

**Development and validation of a QuEChERS and HPLC-MS/MS method for trace analysis of ten
diamide insecticides in agricultural products**

Fajun Tian^{1*}, Zhenzhen Zhou¹, Junfeng Lu, Chengkui Qiao, Caixia Wang, Tao Pang, Linlin Guo, Jun Li,
Rongli Pang, Hanzhong Xie*

Zhengzhou Fruit Research Institute, Chinese Academy of Agricultural Sciences, Zhengzhou 450009,
China

***Correspondence:** Professor Hanzhong Xie, Zhengzhou Fruit Research Institute, Chinese Academy of
Agricultural Sciences, Zhengzhou 450009, China E-mail: xiehanzhong@caas.cn; Dr. Fajun Tian, E-
mail: tianfajun@caas.cn

Table S1. Comparison of the current method with other previously reported methods.

Diamide pesticides	Samples	Method	LOD ($\mu\text{g kg}^{-1}$)	LOQ ($\mu\text{g kg}^{-1}$)	Time analysis (min)	RSD (%)	Reference
Cyantraniliprole	Vegetables	LC-MS/MS	2	5	3.5	2.6-15.1 (intra-day), 3.4-13.3 (inter-day)	1
Cyantraniliprole	Vegetables	LC	—	50	40	9.9-15.2	2
Cyantraniliprole	Vegetables	LC-MS/MS	5	10	5.1	1.6-8.9	3
Cyantraniliprole	Rice	LC-MS/MS	5.4	4.3	3.0	1.1-10.6	4
Cyantraniliprole	Corn	LC-MS/MS	—	10	4.2	4.7-10.1	5
Chlorantraniliprole	Fruits	LC	20	60	14.5	6-11	6
Chlorantraniliprole	Fruits	LC-MS/MS	8.6	17.2	15	2.7-6.1	7
Cyantraniliprole and chlorantraniliprole	Fruits, vegetables and cereals	LC-MS/MS	—	10	16	2-8	8
Chlorantraniliprole	Vegetables	LC	30	100	12.5	1.6-4.4 (intra-day), 5.5-9.1 (inter-day)	9
Chlorantraniliprole	Vegetables	LC	30	100	9.86	1.89-3.56	10
Chlorantraniliprole	Vegetables	LC	30	100	12.5	1.7-3.35	11
Chlorantraniliprole	Rice	LC-MS/MS	0.012-0.015	-	4.5	1.7-7.5	12
Chlorantraniliprole	Rice	LC-MS/MS	0.15	0.5	3	2.1-10.2	13
Chlorantraniliprole	Corn	LC-MS/MS	2-3	5-10	3.5	1.9-11.3 (intra-day) 4.7-10.4 (inter-day)	14
Tetrachlorantraniliprole	Corn	LC-MS/MS	—	1-6	—	2.87-8.21	15
Tetrachlorantraniliprole and cyantraniliprole	Corn	LC-MS/MS	—	10	6	< 10	16
Cyclaniliprole	Fruits, vegetables, and cereals	LC-MS/MS	—	10	10	< 13	17
Cyclaniliprole	Fruits and vegetables	LC-MS/MS	0.08-0.1	10	4	0.41-4.2	18
Cyclaniliprole	Fruits and vegetables	LC-MS/MS	—	10	10	0.4-12.1	19
Flubendiamide	Vegetables	LC	—	10	15	1.15-4.80	20
Flubendiamide	Vegetables	LC	—	10	10	<5%	21
Flubendiamide	Vegetables	LC	—	50	15	2.87-6.51	22
Flubendiamide	Vegetables	LC-MS/MS	0.3	—	12	1.79-4.81	23
Flubendiamide	Vegetables	LC	3	10	20	1.62-5.39	24
Cyhalodiamide	Rice	LC-MS/MS	0.5	2-10	5	1.2-10.7	25

Broflanilide		Fruits, vegetables, and cereals	LC-MS/MS	—	5	10	<1.8	26
Broflanilide		Rice	LC	0.16-1.67	0.54-5.48	14	3.29-8.15	27
Broflanilide		Fruits, vegetables, and cereals	LC-MS/MS	4	10	10	<21	28
Tetraniliprole		Rice	LC-MS	1.55-3.09	5.16-10.29	3.2	2.58-15.92	29
Tetraniliprole		Corn	LC-MS/MS	—	1	4.2	<13.52	30
Tetraniliprole		Vegetables	LC-MS	10	50	15	2.91-15.32	31
Tetraniliprole		Vegetables	LC-MS/MS	3	10	10	1.4-5.5	32
Fluchlordiniliprole		Rice	LC-MS	0.15-7.0	0.51-2.33	8	1.77-4.35 (intra-day) 1.73-4.20 (inter-day)	33
Five insecticides	diamide	Fruits and cereals	LC-MS/MS	—	5-10	5	0.4-9.9 (intra-day) 1.7-13.5 (inter-day)	34
Five insecticides	diamide	Edible mushrooms	LC-MS/MS	0.05-2	5	6	0.8-12.7 (intra-day) 2.8-12.2 (inter-day)	35
Five insecticides	diamide	Vegetables	LC-MS/MS	—	0.03-0.8	6	3.8-9.4	36
Six insecticides	diamide	Vegetables	LC	<15	34-51	20	1.1-9.7 (intra-day) 3.0-11.0 (inter-day)	37
Five insecticides	diamide	Fruits and vegetables	LC-MS/MS	—	5	10	<10.9	38
Ten insecticides	diamide	Fruits, vegetables, and cereals	LC-MS/MS	0.01-1	5	6	1.0-13.4 (intra-day) 2.3-15.7 (inter-day)	This work

Five diamide insecticides: chlorantraniliprole, cyantraniliprole, flubendiamide, cyclaniliprole, and tetrachlorantraniliprole.

Six diamide insecticides: five diamide insecticides and broflanilide.

References

1. F. S. Dong, X. G. Liu, J. Xu, J. Li, Y. B. Li, W. L. Shan, W. C. Song and Y. Q. Zheng, *Biomed. Chromatogr.*, 2012, **26**, 377-383.
2. F. Malhat, K. M. Kasiotis and S. Shalaby, *Environ. Monit. Assess.*, 2018, **190**, 1-10.
3. J. P. Sun, N. Feng, C. F. Tang and D. M. Qin, *Bulletin of Environmental Contamination and Toxicology*, 2012, **89**, 845-852.
4. C. Zhang, X. Hu, H. Zhao, M. Wu, H. He, C. Zhang, T. Tang, L. Ping and Z. Li, *Chemosphere*, 2013, **93**, 190-195.
5. J. F. Ding, C. M. Xu, W. Zhang, N. Zou and W. Mu, *Chin. J. Pestic. Sci.*, 2018, **20**, 83-89.
6. F. M. Malhat, *Food Anal. Methods* 2012, **5**, 1492-1496.

7. X.-m. Liang, W.-y. Zhang, W. Zhang, S.-b. Xie, R.-y. He, J. Xu, L.-j. Su, B.-l. Sun and J. Zhang, 2020.
8. T. Schwarz, T. A. Snow, C. J. Santee, C. C. Mulligan, T. Class, M. P. Wadsley and S. C. Nanita, *J. Agric. Food. Chem.* , 2011, **59**, 814-821.
9. B. Singh, A. Kar, K. Mandal, R. Kumar and S. K. Sahoo, *J. Food Sci.* , 2012, **77**, T208-T215.
10. A. Kar, K. Mandal and B. Singh, *Bulletin of Environmental Contamination and Toxicology*, 2012, **88**, 501-506.
11. A. Kar, K. Mandal and B. Singh, *Environ. Monit. Assess.* , 2013, **185**, 1255-1263.
12. J.-M. Zhang, W.-G. Chai and Y.-L. Wu, *Chemosphere*, 2012, **87**, 132-136.
13. G. M. Telo, S. A. Senseman, E. Marchesan, E. R. Camargo, T. Jones and G. McCauley, *J. Agric. Food. Chem.* , 2015, **63**, 2119-2126.
14. F. Dong, J. Xu, X. Liu, J. Li, Y. Li, Z. Kong, W. Shan, Z. Zheng and Y. Zheng, *Chromatographia*, 2011, **74**, 399-406.
15. T. Fan, X. Chen, M. Zhao, J. Wang, Z. Meng, S. Dong, X. Miao and Q. Wu, *Sci. Total Environ.* , 2021, **800**, 149429.
16. X. Li, Z. Sun, T. Yan, Y. Li, X. Zhang, M. Liu, Y. Lin, Z. Zhang and H. Xu, *J. Sci. Food Agric.* , 2022, **102**, 6676-6686.
17. Z. Lu and H. Pan, *Biomed. Chromatogr.* , 2021, **35**, e5056.
18. J. Yu, J. Hou, Z. Xu, R. Yu, C. Zhang, L. Chen and X. Zhao, *Environmental Science and Pollution Research*, 2023, **30**, 125907-125914.
19. Z. Lu, W. Yue, W. Ren, Y. Wang and Y. Li, *Molecules*, 2022, **27**, 6464.
20. R. S. Battu, B. Singh, R. Kooner and B. Singh, *J. Agric. Food. Chem.* , 2008, **56**, 2299-2302.
21. M. Paramasivam and H. Banerjee, *Bulletin of environmental contamination and toxicology*, 2011, **87**, 452-456.
22. G. Singh, S. Sahoo, R. Takkar, R. Battu, B. Singh and G. Chahil, *Chemosphere*, 2011, **84**, 1416-1421.
23. X. Chen, C. Lu, S. Fan, H. Lu, H. Cui, Z. Meng and Y. Yang, *Bulletin of environmental contamination and toxicology*, 2012, **89**, 1021-1026.
24. K. Sharma, I. Mukherjee, B. Singh, S. K. Sahoo, N. Parihar, B. Sharma, V. Kale, R. Nakat, A. Walunj and S. Mohapatra, *Environ. Monit. Assess.* , 2014, **186**, 7673-7682.
25. Y. Liu, Y. Zhang, S. Liu, Y. Lü, R. Lin, M. Li, X. Liao and X. Li, *Chin. J. Chem. Eng.* , 2018, **26**, 2185-2191.
26. H. H. Noh, C. J. Kim, H. Kwon, D. Kim, B.-c. Moon, S. Baek, M.-s. Oh and K. S. Kyung, *PLoS One* 2020, **15**, e0235526.
27. G. Xie, W. Zhou, M. Jin, A. Yu, L. Rao, H. Jia, J. Luo, Y. He and B. Li, *International Journal of Analytical Chemistry*, 2020, **2020**.
28. J.-S. Park, J.-A. Do, S. Han, S. Park, S. M. Cho, J.-Y. Kim, H.-S. Shin, D. E. Jang, Y. Jung and K. Lee, *J Food Hyg Saf*, 2019, **34**, 124-134.
29. W. Li, Y. Zhang, H. Jia, W. Zhou, B. Li and H. Huang, *Microchem. J.* , 2019, **150**, 104168.
30. D. Ma, S. Yang, J. Jiang, J. Zhu, B. Li, W. Mu, D. Dou and F. Liu, *Ecotoxicology and Environmental Safety*, 2021, **213**, 112061.
31. J. Kousika, K. Bhuvaneswari and V. Muralitharan, *Indian Journal of Entomology*, 2023, 209-212.
32. A. Vijay, R. L. Kalasariya, P. H. Rathod, S. Chawla and R. R. Acharya, *Food Additives &*

Contaminants: Part A, 2024, 1-15.

33. T. Wu, L. Wang, H. Chang, Z. Dong, R. Zhou, Y. Li and B. Li, *J. Food Compos. Anal.*, 2023, **121**, 105429

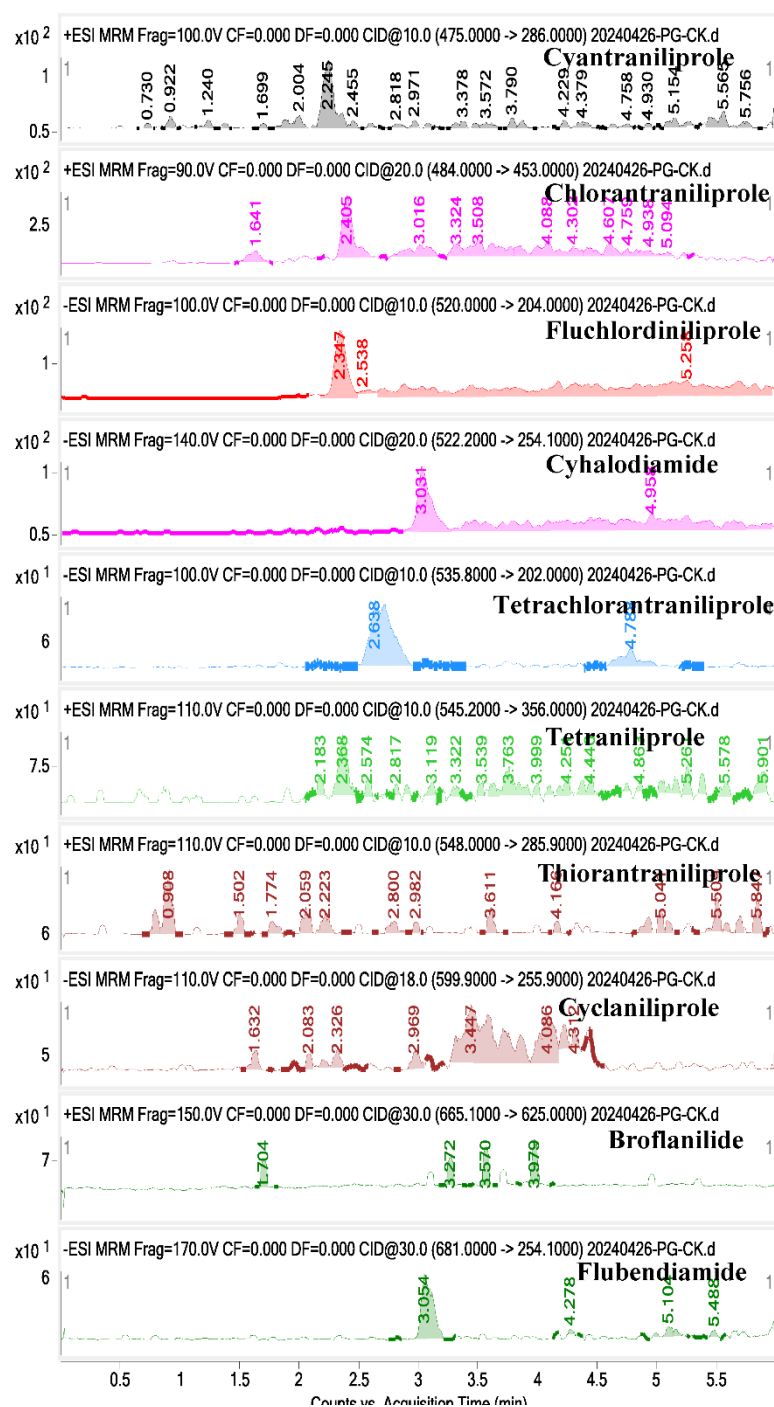


Figure S1. HPLC-MS/MS chromatograms of ten diamide insecticides of blank apple sample.

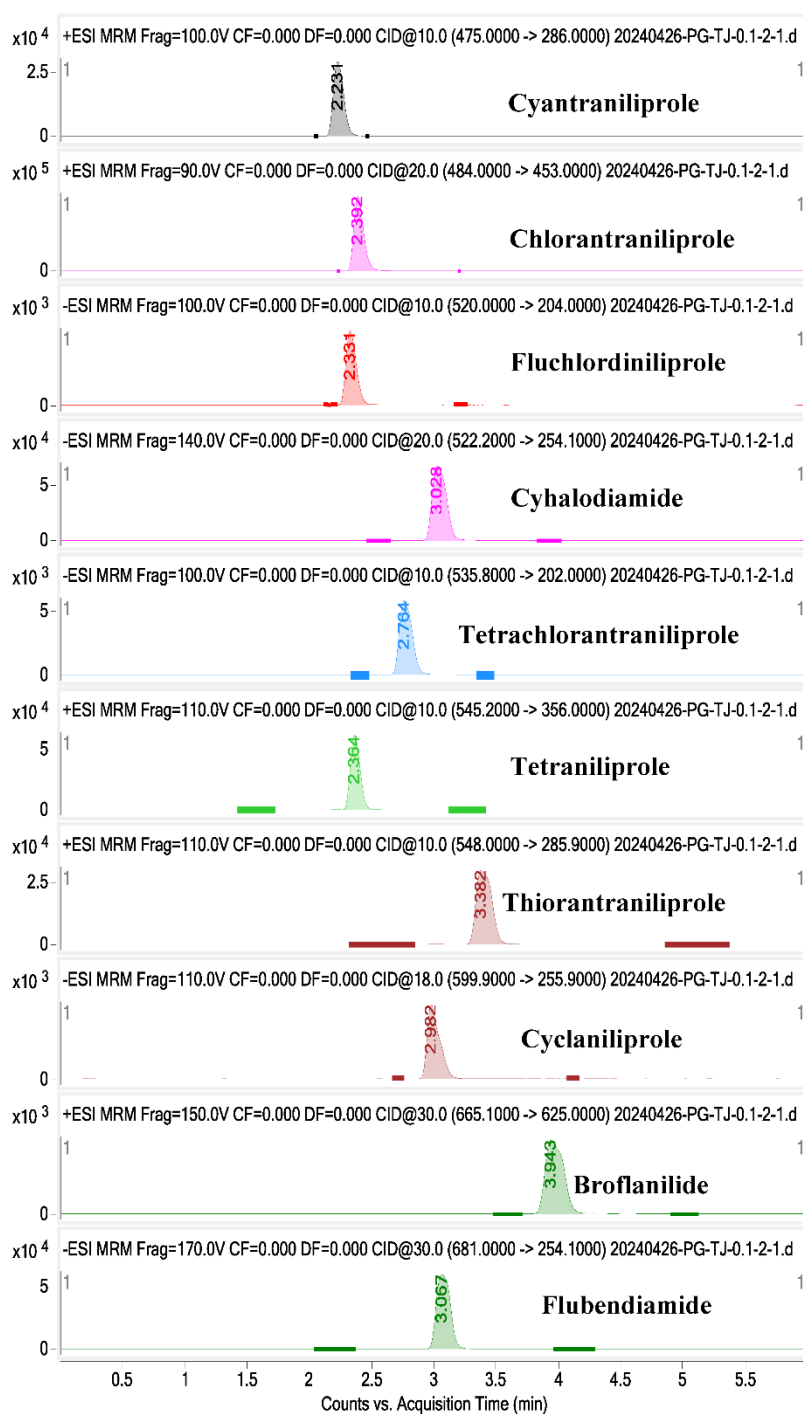


Figure S2. HPLC-MS/MS chromatograms of ten diamide insecticides of spiked apple sample ($100 \mu\text{g kg}^{-1}$).

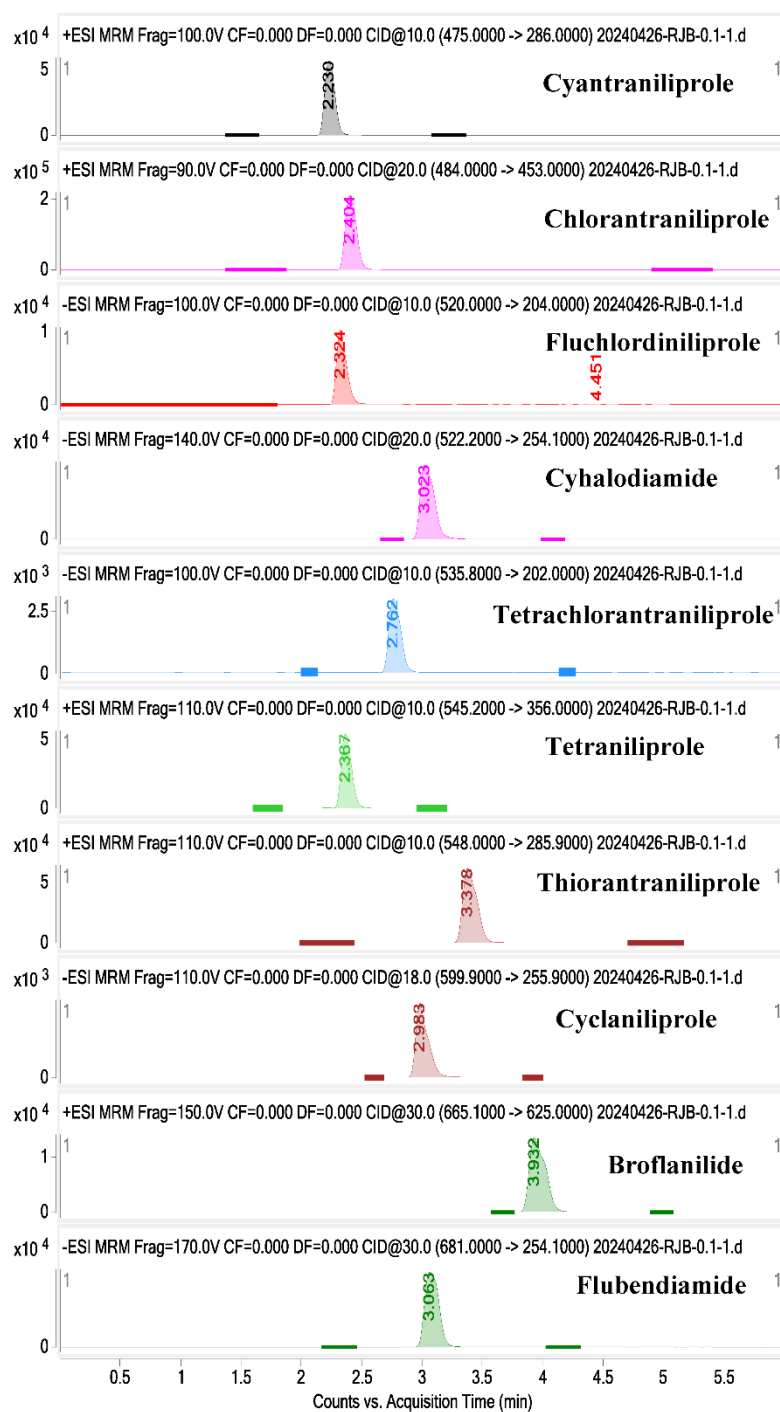


Figure S3. HPLC-MS/MS chromatograms of ten diamide insecticides of standard solution ($100 \mu\text{g kg}^{-1}$).