thermo scientific

Trace-level quantitation of pesticide residues in red chili powder using LC-(HESI)-MS/MS

Authors

Ramiz M. R. Azad, Dasharath Oulkar, and Ashutosh Pathak

Customer Solution Center, Ghaziabad, Thermo Fisher Scientific, India

Keywords

Pesticide residues, chili powder, QuEChERS, LC-MS/MS, TSQ Quantis, TraceFinder

Goal

The objective of this work was to develop a method for the trace-level quantitation of pesticides and their metabolite residues in chili powder, using liquid chromatography-triple quadrupole mass spectrometry. The optimized method performance was verified in accordance with the EU SANTE guidelines and assessed for compliance with the Food Safety and Standards Authority of India (FSSAI) and EU MRLs in chili powder.

Introduction

Spices are widely used for flavoring foods in both commercial catering and households, but potential contaminants that can cause food safety and quality issues receive little attention. This is particularly the case in the myriad of small volume spice trade networks in India and in Asian countries. Food testing of spices generally focuses on microbial impurities or mycotoxins and less on pesticides, perhaps because the difficulties and hence the cost of analyzing a large number of pesticides in a complex matrix are high. Few pesticides are registered for chili crop management to control diseases and pest attacks.¹ Recently, the Rapid Alert System for Food and Feed (RASFF) issued an alert due to flonicamid and formentate residues found in chili powder.² However, the FSSAI does not have MRLs for flonicamid and formentate but the EU has set 0.1 and 0.05 mg/kg, respectively. The lowest MRL set in chili powder is



APPLICATION NOTE 73016

0.005 mg/kg for fipronil and fipronil sulfone (sum of both).^{3,4} Consequently, a robust and sensitive analytical method is required to check that spices on the market are compliant with these new MRLs for LC-amenable compounds.

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method has been widely adopted for the extraction of pesticide residues from a wide range of food samples including spices.⁵ In the case of spices, the instrument method plays a critical role to deliver accurate, precise, and rugged results in compliance with regulatory requirements.

Therefore, the aim of this work was the development, optimization, and validation of a QuEChERS-based multiresidue method for the analysis of pesticide residues in chili powder using LC-MS/MS with the Thermo Scientific[™] TSQ Quantis[™] triple quadrupole mass spectrometer. The data acquisition and processing were carried out using Thermo Scientific[™] TraceFinder[™] software. The optimized method was verified according to the SANTE/11813/ 2017 guidelines⁶ and evaluated for compliance with the EU and FSSAI MRL requirements.

Experimental

Chemicals and apparatus

- Acetonitrile, Optima[™] LC/MS Grade, Fisher Scientific[™]
- Methanol, Optima[™] LC/MS Grade, Fisher Scientific[™]
- Water, Optima[™] LC/MS Grade, Fisher Scientific[™]
- Formic acid (85%), Fisher Scientific[™]
- Acetic acid (100%), Fisher Scientific[™]
- Ammonium formate, LC/MS Grade, Fisher Scientific™
- Anhydrous magnesium sulfate, Fisher Scientific™
- Sodium acetate, Fisher Scientific[™]
- Reference standards procured from Restek[™]
- Other equipment such as a weighing balance, vortex mixer (model, Thermo Scientific), centrifuge, micropipettes, water purification system, ultrasonic bath were used in sample preparation.

LC-MS/MS analysis

The Thermo Scientific[™] Vanquish[™] Flex UHPLC system was coupled to a TSQ Quantis triple quadrupole mass spectrometer (fitted with a heated electrospray ionization (HESI) source). Chromatographic conditions and LC-MS/MS parameters are given in Table 1, while details of collision energy (CE), retention time (RT), precursor and product ion transitions are given in Table 2.

Table 1. LC-MS/MS instrument conditions

Liquid chromato	graphy	method							
Instrumentation:	Vanqui	sh Flex UHP	LC						
Column	Thermo Scientific [™] Hypersil GOLD [™] (100 mm × 2.1 mm × 1.9 µm) (P/N 25002-102130)								
Sample									
compartment temp									
Column oven temp	.: 25 °C								
Mobile phase:	0.19 aceto B: 2 ml 0.19	A: 2 mM ammonium formate + 0.1% formic acid in water: acetonitrile(90:10, v/v) 3: 2 mM ammonium formate + 0.1% formic acid in water: acetonitrile (10:90, v/v)							
Autosampler:	Vanqui	sh (216 vials	capaci	ty)					
Total run time:	18.0 m	in							
Gradient program:	Time	Flow Rate	%B	Curve					
	0.000	0.400	1	5					
	1.500	0.400	1	5					
	5.000	0.400	50	5					
	8.500	0.400	95	5					
	13.500	0.400	95	5					
	14.000	0.400	1	5					
	18.000	0.400	1	5					
Mass spectrome	etry met	hod							
Instrumentation:		antis triple o mass spect							
Method type:		ased selectiv ing (t-SRM)	e-react	ion					
lon source type:	HESI								
Polarity:	Positive	/Negative sv	vitching						
Spray voltage:	Static								
	Positive	: 3500 V							
	Negativ	e: 2500 V							
Sheath gas:	50 Arb								
Aux gas:	10 Arb								
Sweep gas:	1 Arb								
lon transfer									
tube temp.:	325 °C								
Vaporizer temp.:	350 °C								

Sample preparation

The chili powder samples were collected from the local market and mixed well before selecting the test portion for extraction. The particle size was approximately $200-500 \ \mu m.^7$ The QuEChERS method was used for extraction.⁵

Sample extraction:

- Weigh 2 g chili powder into a 50 mL extraction tube.
- For recovery experiment, spike samples before the addition of water and extraction solvent.
- Add 15 mL of HPLC grade water (containing 1% acetic acid) and leave the sample for 10 min soaking.
- Add 15 mL acetonitrile to the above tube.
- Mix vigorously for 1 minute on a vortex mixer at 2500 rpm.
- Add 6 g anhydrous MgSO₄ and 1.5 g sodium acetate to the tube and again mix vigorously for 1 minute on a vortex mixer at 2500 rpm.
- Centrifuge at 5000 rpm for 5 min at ambient conditions.
- Take an aliquot (1 mL) of the acetonitrile supernatant layer.
- Add 50 mg PSA + 7 mg GCB + 150 mg MgSO₄.
- Centrifuge at 5000 rpm for 5 min at ambient conditions.
- Take 0.25 mL supernatant and dilute with 0.75 mL of water.
- Inject 5 μL into the LC-MS/MS.

Data acquisition and processing

The data acquisition was performed by using the instrument conditions in Table 1. The data acquisition and processing methods were carried out using Thermo Scientific[™] TraceFinder[™] software version 4.1. For each analyte two precursor to product ion transitions were acquired in t-SRM mode. For data processing, the user-

defined criteria included an ion ratio (\pm 30%), retention time (\pm 0.1 min), linearity (>0.99 with residuals \pm 20), recovery (70–120%) and precision (\pm 20%) in accordance with the SANTE guidelines.⁶

Results and discussion Sample preparation

Chili powder is a dry powder and complex matrix containing carbohydrates (<9%) and proteins (<2%) with high amounts of alkaloids and colored pigments such as β-carotene, which are verv difficult to remove without incurring losses of pesticides. Chili has a pH in the range 6.2–6.7 and less moisture content (<5%). So, the pH of the sample was reduced by using 1% acetic acid in water, which is essential for liquid-liquid partitioning with acetonitrile. To improve the stability of base-sensitive and organophosphorus compounds during extraction, GCB was added to reduce the concentration of pigments, while PSA was added to remove acidic matrix coextractives. The dSPE cleanup followed by dilution of the extract provided an acceptable recovery by a reduction in matrix co-extractives without substantial losses of the target pesticides. The cleanup and dilution approach increased the instrument uptime by increasing the intervals between cleaning of the sampling cone. The final extract was diluted (30x) as per the defined protocol (e.g., 0.01 mg/kg corresponds to 0.00033 µg/mL), but this low concentration was easily detected by the TSQ Quantis LC-MS/MS system.

LC-MS/MS analysis

The optimized LC-MS/MS method conditions showed excellent sensitivity for 127 compounds. The total ion chromatogram (TIC) is shown in Figure 1. The optimized liquid chromatographic method offered excellent separation for the target analytes (spinetoram and spinosad D, Figure 2). In this method, the dwell time was automatically optimized for the target list of analytes (two transitions per analyte), which offered ≥12 points per peak (Figure 3).

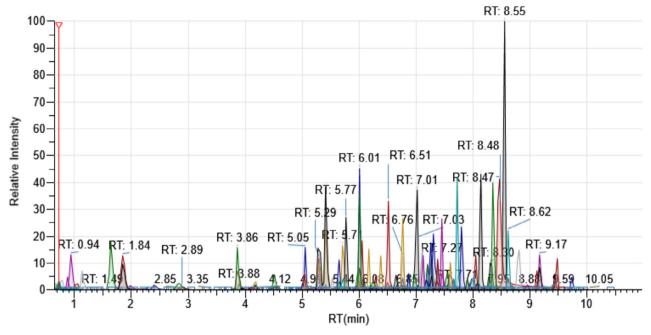


Figure 1. Total ion chromatograms with overlay extraction ions (127 compounds)

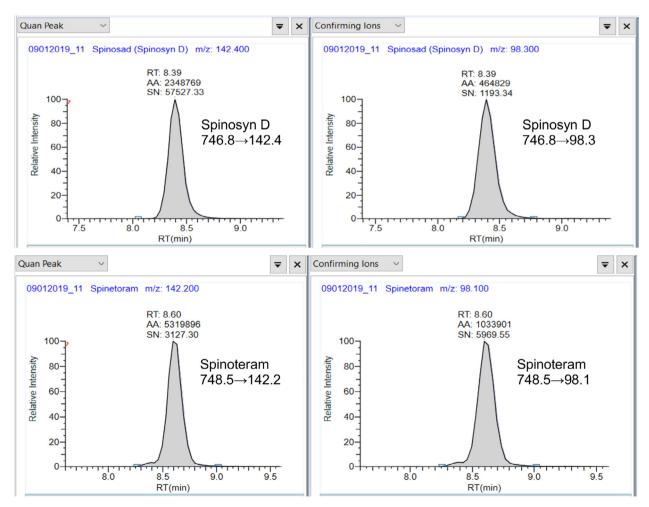


Figure 2. Chromatographic separation of isobaric compounds, i.e. spinosad D and spinetoram

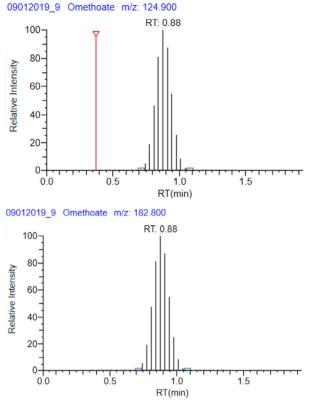


Figure 3. Impact of optimized dwell time on the data points per peak

Identification and quantitation

User-defined parameters for data processing including two transitions per analytes, retention time, correlation coefficient, and residuals were set in the data processing method of TraceFinder software (Master method).

Based on these parameters, the data was processed automatically with flagging. These flags indicate through color codes whether results pass or fail against acceptance criteria set in the processing method. The results that passed user-defined criteria (SANTE guidelines) are shown in green (Figure 4). An identification of aminocarb in chili powder was demonstrated with two transitions, $209 \rightarrow 137$ (quantitative) and $209 \rightarrow 152$ (confirmatory) at the same retention time (0.94 min, ±0.1) with an ion ratio of 75.83% (64.23–119.28%) observed in chili powder in comparison with neat standard. This approach meets the requirement of the SANTE guidelines for identification and quantitation.

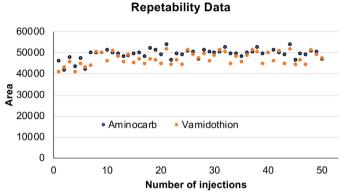
Thermo TraceFinder EFS LC	_	o ×
File View Tools Help	Real time status User: ramiz.	.azad 🕜 🐇
🗋 🐸 🖬 🎒 🕇 🌻 T 🌻	● ● Ⅳ ◇ 卡 砌	(
Analysis	Data Review - MRM in Chilli_25022019 [Quan]*	
 Batch View 	X Sample Results	units ⇔ C
Samples		• =
Auto Samples	2 🖲 1 7 🍽 🌑 T1 Unknown Spike_Chili_10PP8_DD_1 41303 N/A 0.94 N/A 0.281 🗹 N/A ug/k	g
Reference Sample	3 ⊕ 2 8 🍽 🕒 T1 Unknown Spike_Chili_10PP8_DD_2 37896 N/A 0.94 N/A 0.259 🗹 N/A ug/k	g
Threshold Samples	1 4 @ 3 9 ► ● T1 Unknown Spike_Chili_10PP8_DD_3 42283 N/A 0.94 N/A 0.287 🗹 N/A ug/k	-
	5 69 4 10 T1 Unknown Spike_Chili_10PPB_DD_4 38805 N/A 0.94 N/A 0.265 V/A ug/k	-
Data Review	6 69 5 11	
Sample View	7 69 6 12 🕨 💿 T1 Unknown Spike_Chili_10PP8_DD_6 37796 N/A 0.94 N/A 0.258 🗹 N/A ug/k 8 69 7 13 🕨 💿 T1 Unknown Spike_Chili_10PP8_DD_7 45967 N/A 0.94 N/A 0.311 👽 N/A ug/k	
Compound View	9 00 8 1 1 01 01 1 S5,01PP8 1452 N/A 0.94 N/A 0.108 2 8/8 30 ug/k	-
Comparative View	10 🖲 9 2 🍽 🌑 T1 Carta 2 SS_0,5PPB 75721 N/A 0.94 N/A 0.503 🗹 0.55 ug/k	g
comparative view	11 🖲 10 3 🍽 🕒 T1 CalStd 3 SS_1PPB 142940 N/A 0.94 N/A 0.936 🗹 -6.36 ug/k	g
Report View	12 @ 11 4 🍽 🌑 T1 CalStd 4 SS_2,5PPB 379715 N/A 0.94 N/A 2.464 🗹 -1.45 ug/k	g
Local Method	Compound Details	→ ậ :
Acquisition	Quan Peak V Confirming Ions V V Calibration Curve V	∓ ×
Quantitation	Opp12019_3 Aminocarb m/z: 137.100 Aminocarb Minocarb V = 1.5645X - 2.2176R, PE2: Object Web Oppin: Springer, Wit 102: Area	
Processing	RT 0.94 RT 0.94	/
Compounds		×
QAQC		
Groups		
Intel Seg		
Reports		
Acquisition	$0 \xrightarrow{1} 0 \xrightarrow{1} 0 \xrightarrow{1} 1 \xrightarrow{1} $	
•	RT(min) RT(min) socos	
Analysis	m/z: 137.100 Apex RT: 0.94 Left RT: 0.71 Right RT: 1.21 6423% - 119.28% 152.000/137.100 = 75.83% Jon ratio	
Method Development	Area: 1432 Height 134 Noise: 2623 Area: 152.00/157.04 Regin 157.04 Regin 157.107 Right Rft: 1.17	25

Figure 4. Extracted ion chromatogram (XIC) for quantifier ion of aminocarb (A), identification based on qualifier/ confirmatory ions with confirmed with ion ratio (B), and calibration curve (C)

Method performance

The MS response was linear over the range of 0.0001-0.025 mg/L. This range offered excellent correlation coefficients (>0.99) with <15% residuals for all the target analytes in the solvent, which was further used for quantitation. For the quantitative approach, the sensitivity achieved at such low levels (0.1 ng/mL) provided S/N >10:1 supporting with the confirmatory ion (Figure 4). But as per the extraction protocol, the sample gets diluted (30x). Hence, the limit of quantitation (LOQ) values observed in chili powder matrix were 0.005 mg/kg with acceptable recoveries (70-120%) and precision (<20%) for target analytes (>96%) except bitertanol, clethodim, diniconazole, difenoconazole, fluazinam, hexythiazox, monolinuron, and spirodiclofen (LOQ = 0.01 mg/kg). The recovery experiment was carried out at 0.005 mg/kg (LOQ) and 0.01 mg/kg (LOQ \times 2 = reporting limit) to demonstrate the method accuracy and precision. The recoveries were observed in the range of 76-116% with <15 % RSD

(Table 2, Appendix), which were within acceptance criteria (recovery 70–120% and precision <20%).⁶ The XICs of a few compounds at LOQ level spiked in chili matrix are shown in the supplementary information in Appendix II. The optimized method was tested for repeatability of results obtained from a continuous sequence of 50 injections. The repeatability was <15% for area and <±0.05 min retention time (Figures 5 and 6).





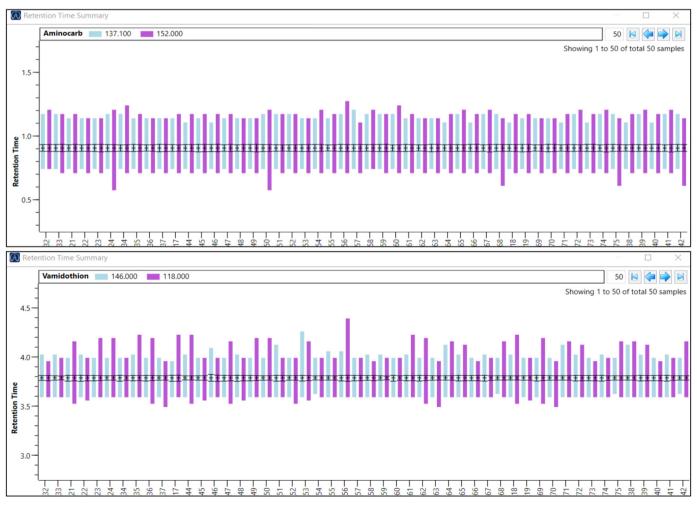


Figure 6. Retention time repeatability for aminocarb and thiabendazole (n=50)

Conclusion

The developed method provides a robust analytical solution for the trace-level (sub ppb) quantitation of more than 120 pesticides in chili powder. The simplicity of the method based on extraction using a QuEChERS method and detection using LC-HESI-MS/MS is suitable for routine analysis in a high-throughput commercial food testing laboratory. The dSPE cleanup followed by the dilution approach minimized the need for cleaning of the sample cone to increase system up time. By following this approach, at least 70 injections (standards, samples, blank) could be completed in a day (24 h cycle). The method validation data at the reporting limit (RL) meets the recovery and precision requirement as per SANTE guidelines. Also, this method complies with the EU and FSSAI MRL requirements by achieving excellent lower limits of quantitation.

References

- Insecticides / Pesticides Registered under section 9(3) of the Insecticides Act, 1968 for use in the Country:(As on 15/05/2019) http://ppqs.gov.in/sites/default/files/ list_of_pesticide_registered_us_93.pdf.
- European Commission RASFF Portal, Notification details 2019.1223, Formetanate (1.3 mg/kg - ppm) and flonicamid (1.5 mg/kg - ppm) in chilli peppers from Italy https://webgate.ec.europa.eu/rasff-window/ portal/?event=notificationDetail&NOTIF REFERENCE=2019.1223
- FSSAI Manual for food safety, 17th Edition-2017 (THE FOOD SAFETY AND STANDARDS ACT, 2006)
- 4. EU Pesticides Database. http://ec.europa.eu/food/plant/pesticides/eu-pesticidesdatabase/public/?event=product.resultat&language=EN&selectedID=237
- Lehotay, S.J.; Maštovská, K.; Lightfield, A. R. Use of buffering and other means to improve results of problematic pesticides in a fast and easy method for residue analysis of fruits and vegetables. *J. AOAC Int.* **2005**, *88*, 615–630; (Note: Basis of the AOAC Method 2007.01).
- SANTE guidelines https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_ mrl_guidelines_wrkdoc_2017-11813.pdf.
- Oh, S.H. Chungbuk National University, Chungbuk, Republic of Korea Kang, Y.R., Chungbuk, Physical Properties of Red Pepper Powder at Different Particle Sizes [2013], National Academy of Agricultural Science, Gyeonggi, Republic of Korea http:// agris.fao.org/agris-search/search.do?recordID=KR2015003122

Appendix I: list of pesticides

Table 2 (part 1). List of pesticides with MRM transitions used

Sr.		RT	ESI			CE	Q3	CE	0.005 mg	g/kg (n=6)	0.01 mg	/kg (n=6)	Ion Ratio	lon ratio
No.	Name of pesticide	(min)	(+/-)	Q1	Q3				% Rec	% RSD	% Rec	% RSD	Absolute	(±30)
1	3-Hydroxycarbofuran	3.89	+	238.1	163	19	181	15	120	7.2	106	6.9	53.7	-0.72
2	Acephate	4.17	+	184.1	49	35	143	11	99	0.2	85	6.3	95.9	5.60
3	Acetamiprid	4.51	+	223	99	53	126	29	94	13.7	88	14.1	10.6	-10.66
4	Aldicarb sulfone	1.46	+	240.1	86.2	28	148.2	19	104	15.1	96	13.5	86.6	1.84
5	Ametryn	5.75	+	228.1	96	35	186.1	25	108	3.9	85	9.1	14.7	-15.86
6	Aminocarb	0.94	+	209.1	137.1	33	152	19	114	1.6	92	4.6	87.2	-5.39
7	Azoxystrobin	6.96	+	404.1	344.1	33	372.1	19	74	7.9	100	2.9	4.3	-18.95
8	Benalaxyl	7.72	+	326.2	148.1	29	294.1	15	102	3.7	85	6.4	20.6	-19.61
9	Benzoximate	8.1	+	364	105	31	199	11	104	7.8	92	6.9	15.5	15.07
10	Bifenazate	7.64	+	301.1	170.1	27	198.1	13	92	4.7	76	9.6	40.6	6.99
11	Bitertanol	7.35	+	338.2	70	29	269.2	13	ND	ND	109	7.3	86.4	-6.07
2	Bupirimate	7.13	+	317	108	35	159.1	33	105	15.4	76	7.1	34.9	-0.26
13	Buprofezin	8.28	+	306.2	116.2	23	201.1	17	108	9.5	114	11.4	30.8	8.94
14	Butafenacil	7.6	+	492.1	331	27	349	19	113	8.7	119	9.1	33.6	0.27
15	Carbendazim	1.64	+	192.2	132.1	41	160.2	25	92	12.5	86	19.1	8.5	-2.51
16	Carbetamide	5.02	+	237.1	118.1	17	192	13	107	12.9	88	9.1	71.1	10.64
17	Carbofuran	5.98	+	222.1	123	29	165.1	17	108	15.8	78	8.6	3.8	2.11
18	Carboxin	5.98	+	236.1	87	33	143	21	106	4.5	109	7.3	8.6	19.33
19	Chlorantraniliprole	6.47	+	484	285.9	17	452.9	21	115	9.3	106	8.8	79.3	3.33
20	Chlorotoluron	5.97	+	213.1	46.2	35	72.2	31	99	3.7	98	4.4	13.3	-13.01
21	Chloroxuron	6.99	+	291.1	72.4	47	218.1	33	102	5.6	81	11.7	22.9	10.07
22	Clethodim	8.27	+	360.1	164	29	268.1	17	ND	ND	75	2.5	31.3	2.69
23	Clothianidin	3.86	+	250	132	21	169	19	118	12.3	80	5.3	72.3	-16.73
24	Cycluron	6.24	+	199.1	89	15	69	21	103	7.8	83	16.2	112.8	7.79

*ND = not detected

*Ion ratio absolute value provided by software and calculated by considering reference value of standard

Table 2 (part 2). List of pesticides with MRM transitions used

No. Number of perturbine Omite Object Object Number of perturbine Number of perurbine Number of perturbine	Sr.		RT	ESI						0.005 mg	/kg (n=6)	0.01 mg	/kg (n=6)	Ion Ratio	lon ratio
28 0 0 167.1 0.51 28 125.1 24 100 11.2 100 4.03 4.0 4.21 27 Demedpion 0.73 - 281.5 11.1 17 11.0		Name of pesticide			Q1	Q3	CE	Q3	CE	% Rec	% RSD	% Rec	% RSD		
27 Democipham 6.73 + 318.1 164 38 162 103 6.77 94 158 0.2 27.88 28 Democnocrow 8.71 - 28.5 112 17 143 183 100 100 2.7 3.8 1.7 4.7 2.7 3.7 2.7 3.7 2.7 3.7 2.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7 3.7	25	Cyproconazole	6.79	+	292	70	31	125	29	103	13.8	94	10.8	70.5	1.08
9 Deroteques 92.8 4 92.8 112 17 183 119 1.5 103 6.00 7.1 8.73 95 Dimensionant 6.01 4 62.3 7.5 4 92.5 103 ND ND ND 103 6.03 6.01 7.2 7.2 92 Dimensionange framer 6.84 4 88.1 105.1 4.5 90.0 92.0 44.0 7.7 7.0 4.0 6.0 7.14 93 Dimensionange framer 6.81 4 88.1 110.7 4.0 90.0 92.0 44.0 107.1 7.0 4.0 10.0 11.0	26	Cyromazine	0.66	+	167.1	85.1	26	125.1	24	108	11.2	106	5.8	53.5	-4.21
19 Dimensionality 6.01 • 660/2 211 1 251 131 N0 N0 <td>27</td> <td>Desmedipham</td> <td>6.73</td> <td>+</td> <td>318.1</td> <td>154</td> <td>35</td> <td>182</td> <td>19</td> <td>93</td> <td>8.7</td> <td>94</td> <td>15.5</td> <td>9.2</td> <td>27.98</td>	27	Desmedipham	6.73	+	318.1	154	35	182	19	93	8.7	94	15.5	9.2	27.98
And Burnersburder Ball	28	Dicrotophos	2.78	+	238.1	112.1	17	193	13	119	1.5	103	5.0	71.1	-8.73
31 Dimethomoph leorney 6.61 + 38.1 16.1 45 30.1 20 10.4 7.1 7.2 7.2 32 Dimethomoph leorney 6.61 + 38.1 16.61 45 30.1 20 28 10.4 10.4 14.4 44.5 -17.4 33 Dimocacie 7.41 + 22.2 7.0 10.7 11.6 20 11.6 10.8 16.7 0.4 0.0 17.4 0.0 17.4 11.6 11.6 11.6 10.8 16.7 0.4 0.0 17.4 11.6 11.4 10.8 16.7 0.4 0.0 17.4 10.8 11.6 10.8 11.7 0.8 10.2 0.2 17.4 10.8 10.1 10.8 11.1 0.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8	29	Difenoconazole	8.01	+		251.1	41	253.1	31	ND	ND	102	2.8	40.4	-18.05
32 Dimethomorphisame? 6.61 * 38.1 165.1 45 901 103 19.7 76 1.4.4 48.5 1.0.0 33< Dimosynchin 7.41 * 302.7 110 29 205 28 44 12.9 74 6.0 77.4 4.0 28.2 28.3 28.3 28.3 28.3 28.3 28.3 28.3 28.3 28.3 28.3 28.3 27.2 6.0 19.9 48 14.6 68.4 14.8 68 14.1 68 14.1 68 14.1 68 14.1 68 14.1 68 14.1 68 14.4 88.4 78.4 <th< td=""><td>30</td><td>Dimethoate</td><td>4.15</td><td>+</td><td>230</td><td>125</td><td>29</td><td>199</td><td>13</td><td>99</td><td>4.5</td><td>89</td><td>6.3</td><td>61.0</td><td>6.21</td></th<>	30	Dimethoate	4.15	+	230	125	29	199	13	99	4.5	89	6.3	61.0	6.21
33 Dimonystechin 7.41 + 0.27.1 11.8 29 20.6 20.8 6.44 12.9 7.4 5.00 10.9 10.80 10.80 10.80 10.80 10.80 10.80 10.80 10.80 10.80 10.80 10.80 10.80 10.81 10.80 10.81	31	Dimethomorph Isomer 1	6.38	+	388.1	165.1	45	301	29	94	7.1	79	15.2	51.7	7.02
34 Dinkonzable 7.61 + 308.2 70.2 80 119 43 ND ND ND 103 11.9 20.6 -281.53 35 Dinkelkann 1.07 + 20.31 178 17 15.7 11 68 15.7 68 8.0 75.0 27.5 37 Envanschr-barczate bra 8.84 + 885.5 82.1 65 112.1 48 181 12.3 68 12.2 5.7 14.91 38 Eprinterench 65.4 9.14 162 49 180.2 5.6 611 11.1 62 12.5 3.84 41 Ebacezacle form 1 7.17 + 32.81 179 131 205 23 161 159 161 67 163 16.2 5.5 16.4 42 Ethion 4.9 4.01 67 151.5 17 151.5 161 71 16.4 71 16.5	32	Dimethomorph Isomer 2	6.61	+	388.1	165.1	45	301	29	103	19.7	76	14.4	48.5	-1.00
38 Divoletirun 1.07 + 203.1 129.2 17 157.2 11 88 15.7 94 8.07 68.8 -1213 38 Disocatarb 4.11 + 224.1 132 21 117 11 18 15.7 94 8.00 7.60 7.75 7.7 14.01 38 Epochocnazole 7.1 + 330 10.1 66 12.1 49 81 12.3 88 12.8 35.8 -35.8 39 Epiconochanazole former 1 7.17 + 328.1 190 31 205 23 101 10.5 7.8 10.2 65.5 -31.7 42 Environic 4.2 + 21.1 92 13 20.5 131 10.5 7.8 10.2 65.5 -31.7 42 Environic 4.3 30.1 17.7 2.1 11.1 27 103 10.7 87 10.8 40.3 40.9 10.1 40.7 40.8 40.8 40.9 10.1 40.7	33	Dimoxystrobin	7.41	+	327.1	116	29	205	23	84	12.9	74	5.0	6.0	-17.49
B Doxacarb 4.11 + 22.41 123 21 167 11 B3 15.77 B4 B.0 75.0 2.78 37 Emamedin-bernoaltrin B.54 + B.B5.1 65 19.8.1 49 B8 14.8 B7 12.2 45.7 14.91 38 Eparodinazole 7.1 + 330 10.1.1 65 11.1 02 198 11.1 02 198 2.5.5 -3.89 40 Ehandine 7.77 + 28.1.1 199 31 205 23 101 15.0 78 16.2 5.5. -3.17 42 Ehandine 6.9 + 30.1 57.2 51 14.1 59 10.0 11.60 74 10.5 6.5.5 1.147 44 Ferandin 6.98 + 30.1 177 25 161.7 49 16.7 47 16.8 76.5 16.5. 1.477	34	Diniconazole	7.61	+	326.2	70.2	50	159	43	ND	ND	103	18.9	20.6	-28.53
37 Ensamectin-bernante bia 8.8 + 886 18.1 49 88 14.6 97 12.2 5.7 14.91 38 Epinolocinacile 7.1 + 330 101.1 65 121.1 49 81 12.3 88 12.3 88 12.3 98 121.1 198 121.1 49 192 191 121.2 22 121 141 123.2 123 123.2 123 123.2 123 123.2 123 123.2 123 123.2 123 123.2 123 123.2 123 123.2 123 123.2 124.2 123.2 124.2 124.2 124.2 124.2 124.2 124.2 124.2 124.2 124.2 124.2 124.2 124.2 1	35	Dinotefuran	1.07	+	203.1	129.2	17	157.2	11	86	15.7	96	8.7	68.8	-12.13
38 Eposeconazole 7.1 + 330 101.1 65 121.1 49 81 12.3 98 12.8 35.5 3.69 99 Epriormechn 6.65 + 014.6 154.2 40 180.2 25 61 11.1 62 10.9 35.4 20.15 40 Etaconazole leome 7.77 + 328.1 169 31 205 23 61 15.9 78 16.0 8.5 6.817 42 Ethimol 4.2 + 210.2 98.1 39 140.1 31 98 14.0 88 14.0 80.5 16.81 43 Ecoazole 8.9 + 300.1 17.2 25 101.1 27 97 15.4 71 5.7 70.5 10.72 44 Fenerpromoph 7.3 + 307 70 39 124.9 57 16.8 15.7 70.5 10.72 71.5	36	Dioxacarb	4.11	+	224.1	123	21	167	11	83	15.7	94	8.0	75.0	2.75
39 Eprinomedin 8.65 + 914.8 154.2 49 186.2 25 61 11.1 92 199 35.4 2015 40 Ebaconazole Isomer 1 7.77 + 328.1 159 31 205 23 102 5.7 106 8.2 5.6 3.46 41 Ebaconazole Isomer 2 7.27 + 328.1 159 31 265 23 61 14.6 66 14.0 60.5 0.89 43 Ebranzole 8.9 + 302.1 57.2 51 141 59 100 11.6 74 19.5 5.5 1.84 44 Fenanzouln 0.69 + 307.1 17.2 51.17 29 7.5 7.15 7.0 8.9 1.94 1.94 4.5 7.99 1.344 47 Fenanzouln 0.69 + 1.35 1.17 65 1.72 1.65 7.8 1.64 7.99 </td <td>37</td> <td>Emamectin-benzoate b1a</td> <td>8.54</td> <td>+</td> <td>886.5</td> <td>82.1</td> <td>65</td> <td>158.1</td> <td>49</td> <td>88</td> <td>14.6</td> <td>87</td> <td>12.2</td> <td>5.7</td> <td>14.91</td>	37	Emamectin-benzoate b1a	8.54	+	886.5	82.1	65	158.1	49	88	14.6	87	12.2	5.7	14.91
40 Etaconazole Isomer 1 7.17 + 328.1 159 31 205 23 161 15.9 78 162 5.5 8.17 42 Ethermache Isomer 2 7.27 + 328.1 159 31 205 23 61 15.9 78 162 5.5 8.17 42 Ethermache 4.2 + 210.2 88.1 39 140.1 31 98 140.4 86 14.0 80.5 0.83 0.83 44 Ferazaquin 9.69 + 301.1 17.2 65 161.1 27 97 15.4 71 4.5 79.5 -19.72 45 Fernzaquin 9.69 + 307.1 170 65 147 69 78 17.9 4.5 79.5 -19.72 46 Fernzaquin 7.23 + 324 157 63 30.1 73 4.65 13.7 63 15.9 16.4 22 16.4 22 13.8 16.7 13.9 10.2 13.9 10.2<	38	Epoxiconazole	7.1	+	330	101.1	65	121.1	49	81	12.3	98	12.8	35.5	-3.69
141 Etaconazole latomer 2 7.27 + 32.81 150 31 205 23 81 150 78 16.2 5.5 -4.317 42 Ethimol 4.2 + 210.2 98.1 39 140.1 31 98 14.6 86 14.0 80.5 0.89 43 Etoazole 8.9 + 300.1 57.2 51 141 69 100 11.7 74 19.5 79.3 19.72 44 Fenaropimoth 9.89 + 307.1 147 25 161.1 27 97 15.4 71 5.7 79.3 19.72 46 Fenrypompth 7.23 + 307.1 147 25. 161.1 27 97 15.4 78 79.3 17.9 74 4.5 79.9 13.84 47 Fenrypompth 7.23 4 307.1 15.1 65.3 16.1 28 27.1 45.0 16.4 16.7 16.4 16.7 16.4 16.7 16.4 16.7 16	39	Eprinomectin	8.65	+	914.6	154.2	49	186.2	25	81	11.1	92	19.9	35.4	20.15
42 Ethimol 4.2 + 210.2 98.1 39 14.0 98 14.8 88 14.0 90.5 0.89 43 Enoxocle 8.9 + 380.1 67.2 61 111 69 100 11.8 74 19.5 5.5 1.64 44 Fenandone 6.98 + 392.1 12.2 53 12.4 93 10.7 67 18.8 34.0 1.47 45 Fenandone 0.98 + 307.1 147 25 161.1 27 97 15.4 74 4.5 79.9 13.4 47 Fenpopinooph 7.31 + 304 117 65 147 29 78 15.7 80 5.9 84.9 99.9 12.51 50 Fiponin 7.7 4 435 250 35 30.20 74 16.8 74 14.1 22.5 2.444 51 Fuponichande 7.63 4 43.1 24.4 415.7 28 ND ND				+	328.1	159	31	205				106			
42 Ethimol 4.2 + 210.2 98.1 30 140.1 31 98 14.6 86 14.0 90.5 0.089 43 Boxacole 8.9 + 380.1 67.2 61 141 99 100 11.6 74 19.5 5.5 1.64 44 Fenzuagin 0.90 + 307.1 147 25 101.1 27 97 15.4 71 5.7 79.9 13.84 47 Fenzuagin 0.90 + 337 70 39 124.9 55 78 17.9 74 4.5 79.9 13.84 47 Fenzyoximate 8.92 + 422 155.1 46 29 72.1 450 88 15.0 90.9 12.51 50 Fpront 7.7 - 435 250 35 30.20 74 16.6 74 14.1 22.5 -24.44 61 Fuzzionan 6.83 - 462.7 397.8 24 415.7 28 ND	41	Etaconazole Isomer 2	7.27	+	328.1	159	31	205	23	81	15.9	78	16.2	5.5	-8.17
4.3 Eloxacole 8.9 + 360.1 57.2 51 141 69 100 11.6 74 19.5 5.5 1.64 4.4 Fenandone 0.66 + 312.1 92 35 23.1 21 93 10.7 87 18.8 34.0 1.47 45 Fenazaquin 9.69 + 307.1 147 25 161.1 27 97 16.4 71 5.7 73.9 -19.72 46 Fenopoincorpin 7.23 + 304 117 65 147 39 78 15.7 80 5.9 84.9 19.87 47 Fenopoincorpin 7.23 + 304 117 65 144 63 104 80.2 85 86.3 6.08 88.8 49 Fenoren 3.8 4 42.2 135.1 44 45.7 28 101 81.9 72.1 33 102 10.8 75 10.4 42.3 22.1 21.1 101 10.8 117 11.4 </td <td>42</td> <td>Ethirimol</td> <td>4.2</td> <td>+</td> <td>210.2</td> <td>98.1</td> <td>39</td> <td>140.1</td> <td>31</td> <td></td> <td>14.6</td> <td>86</td> <td>14.0</td> <td>80.5</td> <td>0.89</td>	42	Ethirimol	4.2	+	210.2	98.1	39	140.1	31		14.6	86	14.0	80.5	0.89
44 Fenamidone 6.06 + 312.1 92 35 236.1 21 93 10.7 87 18.8 34.0 1.47 45 Fenzanquin 9.69 + 307.1 147 25 161.1 27 97 15.4 71 5.7 79.5 -19.72 46 Fenzyonimate 7.3 + 337 70 93 124.9 65 78 17.9 74 4.5 79.9 13.84 47 Fenzyonimate 8.32 + 422 135.1 63 396.1 23 104 8.2 85 3.6 0.8 8.88 49 Fenuron 3.8 + 165.1 46 29 72.1 45 888 15.7 0.2 13.9 63.9 -12.51 50 Fipronil 7.7 - 452 250 35 33.0 20 74 16.6 74 14.1 22.5 -24.44 51 Fuzeram 8.63 - 42.7 37.8 72.1 35															
45 Fentazaquin 9.69 + 307.1 147 25 161.1 27 97 15.4 71 5.7 79.3 1-19.72 46 Fentprojmorph 7.31 + 337 70 39 124.9 65 78 17.9 74 4.5 79.9 13.84 47 Fentprojmorph 7.23 + 422 135.1 53 366.1 23 104 8.2 3.6 3.6 6.8 3.6 0.8 6.9 9.12.51 50 Fpronit 7.7 - 435 250 35 330 20 74 16.6 74 14.1 22.5 -24.44 51 Fluorent 8.63 - 465.7 397.8 24 415.7 26 ND ND 72 13.5 60.1 121 52 Fluorenturon 5.55 + 233.1 46.31 72.1 25 112 8.6 102 8.8 13.1 -16.73 54 Fuurenturon 5.55 189.1 72.1 <td></td>															
46 Fenbuconazole 7.31 + 337 70 39 124.9 55 78 17.9 74 4.5 79.9 13.84 47 Fenpropimorph 7.23 + 304 117 65 147 39 78 15.7 80 5.9 84.9 19.87 48 Fenuron 3.8 + 165.1 46 29 72.1 45 88 15.9 92 13.9 69.9 -12.51 50 Finorill 7.7 435 250 35 330 20 74 16.6 74 16.1 24 12.1 50 Finorill 7.7 435 250 35 330 20 74 16.6 74 14.1 22.5 24.4 51 Fluzzham 8.63 - 462.7 397.8 24 415.7 26 ND ND 72 13.5 50.1 12.1 52 Fluzzham 8.63 - 462.7 397.8 24.7 12 73 16.2 <															
47 Fenpropimorph 7.23 + 304 117 65 147 39 78 15.7 80 5.9 84.9 19.87 48 Fenpropimorph 3.8 + 422 135.1 53 366.1 23 104 8.2 85 3.6 0.8 8.86 49 Fenuron 3.8 + 165.1 46 29 72.1 45 88 15.9 92 13.9 60.9 -12.51 50 Fipronil 7.7 - 435 250 35 330 20 74 16.6 74 14.1 22.5 -24.44 51 Fluxamm 8.63 - 462.7 37.8 74 415.7 26 ND ND 72 13.5 60.1 121 52 Fubandiamide 7.63 + 633.1 174.1 447 22.5 135 1102 8.8 13.1 -16.73 54 Fubandiamide 7.4 + 431.1 70 55 151.1 25 25.1															
Heapy contraite 8.92 + 422 135.1 63 366.1 23 104 8.2 85 3.6 0.8 8.88 49 Fenuron 3.8 + 165.1 46 29 72.1 45 88 15.9 92 13.9 69.9 -12.51 50 Fipronil 7.7 - 435 250 35 330 20 74 16.6 74 14.1 22.5 -24.44 51 Flucendiamide 7.83 + 483.1 274.1 41 408 9 100 19.8 75 16.4 28.7 66.2 53 Fluonediuron 5.55 + 23.1 46 37 72.1 23 120 6.1 117 1.44 24.3 -21.97 55 Fluosabrobin 7.46 + 452.1 165 137 7.5 7.6 11.7 18.4 13.7 56 Fororbiorfenuron															
49 Fundon 3.8 + 165.1 46 29 72.1 45 88 15.9 92 13.9 69.9 -12.51 50 Fipronil 7.7 - 435 250 35 330 20 74 16.6 74 14.1 22.5 -24.44 51 Fluzenam 8.63 - 462.7 397.8 24 415.7 26 ND ND 72 13.5 50.1 1.21 52 Flubendiamide 7.63 + 683.1 274.1 41 408 9 100 19.8 75 16.4 28.7 -6.62 53 Fluoratoron 5.95 + 233.1 46 37 247.1 21 73 14.2 90 9.7 64.3 -13.78 55 Fluolazole 7.4 + 438.1 195.1 25 252.1 17 116 13.0 110 5.1 38.3 -5.56															
Feyronl 7.7 - 435 260 35 330 20 74 16.6 74 14.1 22.5 -24.44 51 Fluzzinam 8.63 - 462.7 397.8 24 415.7 26 ND ND 72 13.5 50.1 1.21 52 Flubendiamide 7.63 + 683.1 274.1 41 408 9 100 19.8 75 16.4 28.7 -66.2 53 Fluometuron 5.95 + 233.1 46 37 72.1 35 112 8.5 102 8.8 13.1 -16.73 54 Fluoxastrobin 7.46 + 459.2 188 47 427.2 23 120 6.1 117 11.4 24.3 -21.97 55 Fusiaxpl 6.76 + 302.1 95 39 242.1 21 73 7.5 76 11.7 18.4 13.4 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>															
Fluzinam 8.63 - 462.7 397.8 24 415.7 26 ND ND 72 13.5 50.1 1.21 52 Flubendiamide 7.63 + 683.1 274.1 41 408 9 100 19.8 75 16.4 28.7 -66.2 53 Fluometuron 5.95 + 233.1 46 37 72.1 35 112 8.5 102 8.8 13.1 -16.73 54 Fluoxastrobin 7.46 + 459.2 188 47 427.2 23 120 6.1 117 11.4 24.3 -21.97 55 Fluoxastrobin 6.05 + 248 93.1 49 129.1 25 73 7.5 76 11.7 18.4 13.74 57 Furakovit 6.76 + 331.1 195.1 25 252.1 11 10.5 110 51.3 64.4 64				-											
52 Flubendiamide 7.63 + 683.1 274.1 41 408 9 100 19.8 75 16.4 28.7 -6.62 53 Fluometuron 5.95 + 233.1 46 37 72.1 35 112 8.5 102 8.8 13.1 -16.73 54 Fluoxastrobin 7.46 + 459.2 188 47 427.2 23 120 6.1 117 11.4 24.3 -21.97 55 Fluxilazole 7.34 + 316.1 165.1 37 247.1 21 73 7.5 76 11.7 18.4 13.74 57 Furalaxyl 6.76 + 230.1 95 39 242.1 21 110 10.5 104 10.8 81.0 -5.6 58 Furathiocarb 8.43 + 383.1 195.1 25 252.1 17 116 13.0 110 5.1 6.6															
53 Fluometuron 5.95 + 23.1 46 37 72.1 35 112 8.5 102 8.8 13.1 -16.73 54 Fluoxastrobin 7.46 + 459.2 188 47 427.2 23 120 6.1 117 11.4 24.3 -21.97 55 Fluslazole 7.34 + 316.1 166.1 37 247.1 21 73 14.2 90 9.7 64.3 -13.78 56 Forchlorfenuron 6.05 + 248 93.1 49 129.1 25 73 7.5 76 11.7 18.4 13.74 57 Furaloxyl 6.76 + 302.1 95 39 242.1 21 110 10.5 104 10.8 81.0 -5.5 58 Furaloxyl 6.76 7.4 + 31.1 70 55 159 33 73 6.7 119 6.5															
54 Fluxastrobin 7.46 + 459.2 188 47 427.2 23 120 6.1 117 11.4 24.3 -21.97 55 Flusilazole 7.34 + 316.1 165.1 37 247.1 21 73 14.2 90 9.7 64.3 -13.78 56 Forchlorfenuron 6.05 + 248 93.1 49 129.1 25 73 7.5 76 11.7 18.4 13.74 57 Furalaxyl 6.76 + 302.1 95 39 242.1 21 110 10.5 104 10.8 81.0 -5.45 58 Furathiocarb 8.43 + 331.1 195.1 25 252.1 17 116 13.0 110 5.1 36 7.3 6.7 119 6.5 91.3 6.4 60 Hexornazole 7.44 + 353.1 168 37 228 119															
55 Flusilazole 7.34 + 316.1 165.1 37 247.1 21 73 14.2 90 9.7 64.3 -13.8 56 Forchlorlenuron 6.05 + 248 93.1 49 129.1 25 73 7.5 76 11.7 18.4 13.74 57 Furalaxyl 6.76 + 302.1 95 39 242.1 21 110 10.5 104 10.8 81.0 -5.45 58 Furathiocarb 8.43 + 383.1 195.1 25 252.1 17 116 13.0 110 5.1 38.3 73 6.7 119 6.5 91.3 6.44 60 Hexotonazole 7.44 + 363.1 168 37 228 19 ND 83 14.0 62.3 4.20 61 Hydramethylnon 9.17 + 495.2 151.1 65 323.2 41 83															
66 Forchlorfenuron 6.05 + 248 93.1 49 129.1 25 73 7.5 76 11.7 18.4 13.74 57 Furalaxyl 6.76 + 302.1 95 39 242.1 21 110 10.5 104 10.8 81.0 -5.45 58 Furathiocarb 8.43 + 383.1 195.1 25 252.1 177 116 13.0 110 5.1 38.3 -15.36 59 Hexaconazole 7.44 + 314.1 70 55 159 33 73 6.7 119 6.5 91.3 6.4 60 Hexatonazole 7.44 + 353.1 168 37 228 19 ND ND 83 14.0 52.3 42.0 61 Hydramethylnon 9.17 + 495.2 151.1 65 323.2 41 83 7.1 71 6.9 72.4															
57 Furalaxyl 6.76 + 302.1 95 39 242.1 21 110 10.5 104 10.8 81.0 -5.45 58 Furathiocarb 8.43 + 383.1 195.1 25 252.1 177 116 13.0 110 5.1 38.3 -16.36 59 Hexaconazole 7.44 + 314.1 70 55 159 33 73 6.7 119 6.5 91.3 6.44 60 Hexythiazox 8.67 + 353.1 188 37 228 19 ND ND 83 14.0 52.3 4.20 61 Hydramethylnon 9.17 + 495.2 151.1 65 323.2 411 83 7.1 71 6.9 27.4 7.06 62 Imazali 6.28 + 297 159 29 201 25 87 18.6 75 9.2 13.9 2.0 6.3 10.6 16.4 97 2.5 74.7 13.99 2.6															
58 Furthiocarb 8.43 + 383.1 195.1 25 252.1 17 116 13.0 110 5.1 38.3 15.6 59 Hexaconazole 7.44 + 314.1 70 55 159 33 73 6.7 119 6.5 91.3 6.44 60 Hexaconazole 7.44 + 333.1 188 37 228 19 ND ND 83 14.0 52.3 4.20 61 Hydramethylnon 9.17 + 495.2 151.1 65 323.2 41 83 7.1 71 6.9 27.4 7.06 62 Imazall 6.28 + 297 159 29 201 25 87 18.6 75 9.2 13.9 2.00 63 Imidacloprid 4.09 + 256 175.1 25 209.1 21 106 16.4 97 2.5 74.7 13.99 <td></td>															
59 Hexaconazole 7.44 + 314.1 70 55 159 33 73 6.7 119 6.5 91.3 6.44 60 Hexythiazox 8.67 + 353.1 168 37 228 19 ND ND 83 14.0 52.3 4.20 61 Hydramethylnon 9.17 + 495.2 151.1 65 323.2 41 83 7.1 71 6.9 27.4 7.06 62 Imazalii 6.28 + 297 159 29 201 25 87 18.6 75 9.2 13.9 -2.00 63 Imidacloprid 4.09 + 256 175.1 25 209.1 21 106 16.4 97 2.5 74.7 13.99 64 Ipconazole 7.68 + 334.2 70 37 125 47 119 13.0 89 16.5 92.8 12.04 65 Isoproturon 6.14 + 207.2 46.1 35 7															
60Hexythiazox8.67+353.11683722819NDND8314.052.34.2061Hydramethylnon9.17+495.2151.165323.241837.1716.927.47.0662Imazalil6.28+29715929201258718.6759.213.9-2.0063Imidacloprid4.09+256175.125209.12110616.4972.5574.713.9964Ipconazole7.68+334.270371254711913.08916.592.812.0465Isoproturon6.14+207.246.13572.129878.58513.611.64.9466Ivermectin9.78+892.6307.331569.51910711.510110.192.89.7867Mandipropamid7.08+412.1328.119356.1159715.5897.923.47.3168Mefenacet7.06+299120.135148.121857.3737.281.99.7169Metalaxyl6.02+280.1192.225220.2191045.6959.939.7-13.1170Methabenzthiazuron5.98 <td></td>															
61 Hydramethylnon 9.17 + 495.2 151.1 65 323.2 41 83 7.1 71 6.9 27.4 7.06 62 Imazalil 6.28 + 297 159 29 201 25 87 18.6 75 9.2 13.9 -2.00 63 Imidacloprid 4.09 + 256 175.1 25 209.1 21 106 16.4 97 2.5 74.7 13.99 64 Ipconazole 7.68 + 334.2 70 37 125 47 119 13.0 89 16.5 92.8 12.04 65 Isoproturon 6.14 + 207.2 46.1 35 72.1 29 87 8.5 85 13.6 11.6 4.94 66 Ivermectin 9.78 + 892.6 307.3 31 569.5 19 107 11.5 810 10.1 10.1 92.8 92.8 97.8 67 Mandipropamid 7.08 + 29.9															
62 Imazalii 6.28 + 297 159 29 201 25 87 18.6 75 9.2 13.9 -2.00 63 Imidacloprid 4.09 + 256 175.1 25 209.1 21 106 16.4 97 2.5 74.7 13.99 64 Ipconazole 7.68 + 334.2 70 37 125 47 119 13.0 89 16.5 92.8 12.04 65 Isoproturon 6.14 + 207.2 46.1 35 72.1 29 87 8.5 85 13.6 11.6 4.94 66 Ivermectin 9.78 + 892.6 307.3 31 569.5 19 107 11.5 101 10.1 92.8 97.8 67 Mandipropamid 7.08 + 412.1 328.1 19 356.1 15 97 15.5 89 7.9 23.4 7.3 7.2 81.9 9.7 68 Mefenacet 7.06 +															
63 Imidacloprid 4.09 + 256 175.1 25 209.1 21 106 16.4 97 2.5 74.7 13.99 64 Ipconazole 7.68 + 334.2 70 37 125 47 119 13.00 89 16.5 92.8 12.04 65 Isoproturon 6.14 + 207.2 46.1 35 72.1 29 87 8.5 85 13.6 11.6 4.94 66 Ivermectin 9.78 + 892.6 307.3 31 569.5 19 107 11.5 101 10.1 92.8 97.8 97.8 67 Mandipropamid 7.08 + 412.1 328.1 19 356.1 15 97 15.5 89 7.9 23.4 7.31 7.3 68 Mefenacet 7.06 + 299 120.1 35 148.1 21 85 7.3 73 7.2 81.9 9.71 69 Metalaxyl 6.02 + 280.1															
64 Ipconazole 7.68 + 334.2 70 37 125 47 119 13.0 89 16.5 92.8 12.0 65 Isoproturon 6.14 + 207.2 46.1 35 72.1 29 87 8.5 85 13.6 11.6 4.94 66 Ivermectin 9.78 + 892.6 307.3 31 569.5 19 107 11.5 101 10.1 92.8 97.8 97.8 67 Mandipropamid 7.08 + 412.1 328.1 19 356.1 15 97 15.5 89 7.9 23.4 7.3 7.2 68 Mefenacet 7.06 + 299 120.1 35 148.1 21 855 7.3 73 7.2 81.9 9.7 69 Metalaxyl 6.02 + 280.1 192.2 25 220.2 19 104 5.6 95 9.9<															
65 Isoproturon 6.14 + 207.2 46.1 35 72.1 29 87 8.5 85 13.6 11.6 4.94 66 Ivermectin 9.78 + 892.6 307.3 31 569.5 19 107 11.5 101 10.1 92.8 97.8 67 Mandipropamid 7.08 + 412.1 328.1 19 356.1 15 97 15.5 89 7.9 23.4 7.31 68 Mefenacet 7.06 + 299 120.1 35 148.1 21 85 7.3 73 7.2 81.9 9.71 69 Metalaxyl 6.02 + 280.1 192.2 25 220.2 19 104 5.6 95 9.9 39.7 -13.11 70 Methabenzthiazuron 5.98 + 222.1 150.3 45 165.2 21 99 4.3 80 2.7 20.0 21.31 71 Methamidophos 0.63 + 142 94															
66 Vermectin 9.78 + 892.6 307.3 31 569.5 19 107 11.5 101 10.1 92.8 9.78 67 Mandipropamid 7.08 + 412.1 328.1 19 356.1 15 97 15.5 89 7.9 23.4 7.31 68 Mefenacet 7.06 + 299 120.1 35 148.1 21 85 7.3 73 7.2 81.9 9.71 69 Metalaxyl 6.02 + 280.1 192.2 25 220.2 19 104 5.6 95 9.9 39.7 -13.11 70 Methabenzthiazuron 5.98 + 222.1 150.3 45 165.2 21 99 4.3 80 2.7 20.0 21.31 71 Methamidophos 0.63 + 142 94 19 125 19 88 18.0 82 19.2 35.8															
67 Mandipropamid 7.08 + 412.1 328.1 19 356.1 15 97 15.5 89 7.9 23.4 7.31 68 Mefenacet 7.06 + 299 120.1 35 148.1 21 85 7.3 7.3 7.2 81.9 9.71 69 Metalaxyl 6.02 + 280.1 192.2 25 220.2 19 104 5.6 95 9.9 39.7 -13.11 70 Methabenzthiazuron 5.98 + 222.1 150.3 45 165.2 21 99 4.3 80 2.7 20.0 21.31 71 Methamidophos 0.63 + 142 94 19 125 19 88 18.0 82 19.2 35.8 11.5															
68 Mefenacet 7.06 + 299 120.1 35 148.1 21 85 7.3 73 7.2 81.9 9.71 69 Metalaxyl 6.02 + 280.1 192.2 25 220.2 19 104 5.6 95 9.9 39.7 -13.11 70 Methabenzthiazuron 5.98 + 222.1 150.3 45 165.2 21 99 4.3 80 2.7 20.0 21.31 71 Methamidophos 0.63 + 142 94 19 125 19 88 18.0 82 19.2 35.8 11.54															
69 Metalaxyl 6.02 + 280.1 192.2 25 220.2 19 104 5.6 95 9.9 39.7 -13.1 70 Methabenzthiazuron 5.98 + 222.1 150.3 45 165.2 21 99 4.3 80 2.7 20.0 21.31 71 Methamidophos 0.63 + 142 94 19 125 19 88 18.0 82 19.2 35.8 11.54		Mandipropamid	7.08	+											
70 Methabenzthiazuron 5.98 + 222.1 150.3 45 165.2 21 99 4.3 80 2.7 20.0 21.31 71 Methamidophos 0.63 + 142 94 19 125 19 88 18.0 82 19.2 35.8 11.54				+											
71 Methamidophos 0.63 + 142 94 19 125 19 88 18.0 82 19.2 35.8 11.54	69	Metalaxyl	6.02	+	280.1	192.2	25	220.2	19	104	5.6	95	9.9	39.7	-13.11
	70	Methabenzthiazuron	5.98	+	222.1	150.3	45	165.2	21	99	4.3	80	2.7	20.0	21.31
72 Methoprotryne 5.72 + 272.2 198 31 240.2 27 74 10.3 73 11.4 50.9 50.0	71	Methamidophos	0.63	+	142	94	19	125	19	88	18.0	82	19.2	35.8	11.54
	72	Methoprotryne	5.72	+	272.2	198	31	240.2	27	74	10.3	73	11.4	50.9	-5.00

*ND = not detected

*Ion ratio absolute value provided by software and calculated by considering reference value of standard

Table 2 (part 3). List of pesticides with MRM transitions used

Sr.		RT	ESI						0.005 mg/kg (n=6)		0.01 mg/kg (n=6)		Ion Ratio	lon ratio
No.	Name of pesticide	(min)	(+/-)	Q1	Q3	CE	Q3	CE	% Rec	% RSD	% Rec	% RSD	Absolute	(±30)
73	Methoxyfenozide	7.25	+	369.1	149.1	21	313.2	11	72	9.2	77	7.7	49.2	-13.15
74	Metribuzin	5.28	+	215.1	84.1	31	187.1	25	88	8.5	106	4.7	4.5	13.15
75	Mevinphos Isomer 1	3.91	+	225.1	127.1	21	193.2	11	109	15.3	97	11.3	25.7	-9.89
76	Mevinphos Isomer 2	4.55	+	225.1	127.1	21	193.2	11	90	17.1	84	8.9	28.6	-4.73
77	Mexacarbate	1.88	+	223.2	151	31	159.1	21	106	2.6	95	5.2	59.2	-6.91
78	(Monceren) Pencycuron	7.95	+	329.1	125	31	218.1	23	83	1.8	73	3.2	3.3	11.49
79	Monocrotophos	1.94	+	224.1	98	17	127.1	21	82	12.8	79	4.0	38.3	22.28
80	Monolinuron	6.07	+	215.1	99	47	126.1	23	ND	ND	74	18.8	32.9	11.01
81	Myclobutanil	6.99	+	289	70	41	125	39	109	15.4	117	2.4	93.6	20.61
82	Nitenpyram	2.22	+	271	126	35	225.2	17	97	12.6	97	10.3	58.1	-14.21
83	Omethoate	0.85	+	214	124.9	31	182.8	17	77	10.0	96	6.4	65.2	-1.86
84	Oxadixyl	5.26	+	279.1	132.1	43	219.1	15	92	9.1	87	5.5	33.2	18.47
85	Penconazole	7.57	+	284.1	70	37	159	35	100	15.2	75	6.5	41.8	-15.33
86	Phenmedipham	6.72	+	301.2	107.9	44	168	12	101	16.2	71	9.1	36.5	0.44
87	Picoxystrobin	7.62	+	368	145	29	205	13	108	6.4	99	7.1	67.7	-8.28
88	Piperonyl butoxide	8.37	+	356.2	119.1	47	177.2	13	97	4.6	110	6.3	7.5	-14.22
89	Pirimicarb	3.89	+	239.2	72.1	33	182.1	21	98	4.3	89	4.1	62.6	-5.18
90	Prochloraz	7.56	+	376	70	43	308	15	72	11.2	91	12.9	9.3	5.06
91	Prometon	5.32	+	226.1	86	39	142	33	87	7.4	82	8.1	82.2	17.06
92	Prometryne	6.41	+	242.2	158.1	33	200.1	25	80	12	73	6.2	59.5	0.91
93	Propiconazole	7.65	+	342.1	69	39	159	31	94	14.5	77	17.5	9.6	8.09
94	Pyracarbolid	5.78	+	218.1	97	37	125	25	73	8.7	72	5.9	8.3	-1.53
95	Pyraclostrobin	7.83	+	388	163	31	194	17	91	19.9	85	14.7	137.9	5.46
96	Pyridaben	9.23	+	365	147	33	309	19	74	11.7	73	8.4	75.1	15.50
97	Pyrimethanil	6.24	+	200	82	37	107	33	102	16.2	82	13.3	36.9	-0.19
98	Pyriproxyfen	8.57	+	322	96	21	185	31	76	9.6	74	10.9	18.3	-0.43
99	Quinoxyfen	8.91	+	308.1	162.1	63	197.1	45	92	8.6	70	8.3	78.0	-9.86
100	Secbumeton	5.38	+	226.2	100	37	170.1	25	94	3.5	83	2.9	20.4	-13.40
101	Siduron	6.61	+	233.3	94	31	137.2	23	72	12.1	74	2.9	72.9	0.65
102	Simetryn	5.04	+	214	124	29	144	29	115	12.2	79	11.5	42.0	-11.16
103	Spinetoram	8.44	+	748.5	98.1	65	142.2	43	111	14.1	97	11.9	21.6	4.18
104	Spinosad (Spinosyn A)	7.85	+	732.5	98.1	65	142.2	39	77	12.1	84	15.6	15.5	-10.79
105	Spinosad (Spinosyn D)	8.24	+	746.8	98.3	65	142.4	41	105	13.4	97	9.1	32.3	28.50
106	Spirodiclofen	9.91	+	411.3	71.3	31	313.3	17	ND	ND	94	1.2	41.9	8.93
107	Spiromesifen	9.21	+	371.2	255.2	31	273.2	11	108	11.8	82	7.2	11.5	-17.41
108	Spirotetramat	6.8	+	374.2	302.2	27	330.2	23	104	10.4	115	2.7	145.2	-10.21
109	Spiroxamine 1	7.3	+	298.2	100.1	43	144.2	29	92	12.9	77	6.0	25.9	0.23
110	Spiroxamine 2	7.3	+	298.2	100.1	43	144.2	29	91	3.4	75	9.2	28.6	-8.69
111	Tebufenozide	7.59	+	353.2	133	23	297.2	11	95	6.5	107	16.8	73.9	-1.44
112	Tebufenpyrad	8.28	+	334	117	47	145	37	85	7.8	93	4.1	30.9	-25.80
113	Tebuthiuron	5.05	+	229.1	116.1	37	172.4	25	92	11.6	89	10.6	21.0	3.74
114	Terbumeton	5.38	+	226.1	100	41	170.1	23	87	3.2	82	3.8	8.7	5.31
115	Terbutryn	6.51	+	242.1	68.1	61	186.1	25	91	6.8	72	5.7	27.6	6.84
116	Tetraconazole	7.18	+	372.1	70	47	159	35	75	11.8	76	12.2	24.3	10.37
117	Thiabendazole	2.41	+	202.1	131.2	45	175.1	35	78	4.6	71	3.1	61.9	-10.93
118	Thiacloprid	5.03	+	253	99	59	126	29	77	10.0	92	14.0	5.6	-24.70
119	Thiamethoxam	2.86	+	292	181	31	211	17	83	19.2	96	11.2	16.4	-5.08
120	Thiophanate-methyl	5.5	+	343	151.1	31	311	17	98	16.5	96	12.1	5.7	26.42

*ND = not detected

*Ion ratio absolute value provided by software and calculated by considering reference value of standard

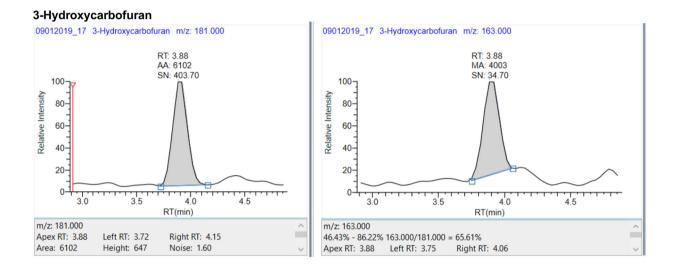
Table 2 (part 4). List of pesticides with MRM transitions used

Sr.		RT	ESI	01	00	05	Q3	05	0.005 mg/kg (n=6)		0.01 mg/kg (n=6)		Ion Ratio	lon ratio
No.	Name of pesticide	(min)	(+/-)	Q1	Q3	CE		CE	% Rec	% RSD	% Rec	% RSD	Absolute	(±30)
121	Triadimefon	7.06	+	294	197.1	21	225	19	119	4.8	82	15.6	36.8	-8.26
122	Triadimenol	6.65	+	296.1	70	33	227.1	17	102	18.4	86	9.8	2.0	-4.63
123	Tricyclazole	5.03	+	190	136	39	163	33	97	19.7	72	14.1	70.8	13.32
124	Trifloxystrobin	8.2	+	409	186	21	206	19	84	16.0	81	7.8	29.4	13.41
125	Triflumizole	7.85	+	346.1	73	27	278.1	17	76	5.7	77	5.2	7.8	-26.68
126	Vamidothion	3.86	+	288	118	37	146	17	102	3.7	89	4.0	8.6	10.06
127	Zoxamide	7.93	+	336.1	159	55	187	29	111	13.1	77	4.4	14.9	-0.47

*ND = not detected

*lon ratio absolute value provided by software and calculated by considering reference value of standard

Appendix II: supplemental information



Vamidothion

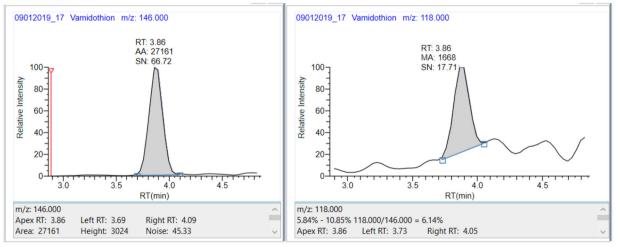


Figure 7 (part 1). Supplemental information for 3-hydroxycarbofuran and vamidothion

thermo scientific

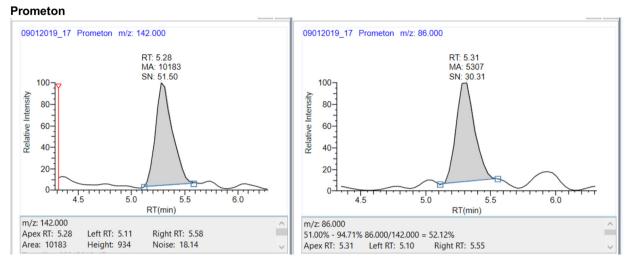


Figure 7 (part 2). Supplemental information for prometon

Find out more at thermofisher.com



©2019 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representatives for details. **AN73016-EN 0719S**