Residual Status and Dietary Risk Assessment of Clothianidin in Chinese Chives

Lin LI[1,2,3,4#], Yao TONG[1,2,3,4#], Huihui LIU[1,2,3,4], Yancheng ZHOU[1,2,3,4], Yuping LIU[1,2,3,4], Lei WANG[1,2,3,4*], Baiqin ZHENG[1,2,3,4*], Shuai WANG[1,2,3,4*]

1. Tangshan Food and Drug Comprehensive Testing Center, Tangshan 063000, China; 2. Tangshan Institute of Industrial Technology for Functional Agricultural Products, Tangshan 063000, China; 3. Hebei Agricultural Products Quality and Safety Testing Innovation Center, Tangshan 063000, China; 4. Hebei Engineering Research Center for Full-laboratory Automation Technology of Food Inspection, Tangshan 063000, China

Abstract [**Objectives**] This study was conducted to evaluate the residual status and dietary intake risk of clothianidin in Chinese chives. [**Methods**] From various markets in Tangshan City, 147 batches of Chinese chive samples were randomly collected for the detection of clothianidin pesticide residue, and the dietary risk of the detected samples was evaluated by using SiO-6512 automatic pretreatment equipment extraction and LCMS-8050 high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). [**Results**] Among the 147 batches of Chinese chive samples, clothianidin was detected in 46 batches, with a detection rate of 31.29%; and the residual level ranged from 0.012 0 to 3.516 mg/kg, with an average value of 0.274 mg/kg. The results of dietary risk assessment showed that the index of food safety (IFS) of clothianidin in Chinese chives ranged from 0.000 004 5 to 0.004 605 5, with an average value of 0.000 220 9. The average IFS values for minors, adults, the elderly and the entire population were, respectively, 0.000 358 9, 0.000 210 7, 0.000 102 6 and 0.000 211 3, which were far less than 1, indicating that it had no impact on human health. [**Conclusions**] This study provides reference for establishing the residue limit standard of clothianidin in Chinese chives.

Key words Clothianidin; Chinese chive; Dietary risk assessment
DOI:10.19759/j.cnki.2164-4993.2024.06.010

Chinese chives are a perennial herbal plant, and Tangshan area is also one of the important areas for chive cultivation[1]. *Bradysia odoriphaga* is a common pest in Chinese chive production, which mainly affects root absorption, causes premature aging and reduces production. The most common control method is root irrigation. Compared with other methods, irrigated roots are more likely to produce pesticide residues[2]. Clothianidin is a new type of insecticide with the structural formula shown in Fig. 1. It has the good safety, high efficiency and high selectivity of neonicotinoids[3], as well as good root absorption and strong penetration[4]. Studies have shown that clothianidin has a good control effect on *B. odoriphaga* and can affect the growth and development of its larvae[5]. The mechanism of clothianidin is different from other pesticides, and it is not easy to produce cross-resistance when mixed with beta-cypermethrin and other pesticides, which can prolong the service life of pesticides[6]. Because of its good control effect and high cost performance, clothianidin is widely used in Chinese chive production, and its residue problem is becoming more and more serious.

In recent years, clothianidin is widely used in vegetable cultivation, and the research of clothianidin mainly focuses on vegetables[7]. In addition, there are many related studies on the residue of procymidone in Chinese chives and dietary risk assessment[8]. However, few studies have been conducted on the residue and dietary risk assessment of clothianidin in Chinese chives in different months of the year, and the maximum residue limit standard of clothianidin in Chinese chives has not been established in GB 2763-2021. Therefore, in this study, high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) was applied to determine the residues of clothianidin in 147 batches of Chinese chive samples and assess the dietary risk, aiming to provide basic data for the supervision and management of pesticide residues of clothianidin in Chinese chives and reference for establishing the residue limit standard of clothianidin in Chinese chives.

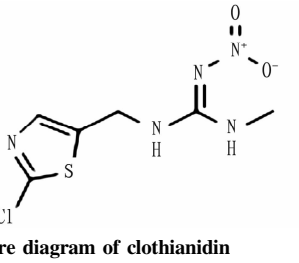

Fig. 1 Structure diagram of clothianidin

Materials and methods

Sample collection

From various markets in Tangshan, 147 batches of Chinese chive samples were randomly collected, and each sample was not less than 3 kg. Sampling was carried out by the quartering

Received: July 3, 2024 Accepted: September 9, 2024
Supported by The Fourth Batch of High-end Talent Project in Hebei Province; The Special Fund of the Central Government Guiding Local Science and Technology Development (226Z5504G).
Lin LI (1997-), female, P. R. China, agronomist, master, devoted to research about detection of pesticide residues in agricultural products.
Yao TONG (1996-), female, P. R. China, agronomist, master, devoted to detection of pesticide residues in agricultural products.
#These authors contributed equally to this work.
*Corresponding author.

method. After division, each sample was treated in a wall-breaking machine, and the homogenate was added in a labeled polyethylene sample bottle, and stored at -18 ℃ for testing.

Instruments and equipment

LCMS-8050 high performance liquid chromatography-tandem mass spectrometer (equipped with electrospray ion source ESI, Shimadzu Corporation, Japan); chromatographic column: phenomenex biphenyl (50 mm × 3.0 mm × 2.6 μm); SiO-6512 automatic pretreatment equipment (Beijing Ability Technology Co., Ltd.); TTL-DCLL nitrogen blower (Beijing Tongtai Lianke Development Co., Ltd.); JJ-200 electronic balance (Changshu Shuangjie Instrument Factory); SZ13022-NY 0.22 μm organic microporous membrane (Tianjin Linghang Experimental Equipment Co., Ltd.).

Reagents

Clothianidin reference material (1 000 μg/ml, Agro-environmental Protection Institute, Ministry of Agriculture and Rural Affairs); chromatographically pure methanol and acetonitrile (purity >99.9%, Dikma Technologies); chromatographically pure formic acid (purity >98.0%, Xiya reagent); chromatographically pure ammonium formate (purity >99.9%, Tianjin Guangfu Fine Chemical Research Institute); extraction package (including extractant magnesium sulfate, sodium chloride, sodium citrate buffer salt and purifying agent); R108 zirconia beads and V03S double-layer extraction purification tubes (Beijing Ability Technology Co., Ltd.); experimental water (Guangzhou Watsons Food and Beverage Co., Ltd.).

Experimental methods

Sample pretreatment First, a 10.0 g of Chinese chive sample (accurate to 0.01g) was weighed, and added with 10 ml of acetonitrile, zirconia beads and the material bag for extraction and purification. QuEChERS automatic pretreatment equipment was used for treatment. Then, the supernatant was filtered with 0.22 μm organic microporous membrane and directly determined by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) after.

Detection condition Ion source: electrospray ion source ESI; scanning mode: MRM (+); quantitative ion (*m/z*): 250.0/169.1; qualitative ion (*m/z*): 250.0/132.0; residence time: 4.0 msec. The parameters are shown in Table 1 in details.

Table 1 Mass spectrometry parameters of clothianidin

Name	Quantitative ion (*m/z*)	Qualitative ion (*m/z*)	Residence time (msec)	Q1 Pre deviation (V)	CE (V)	Q3 Pre deviation (V)
Clothianidin	250.0	250.0	4.0	-11.0	-14.0	-18.0
	169.1	132.0	4.0	-16.0	-12.0	-29.0

Chromatographic column: phenomenx biphenyl (50 mm × 3.0 mm × 2.6 μm); column temperature: 40 ℃; flow rate: 0.4 ml/min; nebulizer flow: 3 L/min; DL temperature: 250 ℃; drying gas flow: 10 L/min; sample volume: 2 μl; pump A: water phase, containing 0.05% formic acid and 5 mmol/L ammonium formate; pump B: organic phase, pure methanol. The gradient elution conditions are shown in Table 2.

Table 2 Gradient elution procedure of clothianidin

Time	Flow rate	Concentration of pump A	Concentration of pump B
0.00	0.40	90.00	10.00
0.50	0.40	90.00	10.00
5.00	0.40	5.00	95.00
8.00	0.40	5.00	95.00
8.01	0.40	90.00	10.00
10.00	0.10	90.00	10.00

Detection method and detection basis

The residue of clothianidin in Chinese chives was determined according to GB 23200.121-2021 *Determination of* 331 *Pesticides and Their Metabolic Residues in Plant-derived Foods: LC-MS/MS*[9].

According to GB 2763-2021 *National Food Safety Standard: Maximum Residue Limits of Pesticides in Food*, there is no maximum residue limit for clothianidin in Chinese chives[10].

The calculation formula of sample detection rate is as follows:

Sample detection rate (%) = Detected sample batches/Total sample batches × 100%

Risk assessment method

The whole population was divided into minors (0 - 17), adults (18 - 59) and elderly people (over 60) according to their age. The average weights of minors, adults, elderly people and the entire population were 35.5, 64.1, 63.0, and 57.7 kg, respectively, and the average daily consumption of Chinese chives was 4.65, 4.93, 2.36, and 4.45 g, respectively[1].

The formula for calculating the index of food safety (*IFS*) is as follows:

$$EDI = R \times F \times E \times P \quad (1)$$

$$IFS = (EDI \times f)/(ADI \times bw) \quad (2)$$

In formula (1), *EDI* is the estimated value of actual pesticide intake (mg); *R* is the detected value of pesticide clothianidin residue in Chinese chives (mg/kg); *F* is the estimated daily intake of Chinese chives (kg); *E* is the edible part factor of Chinese chives, $E = 1$; and *P* is processing factor of Chinese chives, $P = 1$.

In formula (2), *IFS* is the index of food safety; *F* is the correction factor of safe intake, $f = 1$; *ADI* is the safe intake of pesticide clothianidin, with the daily allowable intake of 0.1 mg/kg bw[10]; and bw is per capita weight (kg).

IFS is used to evaluate the degree of potential safety hazards in food. When $IFS << 1$, it means that the pesticide residue has no impact on health. When $IFS < 1$, it means that the risk of pesticide residue is acceptable. When $IFS > 1$, it means that the risk of pesticide residue exceeds the acceptable range.

Results and Analysis

Detection results of clothianidin in Chinese chives

Among the 147 batches of Chinese chive samples tested, 46 batches of samples were detected to contain clothianidin, and the

detection rate was 31.29%. The residual level ranged from 0.012 to 3.516 mg/kg, with an average value of 0.274 mg/kg. The lowest residual amount was 0.012 mg/kg, and the highest residual amount was 3.516 mg/kg. Ma *et al.* [12] detected 121 batches of Chinese chive samples to be listed in Shanxi Province from June 2019 to March 2020, and the detection rate of clothianidin was as high as 81.00%. The detection rate of clothianidin obtained by Yan *et al.* [13] among 171 batches of samples was the highest, at 41.20%, which posed a potential risk to human health. In recent years, clothianidin is a recommended pesticide for controlling *B. odoriphaga*, and the detection frequency has increased year by year. The residual levels from January to December are shown in Table 3.

Table 3 Residue levels of clothianidin in Chinese chives

No.	Detection month (month)	Residue level mg/kg	Detection month (month)	Residue level mg/kg	Detection month (month)	Detection month (month)	Residue level mg/kg	Detection month (month)
CJ001	1	0.082	CJ032	3	0.014	CJ105	7	0.048
CJ004	1	0.102	CJ037	3	0.397	CJ107	7	0.061
CJ008	1	0.207	CJ038	3	0.059	CJ108	7	0.057
CJ009	1	0.028	CJ043	4	0.054	CJ110	7	0.292
CJ014	2	0.039	CJ044	4	0.088	CJ113	7	0.241
CJ015	2	0.039	CJ057	5	0.158	CJ120	8	0.044
CJ017	2	0.053	CJ058	5	0.160	CJ123	8	0.111
CJ018	2	0.054	CJ061	5	0.071	CJ127	9	0.049
CJ020	2	0.065	CJ064	5	0.015	CJ133	9	0.306
CJ021	2	0.825	CJ078	5	0.393	CJ136	9	0.061
CJ022	2	0.596	CJ079	5	0.098	CJ139	10	0.012
CJ023	2	0.207	CJ080	5	0.049	CJ141	11	0.997
CJ025	3	0.502	CJ084	6	0.013	CJ142	12	3.516
CJ026	3	0.132	CJ092	6	0.093	CJ146	12	0.517
CJ029	3	0.329	CJ098	6	0.032	Other number	1 – 12	Not detected
CJ031	3	1.209	CJ104	7	0.128			

Residue status of clothianidin in different months

As can be seen from Table 4, the sampling batches in May and June were relatively high, with 28 and 20 batches, respectively, and the detection rates were 25.00% and 15.00%, respectively. The sampling batches in October and November were few, and 1, respectively, and the detection rates were 50.00% and 100.00%, respectively. In other months, the sampling batches ranged from 6 to 17, and the detection rate ranged from 14.29% to 72.73%. The sampling batches were the most in May, and 7 batches were detected, with a detection rate of 25.00%. The sampling batches were fewest in November, and only one batch was detected, and the detection rate was 100.00%. The detection frequency of clothianidin was the highest in February, with 8 batches, and the detection rate was as high as 72.73%. The detection rate was higher in February, July and November, as shown in Fig. 2. There is no overwintering phenomenon in *B. odoriphaga*, which can cause continuous damage throughout the year, and the peak periods of damage are from May to July and November[14], which is basically consistent with the research results of this study. The higher detection rate in February might be due to the influence of different cultivation and management methods on the damage degree of *B. odoriphaga*, or it might be because that farmers applied pesticides in advance to prevent *B. odoriphaga* and did not strictly implement the provision about the harvesting interval, resulting in a higher detection rate of pesticide residue.

Table 4 Detection rate of clothianidin in different months

Month	Sampling batches batches	Detected batches batches	detection rate %
1	13	4	30.77
2	11	8	72.73
3	17	7	41.18
4	14	2	14.29
5	28	7	25.00
6	20	3	15.00
7	11	6	54.55
8	10	2	20.00
9	14	3	21.43
10	2	1	50.00
11	1	1	100.00
12	6	2	33.33

Assessment of dietary intake risk

It can be seen from Table 5 that for juveniles, the IFS of clothianidin in Chinese chives was between 0.000 015 7 and 0.004 605 5, with an average value of 0.000 589. Specifically, the IFS of Chinese chive samples from batches 1 – 42 was far less than 1, indicating that the pesticide residue of clothianidin had no impact on health. The IFS of Chinese chive samples of batches from 43 to 46 was less than 1, indicating that the pesticide residue of clothianidin posed a risk to human health, but the risk was acceptable.

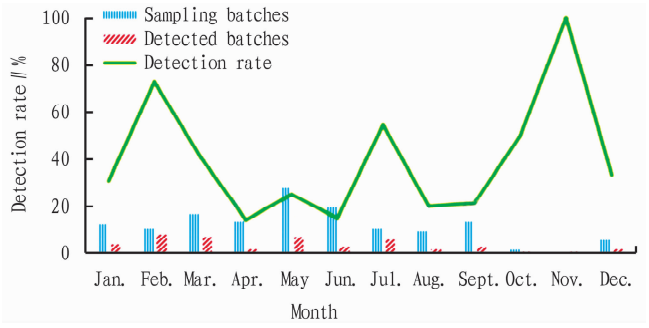

Fig. 2 Detected batches and detection rate of clothianidin in Chinese chives in different months

The IFS of clothianidin in Chinese chives for adults ranged from 0.000 009 2 to 0.002 704 2, with an average value of 0.000 210 7. The IFS of Chinese chives samples from batches 1 – 45 were far less than 1, indicating that the pesticide residues of clothianidin had no impact on health. The IFS of Chinese chive samples from batch 46 was less than 1, indicating that the pesticide residue of clothianidin was hazardous to health, but the risk was acceptable.

The IFS of clothianidin in Chinese chives for elderly people ranged from 0.000 004 5 to 0.001 317 1, with an average of 0.000 102 6. The IFS of Chinese chives samples from batches 1 – 45 was far less than 1, indicating that the pesticide residue of clothianidin had no impact on health. The IFS of Chinese chive samples from batch 46 was less than 1, indicating that the pesticide residue of clothianidin posed a risk to health, but the risk was acceptable.

The IFS of clothianidin in Chinese chives for the entire population ranged from 0.000 004 5 to 0.001 317 1, with an average of 0.000 102 6. The IFS of Chinese chive samples from batches 1 – 45 was far less than 1, indicating that the pesticide residue of thiacloprid had no impact on health. The IFS of Chinese chive samples from batch 46 was less than 1, indicating that the pesticide residue of clothianidin posed a risk to health, but the risk was acceptable.

To sum up, the pesticide residue of clothianidin was risky to the health of people of all ages, but the risk was acceptable.

Table 5 Index of food safety (IFS) of clothianidin in Chinese chives for various age groups

No.	Minors	Adults	The elderly	Entire population
CJ001	0.000 015 7	0.000 009 2	0.000 004 5	0.000 009 3
CJ004	0.000 017 0	0.000 010 0	0.000 004 9	0.000 010 0
CJ008	0.000 018 3	0.000 010 8	0.000 005 2	0.000 010 8
CJ009	0.000 019 6	0.000 011 5	0.000 005 6	0.000 011 6
CJ014	0.000 036 7	0.000 021 5	0.000 010 5	0.000 021 6
CJ015	0.000 041 9	0.000 024 6	0.000 012 0	0.000 024 7
CJ017	0.000 051 1	0.000 030 0	0.000 014 6	0.000 030 1
CJ018	0.000 051 1	0.000 030 0	0.000 014 6	0.000 030 1
CJ020	0.000 057 6	0.000 033 8	0.000 016 5	0.000 033 9
CJ021	0.000 062 9	0.000 036 9	0.000 018 0	0.000 037 0
CJ022	0.000 064 2	0.000 037 7	0.000 018 4	0.000 037 8
CJ023	0.000 064 2	0.000 037 7	0.000 018 4	0.000 037 8
CJ025	0.000 069 4	0.000 040 8	0.000 019 9	0.000 040 9
CJ026	0.000 070 7	0.000 041 5	0.000 020 2	0.000 041 6
CJ029	0.000 070 7	0.000 041 5	0.000 020 2	0.000 041 6
CJ031	0.000 074 7	0.000 043 8	0.000 021 4	0.000 044 0
CJ032	0.000 077 3	0.000 045 4	0.000 022 1	0.000 045 5
CJ037	0.000 079 9	0.000 046 9	0.000 022 9	0.000 047 0
CJ038	0.000 079 9	0.000 046 9	0.000 022 9	0.000 047 0
CJ043	0.000 085 1	0.000 050 0	0.000 024 3	0.000 050 1
CJ044	0.000 093 0	0.000 054 6	0.000 026 6	0.000 054 8
CJ057	0.000 107 4	0.000 063 1	0.000 030 7	0.000 063 2
CJ058	0.000 115 3	0.000 067 7	0.000 033 0	0.000 067 9
CJ061	0.000 121 8	0.000 071 5	0.000 034 8	0.000 071 7
CJ064	0.000 128 4	0.000 075 4	0.000 036 7	0.000 075 6
CJ078	0.000 133 6	0.000 078 4	0.000 038 2	0.000 078 7
CJ079	0.000 145 4	0.000 085 4	0.000 041 6	0.000 085 6
CJ080	0.000 167 7	0.000 098 4	0.000 047 9	0.000 098 7
CJ084	0.000 172 9	0.000 101 5	0.000 049 4	0.000 101 8
CJ092	0.000 207 0	0.000 121 5	0.000 059 2	0.000 121 9
CJ098	0.000 209 6	0.000 123 1	0.000 059 9	0.000 123 4
CJ104	0.000 271 1	0.000 159 2	0.000 077 5	0.000 159 6
CJ105	0.000 271 1	0.000 159 2	0.000 077 5	0.000 159 6
CJ107	0.000 315 7	0.000 185 4	0.000 090 3	0.000 185 9
CJ108	0.000 382 5	0.000 224 6	0.000 109 4	0.000 225 2
CJ110	0.000 400 8	0.000 235 3	0.000 114 6	0.000 236 0
CJ113	0.000 430 9	0.000 253 0	0.000 123 2	0.000 253 7
CJ120	0.000 514 8	0.000 302 3	0.000 147 2	0.000 303 1
CJ123	0.000 520 0	0.000 305 3	0.000 148 7	0.000 306 2
CJ127	0.000 657 5	0.000 386 1	0.000 188 1	0.000 387 2
CJ133	0.000 677 2	0.000 397 6	0.000 193 7	0.000 398 7
CJ136	0.000 780 7	0.000 458 4	0.000 223 3	0.000 459 7
CJ139	0.001 080 6	0.000 634 5	0.000 309 0	0.000 636 3
CJ141	0.001 305 9	0.000 766 8	0.000 373 5	0.000 768 9
CJ142	0.001 583 6	0.000 929 9	0.000 452 9	0.000 932 4
CJ146	0.004 605 5	0.002 704 2	0.001 317 1	0.002 711 6
Mean	0.000 358 9	0.000 210 7	0.000 102 6	0.000 211 3

(Continued) (Table 5)

Conclusions and Discussion

In this study, 147 batches of Chinese chive samples randomly collected from various markets in Tangshan in 2023 were detected for clothianidin pesticide residue. The results showed that 46 batches of samples were detected, with a detection rate of 31.29% and a residue range of 0.012 to 3.516 mg/kg. The sampling batches were more in May and June, but few in October and November, and the detection rate ranged from 14.29% to 100.00%. The maximum residual limit of clothianidin in Chinese chives has not been established, and this study can provide reference for establishing the residual limit standard of clothianidin in Chinese chives in China.

The index of food safety (IFS) was calculated for 46 batches of Chinese chive samples with clothianidin pesticide residues. The results showed that the IFS of minors ranged from 0.000 015 7 to 0.004 605 5. The value of adults ranged from 0.000 009 2 to 0.002 704 2. The value of the elderly ranged from 0.000 004 5 to 0.001 317 1. And the value of the entire population ranged from 0.000 009 3 to 0.002 711 6. The average IFS values of minors, adults, the elderly and the entire population were, respectively, 0.000 358 9, 0.000 210 7, 0.000 102 6 and 0.000 211 3, which were far less than 1, indicating that clothianidin in Chinese chives

detected in this study had no impact on health.

To sum up, the problem of pesticide residue of clothianidin in Chinese chives is serious. Through the assessment of dietary intake risk, the pesticide residue was within the safe range. However, with the increasing demand for Chinese chives, farmers have increased the use of clothianidin and related pesticides in pursuit of yield and pest control, which has increased the pesticide residues to a certain extent, which is likely to pose unacceptable risks to human health. Therefore, it is suggested that relevant departments formulate the maximum residue limit standard of clothianidin in Chinese chives, enhance the supervision and management of pesticide use, and strengthen the detection and evaluation of pesticide residues.

References

[1] PAN LY, WANG Q, YANG GL, *et al.* Residue dynamics and dietary risk assessment of 5 fungicides in Chinese chives under open field and greenhouse conditions[J]. Agrochemicals, 2023, 62(9): 651 – 656. (in Chinese).

[2] YANG D, LI JL, JIN XT, *et al.* Indoor toxicity screening and pesticide mixing study of several insecticides on the larvae of *Bradysia odoriphaga* [J]. Jiangsu Agricultural Sciences, 2017, 45(6): 83 – 85. (in Chinese).

[3] ZHU YF, ZUO WJ, ZHUANG ZX, *et al.* A review of research progress in the development of clothianidin[J]. World Pesticide, 2017, 39(2): 28 – 33. (in Chinese).

[4] WANG YQ. Residual levels of clothianidin and hexaflumuron on chives and spatiotemporal distribution of clothianidin in Chinese chives [D]. Guangzhou: South China Agricultural University, 2020. (in Chinese).

[5] Green prevention and control technical scheme of main diseases and pests of Chinese chives in 2023[J]. China Plant Protection, 2023, 43(3): 99 – 100. (in Chinese).

[6] ZHANG YM, LIU X, JIANG LL, *et al.* Toxicity of clothianidin and other insecticides to *Phyllotreta striolata*[J]. Chinese Journal of Pesticide Science, 2015, 17(2): 230 – 234. (in Chinese).

[7] ZHANG CR, HE HM, XU LY, *et al.* Residue analysis method of clothianidin in rice and its degradation dynamics[J]. Acta Agriculturae Zhejiangensis, 2014, 26(5): 1263 – 1267. (in Chinese).

[8] ZHOU Y, PIAO XY, LIAO XJ, *et al.* Determination and chronic dietary exposure assessment of procymidone residue in Chinese chives[J]. Chinese Journal of Pesticide Science, 2021, 23(2): 373 – 379. (in Chinese).

[9] GB 23200.121-2021 National food safety standard: Determination of 331 pesticides and their metabolic residues in plant-derived foods-LC-MS/MS [S]. (in Chinese).

[10] GB 2763-2021 National food safety standard: Maximum residue limits of pesticides in food[S]. (in Chinese).

[11] ZHANG XS, GAO YG, PENG SJ. Dietary exposure assessment of procymidone residue in Chinese leek (*Allium tuberosum* Rottl. ex Spr.) [J]. Journal of Food Safety and Quality, 2019, 10(10): 3114 – 3119. (in Chinese).

[12] MA XY, LIU J, LI W, *et al.* Risk evaluation of pesticide residues in leeks in Shanxi Province based on food safety index and hazard risk coefficient method[J]. China Vegetables, 2022(7): 92 – 97. (in Chinese).

[13] CAO HH, WANG S, ZHAO HT, *et al.* Detection and analysis of pesticide residues in chinese chives available in Tangshan and risk assessment of the associated dietary intake[J]. Modern Food Science & Technology, 2022, 38(1): 336 – 344. (in Chinese).

[14] DANG ZH, DONG JZ, GAO ZL, *et al.* Detection and analysis of pesticide residues in chinese chives available in Tangshan and risk assessment of the associated dietary intake[J]. Journal of Agricultural University of Hebei, 2001(4): 65 – 68. (in Chinese).

Editor: Yingzhi GUANG Proofreader: Xinxiu ZHU

(Continued from page 36)

[4] NOUGADÈRE A, SIROT V, KADAR A, *et al.* Total diet study on pesticide residues in France: Levels in food as consumed and chronic dietary risk to consumers[J]. Environment International, 2012, 45: 135 – 150.

[5] MAHDAVI V, GHORBANI-PAJI F, RAMEZANI M K, *et al.* Dissipation of carbendazim and its metabolites in cucumber using liquid chromatography tandem mass spectrometry[J]. International Journal of Environmental Analytical Chemistry, 2019, 99(10): 968 – 976.

[6] YU QW, SUN H, WANG K, *et al.* Monitoring of carbendazim and thiabendazole in fruits and vegetables by SiO2@ NiO-based solid-phase extraction coupled to high-performance liquid chromatography-fluorescence detector[J]. Food Analytical Methods, 2017, 10(8): 2892 – 2901.

[7] PATEL GM, ROHIT JV, SINGHAL RK, *et al.* Recognition of carbendazim fungicide in environmental samples by using 4-aminobenzenethiol functionalized silver nanoparticles as a colorimetric sensor[J]. Sensors and Actuators B: Chemical, 2015, 206: 684 – 691.

[8] WANG S, SU L, WANG L, *et al.* Colorimetric determination of carbendazim based on the specific recognition of aptamer and the poly-diallyldimethylammonium chloride aggregation of gold nanoparticles [J]. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2020, 228: 117809.

[9] WANG M, ZHU W, ZHAO L, *et al.* Simultaneous detection of thiabendazole and carbendazim in foods based on two-color upconversion and magnetic separation nanoparticles fluorescence immunoassay[J]. European Food Research and Technology, 2022, 248(1): 85 – 94.

[10] XU X, YAN K, XIAO J, *et al.* Fluorescence spectroscopy detection of carbendazim residue in cucumber juice based on BC[J]. Journal of Food Composition and Analysis, 2024, 130: 106157.

[11] HUANG X, ZHANG N, LI Z, *et al.* Rapid detection of carbendazim residue in apple using surface-enhanced raman scattering and coupled chemometric algorithm[J]. Foods, 2022, 11(9): 1287.

[12] CHEN X, LIN M, SUN L, *et al.* Detection and quantification of carbendazim in Oolong tea by surface-enhanced Raman spectroscopy and gold nanoparticle substrates[J]. Food Chemistry, 2019, 293: 271 – 277.

[13] WANG S-Y, SHI X-C, LIU F-Q, *et al.* Chromatographic methods for detection and quantification of carbendazim in food[J]. Journal of Agricultural and Food Chemistry, 2020, 68(43): 11880 – 11894.

[14] HASSAN YAA, AYAD MF, HUSSEIN LA, *et al.* Hydrophilic interaction liquid chromatography (HILIC) with DAD detection for the determination of relatively non polar fungicides in orange samples[J]. Microchemical Journal, 2023, 193: 109196.

[15] HANOT V, GOSCINNY S, DERIDDER M. A simple multi-residue method for the determination of pesticides in fruits and vegetables using a methanolic extraction and ultra-high-performance liquid chromatography-tandem mass spectrometry: Optimization and extension of scope [J]. Journal of Chromatography A, 2015, 1384: 53 – 66.

[16] YIN XF, FANG B, ZHANG XX, *et al.* Salt-assisted acetonitrile extraction and HPLC-QTOF-MS/MS detection for residues of multiple classes of pesticides in human serum samples[J]. Journal of Separation Science, 2020, 43(17): 3534 – 3545.

[17] SOLTANI S, SERESHTI H, NOURI N. Deep eutectic solvent-based clean-up/vortex-assisted emulsification liquid-liquid microextraction: Application for multi-residue analysis of 16 pesticides in olive oils [J]. Talanta, 2021, 225: 121983.

[18] WEI Q, WU M, XIAO F, *et al.* Development of a fast method for the determination of pesticide multiresidues in tomatoes using QuEChERS and GC – MS/MS [J]. European Food Research and Technology, 2020, 246(8): 1563 – 1572.

Editor: Yingzhi GUANG Proofreader: Xinxiu ZHU