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Study of Imidaclothiz Residues in Cabbage and Soil by HPLC with UV Detection

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Abstract The HPLC method for determination of imidaclothiz residue in cabbage and soil was developed, and its degradation and final residue were studied. The mean accuracies of the analytical method were 92.0–93.0% in soil and 88–93% in cabbage. The precision in cabbage ranged from 2.2% to 5.6%, and in soil from 2.0% to 5.0%. The minimum detectable amount of imidacothiz was 1×10^{-10}g. The minimum detectable concentration was 0.0075 mg kg^{-1} in cabbage and 0.003 mg kg^{-1} in soil. The results showed that imidaclothiz degradation in soil and cabbage coincided with $C = 0.0427e^{-0.0923t}$, $C = 0.739e^{-0.279t}$. The half-lives were about 3.1 days in soil and 2.2 days in cabbage.

Keywords Imidaclothiz · Dynamics · Cabbage · Soil

At present, pesticides are considered to be essential for agricultural development. However, as the pesticides were widely applicated, residues may be rich in environment and food above Maximum Residue Limits (MRLs) (Tariq et al. 2007; Moretto 2008; Tucker 2008). This could produce negative effects on the health of consumers, including acute effect and chronic exposure that could result in serious health hazards (Shiokawa et al. 1988; Sirinyan et al. 1998). So, it is necessary to analyze the residues and dynamics of pesticide in environment and food (Yamamoto et al. 1998; Dai 2005).

Imidaclothiz (1-(2-chloros-5-thiazolylmethyl)-N-nitroimida-zolin-2-ylideneamine) (Fig. 1) belongs to neonicotinoids (Gupta et al. 2008a, b), which is the most newly developed class of synthetic insecticides during the past three decades, and is active against numerous sucking and biting insects, including aphids, whiteflies, beetles and some Lepidoptera species as well (Tomizawa and Casida 1999; Georgakopoulos et al. 2009). It is a kind of broad-spectrum pesticide with good preventive effects while safe for crops, and has been proved to be useful on vegetables and fruits (Zhang 2005). However, experimental study on the method for residue determination of imidaclothiz is limited. In this work, a simple, fast and efficient HPLC method was developed for the determination of imidaclothiz in cabbage and soil. To obtain efficient preconcentration with good reproducibility and accuracy, solid-phase extraction (SPE) was applied. The proposed procedure was validated. The parameters involved calibration and linearity, limits of detection and quantification, precision (repeatability). The present work was also designed to investigate the residues of 10% imidaclothiz wettable powder in cabbage and soil for the safe use of this insecticide and preventing any health problem to consumers.

Materials and Methods

Imidaclothiz standard (purity 99.0%) and 10% imidaclothiz wettable powder were supplied by Nantong Jiangshan Agrochemical & Chemical Co. Ltd. (Jiangsu, China.). Acetonitrile was a chromatograph reagent solvent, and all

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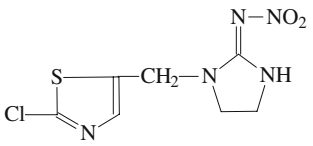

Fig. 1 Chemical structure of imidaclothiz

other chemicals were of analytical grade (Shanghai Experiment Reagent China Co. Ltd.).

A high performance liquid chromatography system, which consisted of two LC-10ATvp pumps and an SPD-10Avp, ultraviolet detector (Shimadzu, Japan) was used for the analysis and separation. A reversed-phase Kromasil ODS C_{18} column (250 mm × 4.6 mm ID, particle size 5 μm) was used for separation at ambient temperature and Chromato Solution Light Chemstation for LC system was employed to acquire and process chromatographic data.

Disposable SPE cartridges containing 100 mg of C_{18} bonded phase (40 mm) were obtained from J.T. Baker. The cartridges were preconditioned with 3 mL of acetonitrile, 3 mL of water and 1 mL of sample.

Field trials were carried out in Wuxue, Hubei Province of China. The content of soil organic matter was 1.22%, and PH was 8.17. Cabbage plants were transplanted in field plots in areas of 4 × 3 m. Each plot contained around 30 plants. The growing plants were treated with the pesticide under investigation at the recommended doses after the formation of plant heads. For each treatment, three plots were used and the plots were distributed in a completely randomized pattern, two untreated plots were sprayed water as control. Imidaclothiz wettable powder was sprayed at two doses 225 g/hm^2 (recommended) and 450 g/hm^2 (double of the recommended) with hand operated gongnong-16 sprayer. Representative samples were taken randomly after 0 (1 h after spraying), 1, 3, 5, 7, 14 and 21 days of spraying for the leaves and soil. The collected samples were placed in a deep freezer at −20°C until analysis.

Ultimate residue field test was designed as above, imidaclothiz wettable powder was sprayed at two doses 225 g/hm^2 (recommended) and 450 g/hm^2 (double of the recommended) with three times succession spraying 7 days interval. After 5 days, the collected samples were placed in a deep freezer at −20°C until analysis.

Pesticide residues were extracted and cleaned up according to the procedures in Abo-El-Seoud et al. (1995).

Soil

Soil was crushed or blended in a hammer mill and then sieved to obtain granules of the same size (40–120 mesh). A total of 20 g soil was socked overnight in a 250 mL cone flask with methanol 50 mL. Subsequently, the extract was shaken for 30 min on a shaker and filtrated. The extracted soil was then washed with 50 mL methanol three times. The volume of the extracts was concentrated to 2 mL with a vacuum rotary evaporator. The sample was transferred to a separator funnel containing 100 mL 5% sodium chloride and 100 mL petroleum ether. The upper level was washed with 50 mL 5% sodium chloride again. Then the petroleum ether phase was discarded and water phase was collected. The water phase was treated using liquid–liquid partitioning with dichloromethane for three times at the volume of 40, 40 and 20 mL, respectively. The sample was dried with sodium sulfate anhydrous column, and through evaporation, the final volume of the extracts reached 2 mL.

Cabbage

Powdered vegetable samples (10 g) were placed in a cone flask with 50 mL methanol and socked overnight. The cone flask was capped and shaken on a shaker for 30 min and then the extracted sample of cabbage was treated in the same way as that of soil.

Clean-up

A certain amount of the concentrated extract was transferred to a glass beaker with 10 mL ethyl acetate/petroleum ether (1:1, v/v). 1 mL of extract was brought into a preconditioned 100 mg C_{18}-bonded silica cartridge and sent to waste. The cartridge was removed from the SPE system and placed on top of a calibrated tube. 1.5 mL of extract sample was transferred to the cartridge, and cleaned up in the condition of over pressure.

All extracts were determined by reversed-phase HPLC with UV detection, which has proved to be a good alternative for imidaclothiz determination. Chromatographic separation in C_{18} columns produced good results, and the detection at 254 nm offered suitable chromatograms for the quantification of imidaclothiz in real samples. The mobile phase was acetonitrile–water (40:60 v/v) with 0.8 mL min^{-1} flow rate, and the volume of the injection was 20 μL. External standard method was adopted. About 0.025 g accurately measured standard imidaclothiz was transferred into a 50 mL volumetric flask, and was made constant volume to 50 mL with acetonitrile. Serial dilutions with acetonitrile were made to produce solutions with final concentrations. Concentrations of imidaclothiz were determined and the peak areas of the standards were recorded. The slope and intercept of the calibration graph were obtained by linear regression of peak area versus concentration: $y = ax + b$, where a is the slope, b is the intercept, x is the concentration and y is the peak area.

First-order kinetics has been extensively used to describe degradation processes of many chemicals (Zhou et al. 2004; Cao et al. 2005; Kyriakidis et al. 2005; Yi and Lu 2006). The degradation kinetics of the imidaclothiz in cabbage and soil was determined by plotting residue concentration against time, and the maximum squares of correlation coefficients were used to determine the equations of best fit curves. For all the samples studied, exponential relations were found to apply corresponding to first order rate equation. Confirmation of the first order kinetics was further made graphically from the linearity of the plots of C against time. The rate equation was calculated from the first order rate equation $C_t = C_0e^{-kt}$ where C_t represented the concentration of the pesticide residue at time t, C_0 represented the initial concentration and k was the rate constant in each day. The half-life ($t_{0.5}$) was determined from the k value for each experiment being $t_{0.5} = \ln 2/k$.

Results and Discussion

Reversed-phase HPLC, with UV detection, was proved to be a good alternative for imidaclothiz determination. Chromatographic separation in C_{18} columns produced good results. The detection at 254 nm offered suitable chromatograms for the quantification of imidaclothiz in real samples. Under the chosen conditions, imidaclothiz showed a retention time of 7.2 min (acetonitrile:water = 40:60 v/v), allowing a complete separation of its signal from that of foreign substances present in the samples (Fig. 2).

For most chromatographic procedures, a linear relation was observed between detector response and analyte concentration (Francotte et al. 1996). The parameters obtained by the selected chromatographic conditions for calibration correspond to: $y = 72.346x + 0.426$, $R^2 = 0.9992$. Linearity was in the range of 0.10–10 mg kg^{-1}. Quantitation of the imidaclothiz in real samples was based on the external standard method. The linearity of method was a measure of range within which the results are directly, or by a well defined mathematical transformation, proportional to the concentration of analyte in samples within a given range.

The limit of detection (LOD) is the lowest concentration of analyte detectable by an analytical method and is expressed in concentration units. The limit of quantification (LOQ) is the lowest solute concentration that can be determined with acceptable precision and accuracy, under the stated experimental conditions. It is also expressed in concentration units. In this study, the LOD and LOQ were determined according to the definition in Francotte et al. (1996), and were defined as follows: $LOD = 2h_nC_s/h_s$, $LOQ = 6h_nC_s/h_s$, where C_s is the amount of analyte injected; h_s is the peak height of the analyte, h_n is the largest deviation of detector signal from the average baseline level, measured at the retention time of the analyte. To measure these parameters, a series of diluted imidaclothiz standard samples were used. From this series, the peak was selected whose height h_s was about three times larger than the signal-to-noise ratio h_n. The h_s value was the height of the analyte measured from the average baseline level to the top of the peak, while h_n was measured over 10 peak widths in the absence of analysis. By comparison of the response with the baseline noise, the LOD was 0.0075 mg kg^{-1}(cabbage), 0.003 mg kg^{-1} (soil), and the LOQ was 1×10^{-10}g.

Precision (repeatability) reflects the variation in results when repetitive analyses are made on the same conditions. The numerical value used is the relative standard deviation for repeatability (RSD). Repeatability of the developed analysis method was determined by adding imidaclothiz in different concentrations to blank samples. The within-batch recovery and repeatability (RSD) of spiked imidaclothiz in sample at the levels of 0.1, 1 and 10 mg kg^{-1} are summarized in Table 1. The precision (repeatability) in cabbage ranged from 2.2% to 5.6%, and in soil from 2.0% to 5.0%. The results were fairly good for the concentration levels investigated. The average recoveries obtained for imidaclothiz at all concentrations and conditions investigated were determined as 92.3% and 90.3% in soil and cabbage.

The residue dynamics of imidaclothiz in cabbage was demonstrated in Fig. 3. The residues were 0.78, 0.56, 0.21, 0.12, 0.071, 0.012 mg kg^{-1} after 0, 1, 3, 5, 7, and 14 days of application. The dynamics regression equation and the half-lives of imidaclothiz in cabbage were as follows: $C = 0.739e^{-0.279t}$, $R^2 = 0.9801$, $T_{0.5} = 2.2$ days.

The residue dynamics of imidaclothiz in soil was shown in Fig. 4. The residues were 0.055, 0.039, 0.032, 0.027, 0.020, 0.011, 0.0021 mg kg^{-1} after 0, 1, 3, 5, 7, 14 and 21 days of application. As expected, a gradual and continuous deterioration of the pesticide residues in the treated plants was observed as a function of time after application. The dynamics regression equation and the half-life of imidaclothiz in soil were as follows: $C = 0.0427e^{-0.0923t}$, $R^2 = 0.9025$, $T_{0.5} = 3.1$ days.

The final levels of the residue were presented in Table 2. The final residues of imidaclothiz in soil were 0.0058–0.01 mg kg^{-1}, and the final residues of imidaclothiz in cabbage were 0.0015–0.0045 mg kg^{-1}, at recommended dosage with three times successive spraying and 5 days harvest interval.

In conclusion, the average half-lives of imidaclothiz were 3.1 days in soil, and 2.2 days in cabbage. It meant that 10% imidaclothiz wettable powder was easy to be degraded. The concentrations of the final residue of 10% imidaclothiz wettable powder in cabbage were from 0.0015

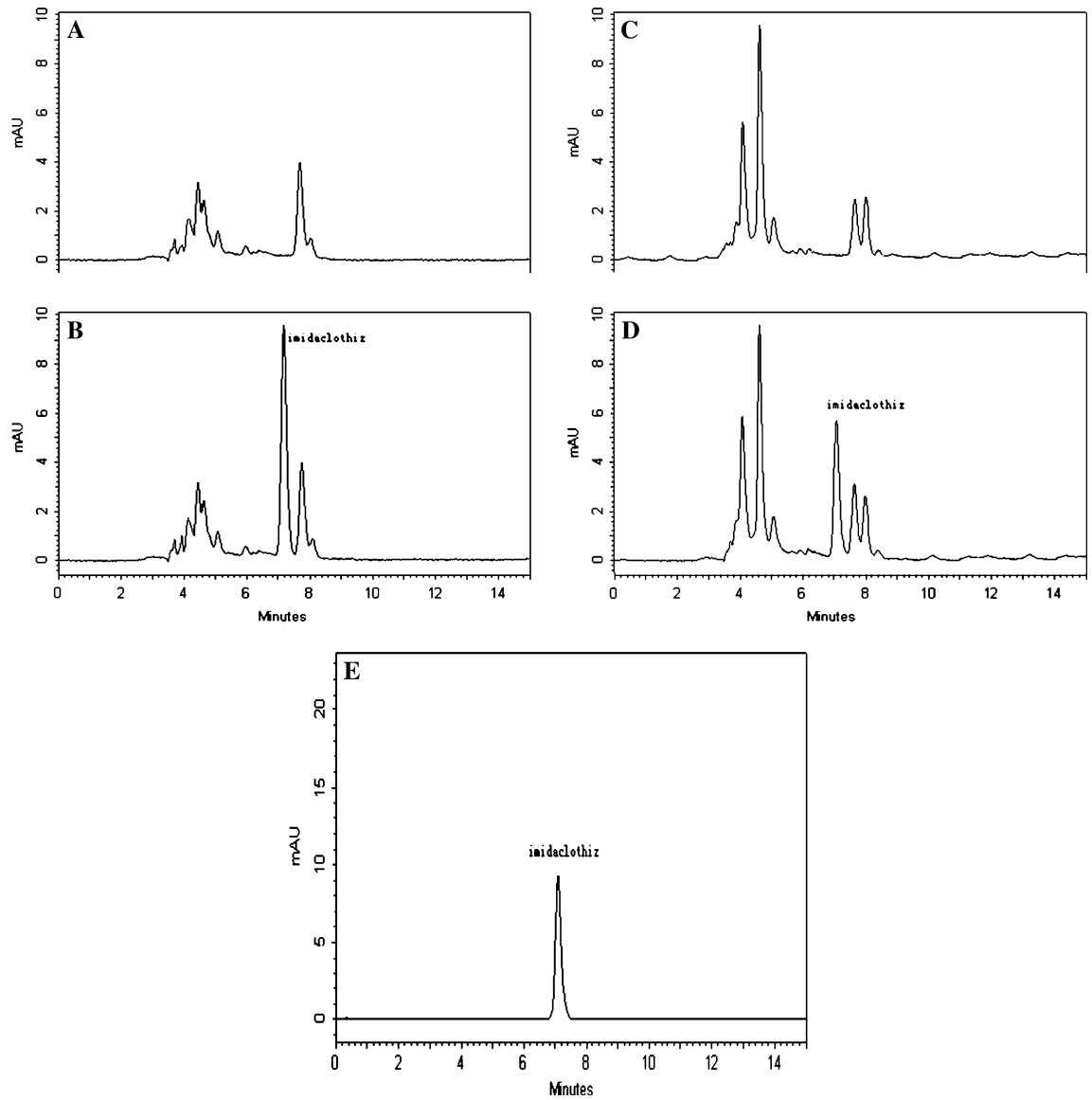

Fig. 2 Chromatograms of imidaclothiz. **a** soil without imidaclothiz; **b** soil spiked with imidaclothiz (0.45 mg kg^{-1}); **c** cabbage without imidaclothiz; **d** cabbage spiked with imidaclothiz (0.30 mg kg^{-1}); **e** the standard chromatogram of imidaclothiz

Table 1 Within-batch recovery and repeatability (RSD) for imidaclothiz in sample spiked at different levels

Matrix	Spiked levels (mg kg^{-1})	Detected (mg kg^{-1})	SD	Recovery (%)	RSD[a] (%)
Cabbage	0.1	0.088	0.1214	88	5.6
	1.0	0.90	0.1253	90	3.3
	10.0	9.3	0.2154	93	2.2
Soil	0.1	0.092	0.1765	92	5.0
	1.0	0.92	0.2845	92	2.0
	10.0	9.3	0.3214	93	3.1

[a] Mean value of six determinations

to 0.0045 mg kg^{-1}. The final residues of 10% imidaclothiz wettable powder in soil were from 0.0058 to 0.01 mg kg^{-1}. A dosage of 225 g/hm^2 was suggested for 10% imidaclothiz wettable powder and a harvest interval should be more than 5 days. This could be considered as safe for human being and animals.

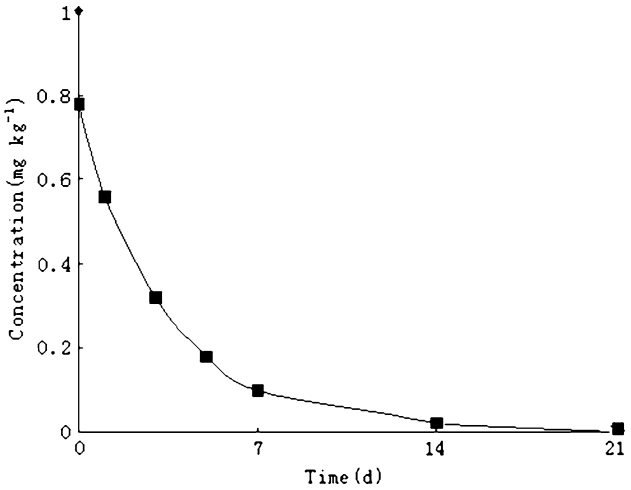

Fig. 3 The degradation curve of imidaclothiz in cabbage

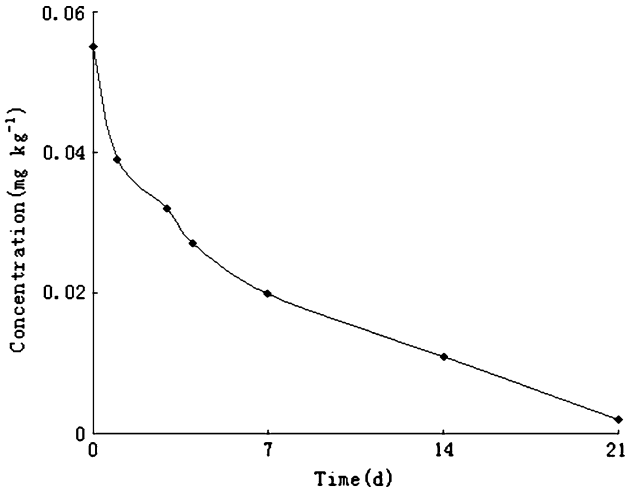

Fig. 4 The degradation curve of imidaclothiz in soil

Table 2 The final residues of imidaclothiz in soil and cabbage

Dosage (g/hm^2)	Times	Interval (days)	Residue[b] (mg kg^{-1})	
			Cabbage	Soil
225	3	5	0.0015	0.0058
	4	5	0.0024	0.0079
450	3	5	0.0039	0.0085
	4	5	0.0045	0.010
CK			UD[a]	UD

[a] UD means undetectable

[b] Mean value of six determinations

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