spiking level of 0.02 mg/kg) was used to investigate the optimal amount of MWCNTs and PSA for purification. As shown in Fig. 3 when the amount of MWCNTs and PSA increased, the recovery rates of the analyte decreased, and the use of 70 mg and 150 mg yielded the recovery rates of 92% and 97%, respectively, which were in the acceptable range of 70%-120%. MWCNTs can be applied to remove high level of pigments. Conversely, it can result in a loss of planar analyte due to the strong affinity and π-π bonding between analyte and MWCNTs. Perhaps more amount of MWCNTs could have better cleanup performance, however, over 90 mg of MWCNTs would lead to low recovery rates (lower than 75%) for the analyte, which greatly limited the usefulness of the cleanup of pigmented matrix. Moreover, we compared the color difference between the unpurified sample extract and the sample extract purified with 70 mg of MWCNTs and 150 of mg PSA. The results showed that the unpurified sample extract was light green and turbid, whereas the purified sample extract was almost colorless and transparent, which indicated that many of the interfering substances especially pigments were removed by the MWCNTs and PSA after the dispersive SPE cleanup procedure. Considering the pesticide recovery rate of the pesticide and the purification effect of the sample extract, the optimized amounts of MWCNTs and PSA for dispersive SPE were 70 mg and 150 mg, respectively.

3.2. Matrix effect

Matrix effect occurs due to the coelution of matrix components in complex samples, which significantly interferes with the detection of the target analytes [45]. Matrix effect may vary substantially for different matrices and with the properties of the target analytes, which could render inaccurate qualitative and quantitative results of the method [44,46]. Thus, accounting for the assessed the matrix effect and/or the use of matrix-matched calibration standards to minimize quantitative errors of the method is essential. As presented in Table 1, in the proposed method, the matrix enhanced the response of the target pesticide at a low concentration, whereas a high matrix concentration yielded a reduced response. Therefore, the matrix-matched calibration curve was recommended in the method for analyte quantification.

3.3. Linearity

The linearity of an analytical method can be defined as the ability of the method to obtain test results that are directly proportional to the concentration of the target analytes, within a given range. In this method, the calibration curve for chlorantraniliprole was linear over a concentration range from 0.02 mg/kg to 1.0 mg/kg, and the linear regression equation was determined as $y = 14517x+289.31$, with a correlation coefficient of 0.9984.

3.4. Accuracy and precision

Recovery and repeatability experiments were performed to assess the trueness and precision of the method. Table 2 provides the recovery and precision values for chlorantraniliprole in spiked samples of fresh tea leaves. Apparently, the obtained mean recovery rates fell into an acceptable range of 95.2%–108.8%. The RSD values for the intraday and interday precisions of the method ranged from 3.4% to 7.9% ($n = 6$) and from 4.8% to 10.3% ($n = 5$), respectively, which were satisfactory within the acceptable limits. Fig. 4 displays typical chromatograms obtained for a blank sample and a spiked sample at a concentration level of 0.02 mg/kg.

3.5. LOD and LOQ

The LOD and LOQ are considered the lowest concentrations of a certain analyte for its confident identification and quantification, respectively. The LOD for chlorantraniliprole was determined as 0.005 mg/kg, and the LOQ was found to be 0.02 mg/kg, which were generally considered satisfactory for the quantitative analysis of the analyte.

Table 1
Matrix effect of chlorantraniliprole in fresh tea leaves.

Mass concentration /(mg/kg)	Response value of solvent standards in peak area (Mean ± standard deviation)	Response value of matrix-matched standards in peak area (Mean ± standard deviation)	Matrix effect
0.02	340.1 ± 6.52	620.8 ± 7.68	71.95
0.05	812.1 ± 6.01	820.7 ± 6.12	15.24
0.1	1410.3 ± 5.11	1992.1 ± 4.80	41.25
0.2	3010.5 ± 4.55	3362.3 ± 4.11	11.68
0.5	7092.6 ± 4.23	7015.0 ± 3.72	−1.09
1.0	15031.3 ± 2.12	15021.2 ± 2.11	−0.067
20	280969.1 ± 1.50	280854.8 ± 1.47	−0.041

Table 2
Spike recovery rate and relative standard deviation of chlorantraniliprole in fresh tea leaves.

Spiking level /(mg/kg)	Intraday precision (n = 6)		Interday precision (n = 5)	
	Mean recovery(%)	RSD(%)	Mean recovery(%)	RSD(%)
0.02	108.8	7.9	105.1	10.3
0.05	102.5	4.7	99.8	5.9
0.2	97.3	5.9	96.5	7.3
1.0	95.2	4.1	97.0	6.7
20.0	96.9	3.4	98.3	4.8

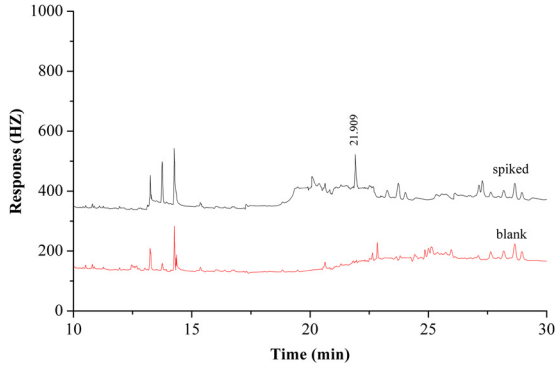

Fig. 4. Chromatogram of fresh tea leaves.

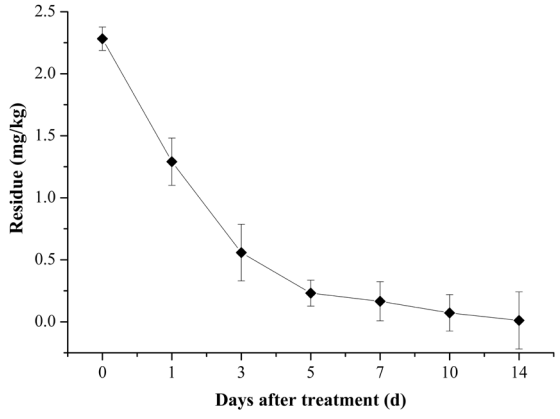

Fig. 5. Dissipation dynamics of chlorantraniliprole in fresh tea leaves.

3.6. Method application

To further demonstrate the method applicability, a field trial of chlorantraniliprole dissipation in fresh tea leaves sprayed with a suspension of 200 g/L chlorantraniliprole was performed using the method established in this work. As illustrated in Fig. 5, the trial results revealed that the residue of chlorantraniliprole in fresh tea leaves reached a maximum of 2.282 mg/kg at 2 h after spraying and then began to decrease, showing a dissipation of 43.4% after 1 d. Furthermore, the residue was significantly reduced after 7 d, with a dissipation of 92.8%, and the digestibility equaled 99.5% after 14 d, yielding a residual amount of 0.011 mg/kg, which was below the MRL value of 0.02 mg/kg set by European Union. The dissipation of chlorantraniliprole in fresh tea leaves followed the pseudo-first-order rate equation, and the regression equation was found to be $C_t = 1.8989e^{-0.3593t}$, with a correlation coefficient of 0.9855 and a half-life of 1.9 d. The residue of chlorantraniliprole in fresh tea leaves dissipated measurably with time, although the rate of loss may have been affected by environmental conditions. Dilution caused by the growth of the tea trees, physical loss and chemical degradation were probably the main factors contributing to this diminution [47].

4. Conclusions

In this work, a simple and reliable method with MWCNTs as dispersive SPE sorbent and GC-ECD detection for determining chlorantraniliprole residues in fresh tea leaves was developed. A mixture of MWCNTs and PSA were used in the cleanup step to obtain a better cleanup performance. It showed that MWCNTs could increase the removal of interfering substances from the fresh tea leaf extracts. The validation parameters of the method including linearity, accuracy, precision, LOD and LOQ, and matrix effect were examined, which demonstrated the developed method fulfilled the requirements for pesticide residue analysis. The developed method was successfully used to determine chlorantraniliprole residues in real field samples. The dissipation dynamics showed that chlorantraniliprole dissipated fast in fresh tea leaves, and the half-life was 1.9 d.

Declaration of Competing Interest

The authors confirm that the contents of this article have no conflict of interest.

Acknowledgment

This work was supported by Science and Technology Project of Suzhou (Grant Nos.: SNG201622 and SNG201644)

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