Application note | 000752

Food safety

Multi-residue analysis of pesticides in edible oils by triple quadrupole GC-MS

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Keywords

Pesticides, sunflower oil, gas chromatography-mass spectrometry, GC-MS, triple quadrupole, TSQ 9610 mass spectrometer, NeverVent Advanced Ionization Ion source (AEI), TRACE 1610 GC, TriPlus RSH autosampler, productivity

Goal

The aim of this application note is to demonstrate the performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer with the Thermo Scientific™ NeverVent™ Advanced Electron Ionization (AEI) source coupled to the Thermo Scientific™ TRACE™ 1610 GC for the determination of pesticide residues in sunflower oil at trace levels.

Introduction

Edible oils are consumed every day for cooking and frying. Among them, sunflower oil with its high content of poly- and monounsaturated fats as well as vitamin E, a potent antioxidant, has proven to be a healthy oil, which can have beneficial effects on the heart, skin, immune system, and overall maintenance of health.[1] The excessive use of pesticides on crops and during their storage can result in residues that remain in edible oils, which negatively impact both the quality and the safety of the products.

As pesticides usually occur at trace levels, sensitivity is key in this analysis as the regulatory maximum residue levels (MRLs) must be consistently met by analytical testing laboratories when assessing food safety. One of the most common techniques for analysis of pesticides is gas chromatography coupled to triple quadrupole mass spectrometry (GC-MS/MS), as it ensures adequate sensitivity and selectivity to achieve both the MRLs and to reduce the risk of false positive results by using the selected reaction monitoring (SRM) acquisition mode.

In this study, the TSQ 9610 triple quadrupole GC-MS/MS system was assessed for the analysis of >300 pesticides in sunflower oil at trace level concentrations. Linearity, limits of detection and quantitation, and an alternative approach based on quantitative analysis following standard addition are demonstrated.

Experimental

In the experiments described here, a TSQ 9610 triple quadrupole mass spectrometer equipped with a NeverVent Advanced Electron Ionization (AEI) ion source was coupled to a TRACE 1610 GC equipped with a Thermo Scientific™ iConnect™ Split/Spiltless (iConnect-SSL) injector and a Thermo Scientific™ TriPlus™ RSH SMART liquid autosampler. The NeverVent technology allows for ion source cleaning, filament replacement, and column exchange without breaking instrument vacuum, therefore ensuring minimum downtime to the laboratory workflow. Chromatographic separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-35MS analytical column, 30 m x 0.25 mm i.d. x 0.25 µm (P/N 26094-1420). Additional method details are reported in Table 1. The list of the target compounds, as well as retention times and monitored transitions are reported in Appendix 1.

Data acquisition, processing, and reporting

Data were acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated instrument control ensures full automation of the analytical workflow combined with an intuitive user interface for data analysis, processing, customizable reporting, and storage in compliance with the Federal Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11). The advanced reprocessing capability of Chromeleon CDS software ensures immediate and easy data analysis, offering the possibility of automated standard addition quantitative analysis. Moreover, Chromeleon CDS software also offers the option to scale up the entire data handling from a single workstation to an enterprise environment.

Standard and sample preparation

Samples for analysis were prepared by adding 1 mL toluene and acetonitrile (60:40 v/v) to sunflower oil, followed by sample freezing. The resulting supernatant was injected into the GC-MS/MS system. In a similar way, to assess instrument linearity, a six-point matrix-matched calibration curve was prepared by spiking an oil sample at 5, 10, 25, 50, 75, and 100 µg/kg with a mixture of pesticides.

Table 1. GC-MS/MS and autosampler experimental conditions for the analysis of pesticides

TriPlus RSH SMART autosampler parameters	
Injection volume (µL)	1
Filling strokes counts	10
Pre-injection wash cycles	3
Pre-injection solvent wash volume (µL)	5
Post-injection wash cycles	3
Pre-injection solvent wash volume (µL)	5
Sample rinse cycles	1
Sample rinse volume (µL)	2

iConnect-SSL parameters	
Inlet module and mode	SSL, splitless
Injection temperature (°C)	280
Liner	4 mm i.d. Taper liner with wool on bottom
Splitless time (min)	1.5
Split flow (mL/min)	50
Septum purge flow (mL/min)	5, constant
Carrier gas, flow (mL/min)	He, 1.8

TRACE 1610 GC parameters	
Oven temperature program	
Temperature (°C)	85
Hold time (min)	1.5
Rate (°C/min)	30
Temperature 2 (°C)	150
Rate (°C/min)	10
Temperature 3 (°C)	320
Hold time (min)	8
GC run time (min)	28.66
Column	
TraceGOLD TG-35MS	30 m, 0.25 mm, 0.25 µm (P/N 26094-1420)

TSQ 9610 mass spectrometer parameters	
Transfer line temperature (°C)	280
Ion source type and temperature (°C)	NeverVent AEI, 280
Ionization type	EI
Emission current (µA)	50
Acquisition mode	*timed*-SRM
Tuning parameters	AEI Smart Tune
Collision gas and pressure (psi)	Argon at 70

Results and discussion

Chromatography

Sunflower oil is a complex matrix, and it is important that the interferences from the matrix are removed to produce a sufficiently resolved chromatogram and, subsequently, quantify pesticides at the MRLs defined by the EU Reference Laboratories for Residues of Pesticides (EURL)[2] at 10 µg/kg. The *t*-SRM acquisition method allowed for simultaneous acquisition of multiple characteristic ions for each pesticide, maintaining high sensitivity combined with high selectivity to discriminate between the individual pesticides under investigation and the matrix, thus ensuring a confident and selective identification of analytes. As an example for the complexity of the analysis, Figure 1 shows the *t*-SRM acquisition at 5 µg/kg for pesticides in sunflower oil.

Some pesticides, can easily degrade in the injector port, leading to active sites and therefore producing matrix effects when repeated injections are made. This results in poor peak profiles with marked tailing and poor reproducibility. The high inertness of the TRACE 1610 GC sample path, combined with the ultra-low bleed of the TraceGOLD column and the effective surface deactivation of the packed splitless quartz liner, ensured Gaussian peak shape across long sequences. Figure 2 shows an example of *ortho*-phenylphenol acquired on samples spiked at 100 µg/mL at the beginning (injection 10), middle (injection 95), and end (injection 204) of a typical sequence. Retention times (RT), peak areas, ion ratios (IR), peak asymmetry, and peak width (measured at 50%) remained stable across the entire sequence as demonstrated in the table reported in Figure 2.

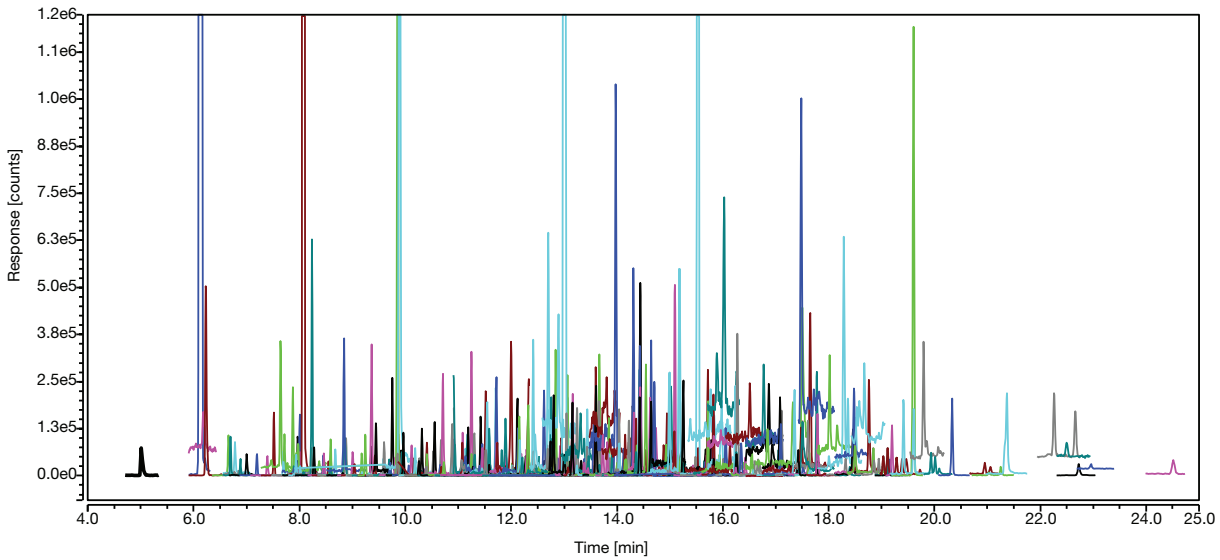
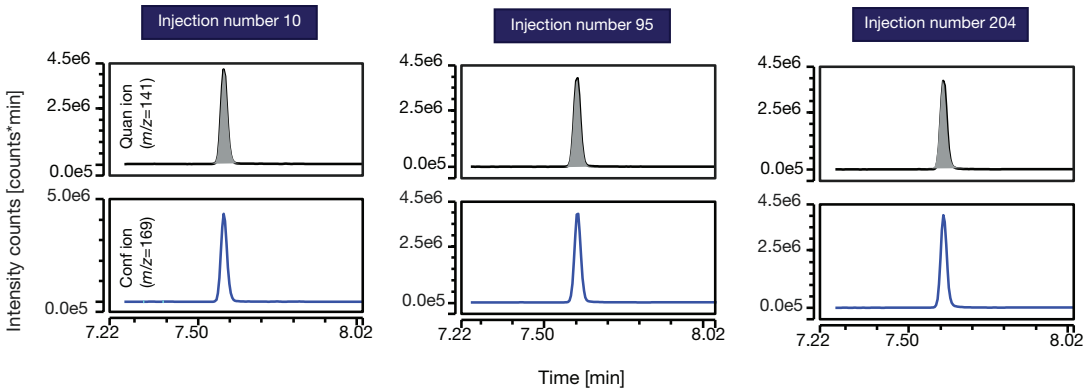


Figure 1. *t*-SRM acquisition for pesticides at 5 µg/kg in sunflower



ortho-phenylphenol					
Injection number	RT (min)	Area (counts*min)	Asymmetry (EP)	Peak width (50%)	IR (%)
10	7.61	106210	1.1	0.024	103
95	7.64	102386	1.0	0.024	113
204	7.64	101050	1.2	0.024	118

Figure 2. Ortho-phenylphenol peak comparison in spiked samples acquired at the beginning (injection 10), middle (injection 95), and end of a typical sequence (injection 204). Retention times (RT), peak areas, ion ratios (IR), peak asymmetry, and peak width (measured at 50%) remained stable across the entire sequence.

Linearity for accurate quantitative analysis

The TSQ 9610 triple quadrupole mass spectrometer is equipped with the Thermo Scientific™ XLXR™ detector, which is an electron multiplier that offers extended dynamic range and longer lifetime. This detector allows expanded calibration curves to be analyzed and significantly limits the need for detector replacement on the system. To test the extended dynamic range of the detector, linearity was evaluated by using a six-point matrix-matched calibration curve ranging from 5 to 100 µg/kg. Figure 3 shows some examples of calibration curves for selected pesticides.

The signal-to-noise ratio (S/N) at the lowest calibration point was used to establish the limit of detection (LOD, S/N > 3) and quantitation (LOQ, S/N > 10). The calculated LODs and LOQs ranged from 0.02 to 19 µg/kg (Figure 4) and from 0.07 to 63 µg/kg, respectively, as reported in Appendix 1.

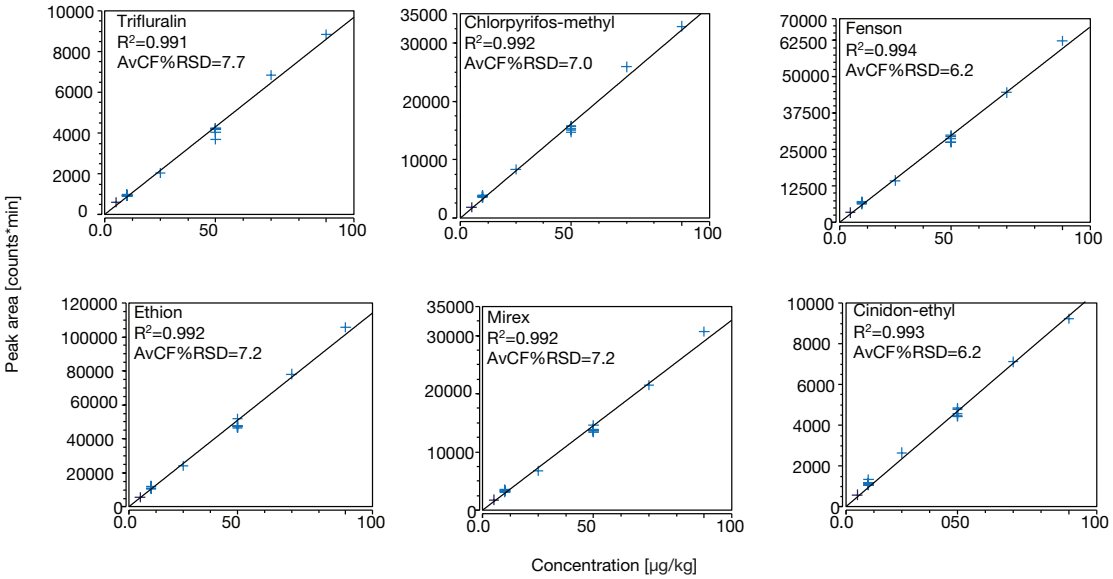


Figure 3. Examples of calibration curves ranging from 5 to 100 µg/kg for selected pesticides. R^2 as well as AvCF %RSD are annotated.

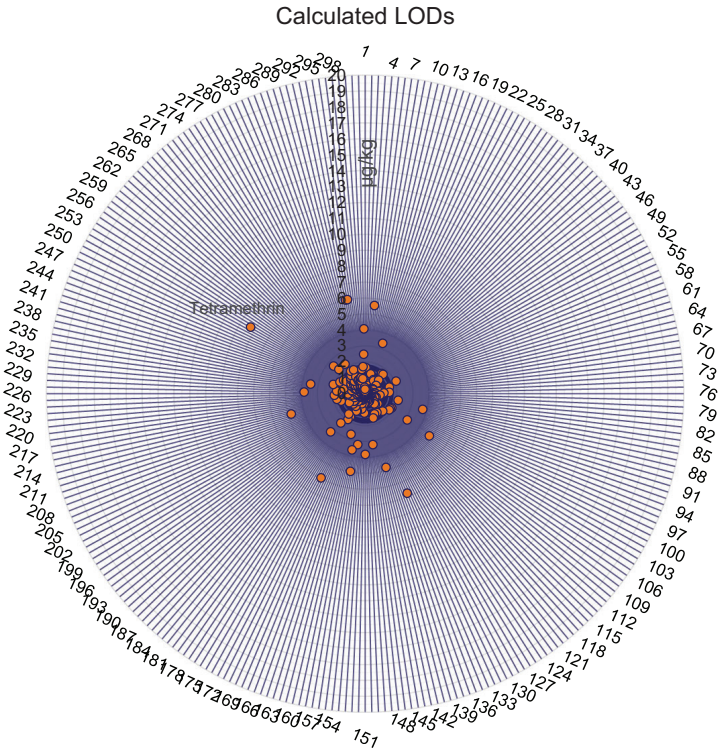


Figure 4. Calculated LODs based on the S/N > 3. For > 90% the LODs were < 2 µg/kg.

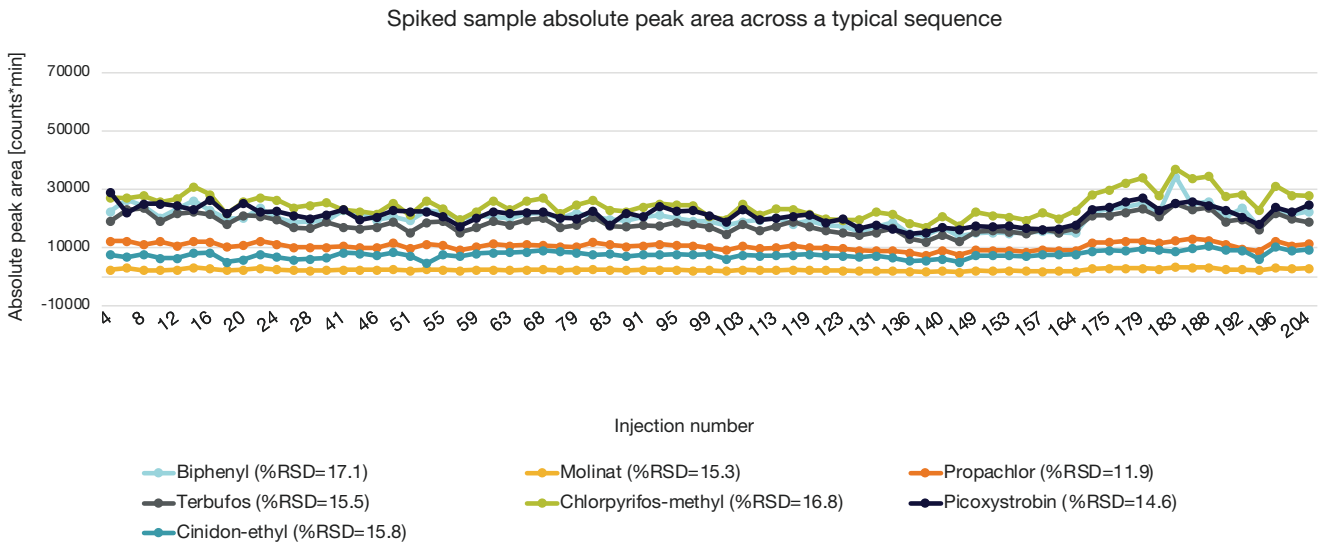


Figure 5. Absolute peak area response obtained for spiked samples at 100 µg/kg across a typical sequence of n=204 consecutive injections of sunflower oil samples, where native samples were alternated to spiked samples

Unparalleled productivity for essential testing

Simplified procedures and robust instruments requiring minimal user intervention are essential for analytical testing laboratories dealing with high sample throughout and looking to minimize instrument idle time and maximize their return on investment. Standard addition can be used as an alternative approach to multi-point calibration curves as it is a simpler approach to compensate for matrix effects. This procedure involves the addition of a known quantity of an analyte to one of two duplicate samples immediately prior to extraction.[3] The difference in response from the two sample extracts (spiked and unspiked) obtained from the detector calibrates the response to the known quantity of analyte added and compensates for incomplete or biased recovery.[3] The quantity of analyte present in the unspiked sample extract is calculated by simple proportion.[3] This technique automatically adjusts for both recovery and calibration. Absolute peak area RSDs for some selected pesticides in spiked samples are reported in Figure 5 as less than 20% across a typical sample sequence where unspiked samples and spiked samples at 100 µg/kg were alternated. Calculated recoveries (%) for the compounds in the example ranged between 97 and 119, with calculated precision within 20%. Neither inlet nor ion source maintenance was performed on the system during this sequence which was equivalent to over 4 days of continuous analysis.

Conclusions

The results obtained in these experiments demonstrate that the TSQ 9610 mass spectrometer equipped with the NeverVent AEI ion source in combination with the TRACE 1610 GC and the TriPlus RSH SMART autosampler delivers robust analytical performance for multi-residue analysis of pesticides in sunflower oil.

- The NeverVent AEI ion source in combination with the *t*-SRM acquisition mode allowed for high sensitivity and high selectivity to discriminate between the investigated pesticides and the matrix, thus ensuring confident and selective identification of analytes combined with sensitive detection of trace level analytes with calculated LODs < 2 µg/kg (ppb) for more than 90% of the target analytes.
- The stability of the AEI ion source, the high inertness of the TRACE 1610 GC sample path combined with the ultra-low bleed and superior inertness of TraceGOLD column, and the effective surface deactivation ensured Gaussian peak shape, retention time, and ion ratio stability across long sequences, ensuring accurate and reliable analyte quantitation.
- The standard addition approach allowed for increased laboratory productivity with minimal instrument idle time.

References

1. Karthik, D.; Vijayarekha, K. Chemometric identification of a few heavy metals, pesticides and plasticides in edible sunflower oil for health risk assessment, International Journal of Food Properties, 2018, 21(1), 1442-1448.
2. EU Reference Laboratories for Residues of Pesticides. https://www.eurl-pesticides.eu/docs/public/home.asp?LabID=100&Lang=EN
3. Quality control procedures for pesticide residues analysis, SANCO/10232/2006, 2006, March,24.

Appendix 1. List of the target compounds, retention times (RT), and monitored transitions (*m/z*)

Ref. number for Figure 3	Compound name	"Retention time (RT, min)"	MS quantitation (m/z)	MS confirming (m/z)	MS confirming (m/z)	Calculated LOD (S/N>3) (µg/kg)	Calculated LOQ (S/N>10) (µg/kg)
1	Dichlorvos	5.03	185 / 93	185 / 109	220 / 185	0.1	0.3
2	Biphenyl	6.20	154 / 115	152 / 126	154 / 102	1.6	5.4
3	Dichlobenil	6.24	171 / 136	173 / 138		0.0	0.1
4	Chlormephos	6.68	154 / 121	234 / 121		0.1	0.4
5	Etridiazole	6.79	211 / 183	213 / 185		0.4	1.5
6	Lufenuron	6.87	176 / 121	176 / 148		5.6	18.5
7	Mevinphos a+b	6.91	127 / 95	127 / 109	192 / 127	0.6	1.9
8	Nitrapyrin	7.00	194 / 133	194 / 158		0.6	1.9
9	Methacriphos	7.21	240 / 180	240 / 208		0.1	0.4
10	Pentachlorobenzene	7.40	248 / 213	250 / 215		0.1	0.3
11	Chloroneb	7.53	191 / 113	191 / 163		0.1	0.2
12	ortho Phenylphenol	7.64	170 / 141	170 / 169		0.1	0.4
13	Phthalimide	7.80	147 / 76	147 / 103		0.2	0.6
14	Molinat	7.81	187 / 98	187 / 126		1.3	4.2
15	Ethalfluralin	7.93	276 / 202	316 / 276		0.2	0.5
16	MCPA-metylester	7.99	214 / 141	214 / 155		0.1	0.4
17	Tetrahydrophthalimide (THPI)	8.10	151 / 79	151 / 122		3.3	11.1
18	Chlorethoxyphos	8.03	153 / 97	153 / 125		0.6	2.2
19	Benfluralin	8.05	292 / 160	292 / 264		0.1	0.5
20	Trifluralin	8.10	264 / 160	306 / 206	306 / 264	0.2	0.8
21	Demeton O	8.25	88 / 60	115 / 97	171 / 97	0.6	1.9
22	Heptenophos	8.26	124 / 89	250 / 89		0.0	0.1
23	Chlorfenprop-methyl	8.29	137 / 102	165 / 101		0.1	0.3
24	Tecnazen	8.47	261 / 203	259 / 201		0.2	0.8
25	MCPA ethyl ester	8.48	228 / 141	228 / 155	228 / 125	0.2	0.8
26	Propachlor	8.57	169 / 120	196 / 120		0.2	0.8
27	Ethoprophos	8.61	158 / 97	200 / 158		1.0	3.3
28	Chlorpropham	8.67	213 / 127	213 / 171		0.2	0.8
29	2,4-D-Methylester	8.84	234 / 147	234 / 175		0.9	3.1
30	Diphenylamin	8.85	169 / 167	169 / 168		0.2	0.7
31	Cadusaphos	8.83	159 / 97	213 / 89		0.1	0.4
32	Diallate (trans cis)	8.71	234 / 150	234 / 192		0.1	0.2
33	Sulfotep	9.02	266 / 146	322 / 146	322 / 202	0.2	0.5
34	Fluchloralin	9.29	264 / 160	306 / 264		1.6	5.4
35	Profluralin	9.05	318 / 199	330 / 248		0.3	1.0
36	Omethoat	9.18	156 / 79	156 / 110		0.3	0.9
37	Naled	9.21	145 / 113	301 / 109		1.6	5.4
38	Flonicamid	9.45	174 / 126	174 / 146		0.1	0.4
39	2,4 D Ethylester	9.33	248 / 175	248 / 185		1.2	3.9
40	Hexachlorbenzol (HCB)	9.37	284 / 249	286 / 251		0.1	0.3
41	Tefluthrin	9.40	177 / 127	177 / 137		0.1	0.3
42	Pentachloranisol	9.44	278 / 235	280 / 237		0.4	1.2
43	Dicrotophos	9.59	127 / 95	192 / 127		0.4	1.3
44	HCH alpha	9.62	183 / 147	217 / 181		0.1	0.4
45	Thiometon	9.72	125 / 47	158 / 125	248 / 88	0.2	0.7
46	Demeton S	9.77	126 / 65	143 / 97	170 / 114	0.8	2.8

47	Dioxabenzofos	9.75	183 / 153	201 / 121		0.5	1.7
48	Terbufos	9.84	231 / 157	231 / 175	288 / 231	0.5	1.6
49	Propyzamid	9.88	173 / 109	175 / 147		0.1	0.4
50	Diazinon	9.96	199 / 93	304 / 179		0.4	1.3
51	Tebupirimfos	9.97	234 / 110	234 / 126		0.4	1.4
52	Propetamphos	9.99	138 / 64	194 / 166		0.2	0.7
53	Atrazine	10.08	200 / 104	200 / 122		0.6	1.9
54	Swep	10.13	187 / 124	219 / 174		0.2	0.7
55	MCPA-1-butyl ester	10.19	256 / 141	256 / 200		0.3	1.0
56	Triallate	10.20	268 / 184	270 / 186		0.2	0.6
57	Quintozen	10.20	214 / 179	249 / 214	295 / 237	0.6	1.9
58	2.4.5-T-Methylester	10.32	233 / 190	268 / 233	270 / 235	2.1	6.9
59	Fonofos	10.33	246 / 109	246 / 137		0.1	0.4
60	Dinobuton	10.40	163 / 116	211 / 117		0.3	0.9
61	Disulfoton	10.41	186 / 97	274 / 88		0.2	0.5
62	HCH gamma_Lindane	10.43	183 / 147	217 / 181		0.3	1.1
63	Etrimfos	10.43	292 / 153	292 / 181		0.1	0.3
64	Bromocyclen	10.49	359 / 243	361 / 245		1.6	5.2
65	Dimethoate	10.55	125 / 47	229 / 87		0.2	0.5
66	Chloramben-Methyl	10.56	160 / 124	188 / 124	188 / 160	0.1	0.3
67	MCPA-thioethyl	10.68	244 / 125	244 / 155		0.2	0.7
68	Cyanophos	10.70	243 / 79	243 / 109		0.9	3.1
69	Iprobenfos	10.70	204 / 91	204 / 122		0.2	0.8
70	Isazophos (Miral)	10.75	257 / 119	257 / 162		0.9	2.9
71	Dichlofenthion	10.87	223 / 159	223 / 205	279 / 223	0.2	0.6
72	Fipronil, desulfinyl	10.89	333 / 231	388 / 333		0.1	0.3
73	HCH beta	10.96	183 / 147	217 / 181		0.6	2.0
74	Plifenate	10.98	242 / 170	242 / 172		1.5	5.1
75	2,4 D Butyl Ester	11.04	276 / 162	276 / 185		1.2	3.9
76	Acetochlor	11.10	223 / 132	223 / 146		0.1	0.3
77	Fenchlorphos oxon	11.09	269 / 224	271 / 256		0.2	0.6
78	Heptachlor	11.15	100 / 65	272 / 237		0.4	1.4
79	Vinclozolin	11.14	212 / 172	285 / 212		0.7	2.3
80	Paraoxon-methyl	11.16	230 / 106	230 / 136	230 / 200	0.3	0.9
81	Benoxacor	11.19	259 / 120	261 / 120		0.1	0.4
82	Terbacil	11.28	160 / 76	161 / 88	161 / 144	0.9	3.1
83	Dimethachlor	11.27	197 / 148	199 / 148		0.1	0.3
84	S421	11.28	130 / 95	132 / 97		0.2	0.7
85	Pentachloroaniline	11.27	263 / 192	265 / 194		0.5	1.8
86	Alachlor	11.34	188 / 131	188 / 160	237/160	2.1	7.0
87	Phosphamidon	11.44	127 / 109	264 / 127		0.3	0.8
88	Tridiphane	11.47	187 / 159	187 / 159		3.8	12.5
89	Chlorpyrifos-methyl	11.47	286 / 93	286 / 271	288 / 273	0.1	0.4
90	Fenchlorphos	11.53	285 / 270	287 / 272		0.2	0.6
91	HCH delta	11.59	183 / 147	217 / 181		0.7	2.4
92	Malaoxon	11.56	127 / 99	127 / 109		0.6	2.0
93	Dimethipin	11.55	118 / 58	124 / 76		0.6	2.1
94	Chlorothalonil	11.69	266 / 133	266 / 170		0.6	2.0
95	Propanil	11.59	217 / 161	219 / 163		0.7	2.2
96	Tolclofos-methyl	11.74	265 / 250	267 / 252		0.2	0.7
97	Pirimiphos-methyl	11.74	290 / 125	305 / 180		0.2	0.5

98	Nitrothal-isopropyl	11.77	236 / 148	236 / 194		0.4	1.5
99	Parathion-methyl	11.80	263 / 79	263 / 109		1.9	6.3
100	N-Desethyl-pirimiphos-methyl	11.82	277 / 135	277 / 168		0.3	1.0
101	Dichlorbenzophenon, o,p	12.12	139 / 111	250 / 139		1.8	6.1
102	Paraoxon-ethyl	11.91	149 / 119	220 / 94	275 / 99	3.1	10.4
103	Metolachlor	12.01	162 / 133	238 / 133	238 / 162	4.8	16.1
104	Pentachlorothioanisole	12.01	296 / 246	296 / 263		1.8	6.1
105	Butralin	12.04	266 / 190	266 / 220		0.3	1.0
106	Isobenzan (Telodrin)	12.05	311 / 275	313 / 277		0.5	1.8
107	Malathion	12.13	173 / 99	285 / 127		0.4	1.3
108	Chlorthal-dimethyl	12.13	301 / 223	332 / 301		1.0	3.4
109	Chlorpyrifos-ethyl	12.15	314 / 258	314 / 286	316 / 260	0.2	0.7
110	Trichloronat	12.16	297 / 269	299 / 271		0.2	0.7
111	Ethofumesat	12.17	207 / 161	286 / 207		0.8	2.6
112	Triadimefon	12.15	208 / 127	208 / 181		0.1	0.3
113	Isopropalin	12.21	280 / 180	280 / 238		1.6	5.2
114	Fenitrothion	12.22	277 / 109	277 / 260		0.4	1.2
115	Isomethiozin	12.28	198 / 82	225 / 57		0.9	3.2
116	Metribuzin	12.29	198 / 89	198 / 110		0.9	2.9
117	Tetraconazol	12.30	336 / 204	336 / 218		0.2	0.7
118	Pirimiphos-ethyl	12.33	304 / 168	318 / 166		0.1	0.2
119	Dichlofluanid	12.34	224 / 123	226 / 123		0.4	1.2
120	Fipronil, sulfide	12.41	351 / 255	420 / 351		0.1	0.2
121	Parathion-ethyl	12.44	291 / 109	291 / 137		0.5	1.5
122	Fipronil	12.70	367 / 178	367 / 213	369 / 215	0.4	1.2
123	Dimethylvinphos	12.61	295 / 109	297 / 109		0.2	0.6
124	Chlorthion	12.65	297 / 79	297 / 109		1.4	4.7
125	Bromophos-methyl	12.68	329 / 314	331 / 316		0.5	1.8
126	Dichlorbenzophenon, p,p	12.70	250 / 139	139 / 111		0.1	0.2
127	Isofenphos-methyl	12.70	199 / 121	241 / 199		0.2	0.6
128	Dicapthon	12.75	262 / 123	262 / 216		0.2	0.7
129	Amidithion	12.75	131 / 59	143 / 111	171 / 125	0.6	1.9
130	Chlozolinate	12.79	259 / 188	331 / 259		1.4	4.7
131	Dinobuton2	12.80	163 / 116	211 / 117		6.8	22.7
132	Pendimethalin	12.82	252 / 162	252 / 191	281 / 252	0.5	1.6
133	Isofenphos	12.84	213 / 121	213 / 185		0.2	0.6
134	MCPA - butoxyethylester	12.89	300 / 182	300 / 200		0.6	1.9
135	Isocarbofos	12.89	136 / 108	230 / 212		1.6	5.4
136	Heptachlorepoxid-cis	12.91	353 / 263	353 / 282		0.4	1.5
137	Crufomate	12.90	182 / 147	256 / 226	276 / 182	4.8	16.1
138	Haloxyfop-methyl	12.94	375 / 288	375 / 316		0.5	1.6
139	Flumetralin	12.96	143 / 107	143 / 108		0.2	0.6
140	Penconazol	13.05	248 / 157	248 / 192		0.2	0.5
141	Antrachinon	13.05	208 / 152	208 / 180		0.3	0.9
142	Heptachlorepoxid-trans	13.07	272 / 237	289 / 219	289 / 253	0.2	0.8
143	Triadimenol (Doppelpeak)	13.11	128 / 100	168 / 70		3.3	10.9

144	Fenson	13.17	268 / 77	268 / 141		0.3	1.0
145	Chlorfenvinphos (2Peaks)	13.16	323 / 267	325 / 269		0.2	0.6
146	Butachlor	13.16	237 / 160	176 / 146		0.1	0.2
147	Mecarbam	13.20	131 / 42	131 / 86	329 / 131	0.5	1.6
148	Bromophos-ethyl	13.22	359 / 303	359 / 331		0.4	1.3
149	Tolylfluanid	13.24	238 / 137	240 / 137		0.2	0.6
150	Metazachlor	13.30	133 / 117	209 / 132		3.8	12.8
151	Procymidon	13.31	283 / 67	283 / 96		1.3	4.2
152	Chlordan-trans (gamma)	13.40	272 / 237	373 / 266		1.2	4.1
153	Quinalphos	13.38	193 / 129	298 / 156		0.7	2.2
154	DDE o,p	13.43	318 / 246	246 / 176		0.6	2.1
155	Phenthoat	13.43	274 / 121	274 / 125		0.2	0.8
156	Diclocymet	13.40	221 / 155	277 / 221		0.7	2.3
157	Crotoxyphos	13.47	193 / 109	193 / 127	127 / 109	3.3	10.9
158	Propaphos	13.56	304 / 140	304 / 220		0.2	0.7
159	2,4 D Ethylhexyl ester	13.60	220 / 162	222 / 164	332 / 220	5.0	16.7
160	Chlordan-cis (alpha)	13.58	272 / 237	373 / 266		1.0	3.4
161	Bromfenvinphos_1_2	13.50	267 / 159	323 / 267		3.7	12.2
162	Benazolin-ethyl	13.59	170 / 134	198 / 170		0.2	0.8
163	Paclobutrazole	13.70	236 / 125	238 / 127		0.2	0.6
164	Chlorbenside	13.66	125 / 89	268 / 125		0.1	0.3
165	Endosulfan-alpha	13.67	241 / 206	272 / 237		0.7	2.3
166	Pyrifenox	13.63	262 / 192	262 / 200		2.7	9.1
167	Oxadiazon	13.73	258 / 175	302 / 258		0.4	1.3
168	Tetrachlorvinphos	13.83	329 / 109	331 / 109		0.3	0.9
169	Tribuphos DEF(Merphos Abbau)	13.85	202 / 113	234 / 147		0.5	1.5
170	Butamifos	13.90	286 / 185	286 / 202		1.2	4.1
171	Picoxystrobin	13.90	303 / 157	335 / 303		0.4	1.5
172	Hexaconazol GC7	13.94	214 / 133	214 / 187	256 / 82	1.3	4.2
173	Fipronil, sulfone	14.00	383 / 213	385 / 257		6.0	20.0
174	Chlorflurenol-Methyl	13.96	215 / 152	217 / 152		0.1	0.3
175	Oxyfluorfen	14.00	252 / 146	361 / 300		0.4	1.4
176	DDE p,p	14.04	246 / 176	318 / 246		0.1	0.4
177	captan	14.05	117 / 82	149 / 70		1.7	5.8
178	Buprofezin	14.11	172 / 57	249 / 193	305 / 172	2.0	6.6
179	Chinomethionate	14.13	206 / 148	234 / 206		0.5	1.6
180	Profenofos	14.15	337 / 267	339 / 269		1.0	3.4
181	Methidathion	14.15	145 / 58	145 / 85		0.2	0.8
182	Folpet	14.15	117 / 82	260 / 130		1.7	5.6
183	Fluorodifen	14.17	190 / 126	190 / 146		2.4	8.1
184	Iodofenfos	14.21	377 / 362	379 / 364		0.7	2.3
185	Dieldrin	14.24	245 / 173	263 / 193	279 / 243	3.3	10.9
186	Diclobutrazol	14.28	270 / 159	272 / 161		0.4	1.2
187	Genite	14.30	141 / 77	302 / 141		0.3	1.0
188	Disulfoton sulfon	14.30	213 / 125	213 / 153		0.3	1.0
189	Flamprop-methyl	14.34	230 / 170	335 / 105		0.3	1.1
190	Ditalimfos	14.38	271 / 243	299 / 243		1.0	3.4
191	Flusilazol	14.41	220 / 139	233 / 165	315 / 233	0.2	0.8

192	Chlorfenson	14.41	111 / 75	175 / 75	175 / 111	0.1	0.4
193	Chlorpropylat	14.42	251 / 139	253 / 141		0.1	0.3
194	Mephosfolan	14.50	168 / 140	196 / 140		0.8	2.6
195	DDD o,p	14.42	235 / 165	237 / 165		0.2	0.7
196	Vamidothion	14.52	145 / 87	169 / 125		0.9	2.9
197	Perthane	14.55	223 / 167	223 / 179		0.3	1.0
198	Phosfolan	14.60	168 / 60	168 / 140	227 / 140	0.4	1.3
199	Flamprop-isopropyl	14.62	276 / 77	363 / 105		0.3	0.9
200	Kresoxim-methyl	14.62	206 / 89	206 / 116	206 / 131	1.2	3.9
201	Chlorobenzilate	14.63	251 / 111	251 / 139		0.1	0.5
202	Myclobutanil	14.80	179 / 125	179 / 152	288 / 179	0.1	0.4
203	Cyproconazol	14.86	222 / 125	224 / 127		0.4	1.4
204	Diniconazol	14.91	268 / 232	270 / 234		0.2	0.5
205	Nitrofen	14.99	283 / 162	283 / 202		0.4	1.4
206	DDT o,p	14.97	235 / 165	237 / 165		0.4	1.3
207	Ethion	15.00	231 / 129	384 / 231		0.7	2.4
208	Chlorthiophos (2 Peaks)	15.06	325 / 269	325 / 297		0.2	0.6
209	Azaconazol	15.06	217 / 173	219 / 175		0.1	0.4
210	Etaconazol (Doppelpeak)	15.14	245 / 173	245 / 191		1.6	5.3
211	DDD p,p (TDE)	15.16	235 / 165	237 / 165		0.2	0.6
212	Carbophenthion-methyl	15.20	157 / 121	314 / 157		4.8	16.1
213	Tetrasul	15.22	252 / 217	254 / 219		0.5	1.5
214	Carfentrazon-ethyl	15.24	340 / 312	411 / 340		0.1	0.4
215	Endosulfan-beta	15.39	241 / 206	272 / 237	274 / 239	1.8	6.1
216	Sulprofos	15.42	322 / 139	322 / 156		0.5	1.8
217	Haloxyfop-2-ethoxyethyl	15.55	302 / 274	316 / 272		0.9	3.1
218	Trifloxystrobin	15.50	222 / 130	222 / 162		0.8	2.8
219	Fensulfothion	15.49	293 / 97	293 / 125		0.5	1.8
220	Carbophenothion	15.62	342 / 157	342 / 296		0.4	1.2
221	Pyraflufen-ethyl	15.66	339 / 289	349 / 307	412 / 349	0.4	1.3
222	Aclonifen	15.65	212 / 182	264 / 194		1.9	6.5
223	Piperonyl-butoxid	15.68	176 / 103	176 / 131		1.1	3.6
224	DDT p,p	15.69	235 / 165	237 / 165		0.4	1.3
225	Diflufenican	15.70	266 / 246	394 / 266		0.1	0.3
226	Resmethrin (2Peaks)	15.75	171 / 128	171 / 143	128 / 102	3.8	12.8
227	Quinoxyfen	15.79	307 / 237	307 / 272	309 / 237	0.5	1.5
228	Isoxadifen-ethyl	15.75	204 / 176	294 / 204		1.6	5.5
229	Propiconazol (2Peaks)	15.83	259 / 173	261 / 175		1.8	6.0
230	Clodinafop-propargyl	15.80	349 / 238	349 / 266		0.2	0.7
231	Fluopicolid	15.90	209 / 182	347 / 172		0.2	0.8
232	Fenhexamid	16.00	177 / 113	301 / 97		0.8	2.6
233	Bifenthrin	15.92	181 / 141	181 / 165		3.5	11.6
234	Fluotrimazol	15.94	311 / 165	311 / 233		1.3	4.3
235	Spiromesifen	15.98	272 / 209	272 / 254		0.9	2.9
236	Cyanofenphos	15.99	169 / 141	185 / 157		1.4	4.6
237	Diclofop methyl	16.03	253 / 162	340 / 253		0.2	0.8
238	Famophos = Famphur	16.09	218 / 79	218 / 109		2.1	6.9
239	Norflurazon	16.19	303 / 145	305 / 145		0.1	0.4
240	Endosulfan-sulfate	16.24	270 / 235	274 / 239		0.3	1.1

241	Cyenopyrafen	16.24	294 / 156	294 / 184	309 / 156	0.3	1.1
242	Edifenphos	16.23	173 / 109	310 / 173		0.1	0.2
243	Nuarimol	16.31	235 / 139	314 / 139		0.4	1.4
244	Benzoylprop-ethyl	16.39	172 / 145	292 / 105		0.7	2.5
245	Bromopropylat	16.47	185 / 157	341 / 185		1.7	5.8
246	Picolinafen	16.52	238 / 145	376 / 238	376 / 239	0.6	2.0
247	Fenpropathrin	16.56	265 / 89	265 / 210		0.7	2.2
248	Epoxiconazol	16.63	192 / 111	192 / 138		1.0	3.3
249	Cloquintocet-mexyl	16.73	192 / 162	194 / 164		1.0	3.4
250	Tetramethrin (2Peaks)	16.77	164 / 107	164 / 135		8.3	27.8
251	Piperophos	16.81	140 / 98	320 / 122		1.6	5.3
252	Cyhalothrin-lambda&gamma	17.00	208 / 181	181 / 152		1.4	4.7
253	Phenkapton	16.94	341 / 125	378 / 153		1.1	3.6
254	EPN	17.02	157 / 110	169 / 77		0.5	1.6
255	Methoxychlor	17.05	227 / 141	227 / 169	238 / 195	0.9	3.0
256	Pyridaphenthion	17.05	340 / 199	340 / 203		0.4	1.3
257	Chloridazon	17.25	221 / 77	221 / 220		0.8	2.7
258	Furametpyr	17.32	157 / 76	291 / 157		0.2	0.7
259	Bifenox	17.36	341 / 281	341 / 310		2.6	8.8
260	Lactofen	17.39	344 / 223	344 / 300		2.2	7.5
261	Endrin-keton	17.39	315 / 279	317 / 281		1.3	4.2
262	Flurtamone	17.81	199 / 157	333 / 120		0.7	2.2
263	Indanofan	17.46	139 / 75	139 / 111		1.1	3.6
264	Leptophos	17.56	375 / 360	377 / 362		1.3	4.5
265	Fenamidone	17.65	238 / 237	268 / 180		1.0	3.4
266	Mirex	17.59	270 / 235	272 / 237		0.5	1.6
267	Phosmet	17.59	160 / 77	160 / 133		0.4	1.3
268	Tetradifon	17.61	159 / 111	356 / 159	356 / 229	1.4	4.8
269	Phosalone	17.74	182 / 111	367 / 182		0.3	1.0
270	Fenpiclonil	17.90	236 / 201	238 / 201		0.1	0.5
271	Ioxinyl Octanoat	17.90	243 / 88	370 / 243		2.2	7.5
272	Pyrazophos	18.10	221 / 193	265 / 210		1.7	5.6
273	Fenarimol	18.31	139 / 111	251 / 139		0.3	1.1
274	Permethrin (2 Peaks)	18.35	163 / 127	165 / 127		0.6	1.9
275	Metrafenon	18.36	393 / 363	395 / 365		1.2	4.0
276	Bitertanol	18.45	170 / 115	170 / 141		0.9	3.1
277	Azinphos-Methyl	18.46	160 / 51	160 / 77	160 / 132	0.9	3.1
278	Pyridaben	18.77	147 / 132	309 / 147		1.6	5.5
279	Butafenacil	18.74	180 / 124	331 / 124	331 / 180	0.4	1.3
280	Azinphos-Ethyl	18.75	160 / 51	160 / 77	160 / 132	0.9	3.2
281	Cyfluthrin (4 Peaks)	18.90	163 / 127	165 / 127	226 / 199	0.8	2.6
282	Halfenprox	19.20	263 / 169	265 / 115	265 / 131	0.5	1.6
283	Coumaphos	19.26	226 / 163	362 / 226		0.5	1.7
284	Fluquinconazol	19.28	340 / 298	342 / 300		0.1	0.4
285	Cypermethrin (3 Peaks)	19.38	163 / 127	165 / 127		0.8	2.7
286	Flucythrinate (2Peaks)	19.55	157 / 107	199 / 107		0.2	0.8
287	Fenbuconazol	19.90	129 / 102	198 / 129		1.0	3.4
288	Tau-Fluvalinat (Doppelpeak)	20.10	250 / 55	250 / 200		1.0	3.4
289	Boscalid	20.40	342 / 140	344 / 142		0.1	0.2

290	Fenvalerate RR+SS	20.55	225 / 147	419 / 225		6.0	20.0
291	Fenvalerate RS+SR	20.35	225 / 147	419 / 225		6.0	20.0
292	Indoxacarb	21.00	203 / 134	264 / 176		0.9	3.1
293	Deltamethrin (2Peaks)	21.10	251 / 172	253 / 174		1.5	5.1
294	Difenoconazol	21.35	323 / 265	325 / 267		0.1	0.4
295	Dimethomorph	22.35	301 / 165	387 / 301		0.4	1.3
296	Famoxadon	22.62	330 / 224	330 / 237		1.7	5.6
297	Azoxystrobin	22.65	344 / 172	344 / 329	388 / 345	0.3	0.8
298	Cinidon-ethyl	23.09	330 / 210	330 / 302		2.5	8.2
299	Temephos	24.33	466 / 109	466 / 203		4.1	13.5

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