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Application Note 10469

Analysis of Multiresidue Pesticides in Cardamom by GC-MS/MS

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Keywords

Cardamom, pesticides, Fast GC-MS, timed-SRM

Introduction

Cardamom is a seed pod, known since centuries for its culinary and medicinal properties. The spice is native to evergreen rain forest of southern India and grown in only few tropical countries. Botanically, it belongs to the family of "*Zingiberaceae*" and consists of two genera; *Elettaria* and *Amomum*. Cardamom is used in many traditional medicines as antiseptic, local anesthetic, antioxidant in addition to health promoting and disease preventing roles. This delicate spice is commonly used as flavoring agent in foods, soups and refreshing drinks[1].

During cultivation, frequent applications of pesticides are required in order to manage pests in Cardamom. Consequently, the final product may contain pesticides in levels above the safe threshold limit and in some cases, as low as 5 µg/kg. The EU-MRL database lists about 455 pesticides for analysis in Cardamom[2].

Analysis of a multi-residue mixture of pesticides at these trace levels is extremely challenging due to the complex extracts resulting from sample preparation. The instrument method also involves a number of mass transitions making the method even more complex. In order to obtain maximum sensitivity within minimum possible run time the instrument should be capable of detecting a large number of compounds in a single chromatographic run while maintaining superior sensitivity.

Thermo Scientific™ TSQ™ 8000 Evo triple quadrupole GC-MS/MS system is an excellent tool in this regard. Enhanced velocity optics (EVO) driving EvoCell collision cell technology provides high SRM transition speeds, precision, and sensitivity for even the most complex methods involving several pesticides within a short run time. Other advantages include timed-SRM and AutoSRM for SRM optimization.A method was therefore developed for analysis of200 pesticides in Cardamom within only 11 min run time.

Sample Preparation

In brief,the QuEChERS sample preparation (Figure 1) was applied with the extraction of 2 g powdered sample of Cardamom using 10 mL acetonitrile (containing 1% acetic acid) in the presence of 3 g magnesium sulfate, 1.5 g sodium acetate and 10 g NaCl. The supernatant (1 mL) was collected after centrifugation, and dispersive cleanup was performed using 200 mg primary/secondary amine (PSA) and 10 mg graphitized carbon black (GCB). The extract was centrifuged at 10,000 rpm for 5 min and 2 µL of supernatant was injected via autosampler for analysis. For recovery and validation studies, 2 g of residue free Cardamom was fortified with appropriate quantities of the pesticide standard mixture and extracted as per above procedure.

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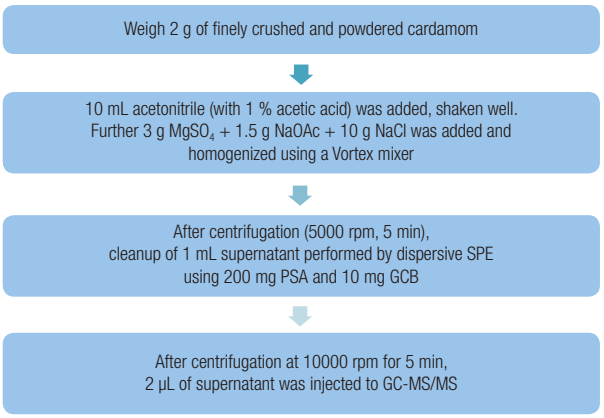

Figure 1. Sample preparation for extraction of pesticides from Cardamom.

Calibration

Stock standard solutions of each pesticide compound were prepared by weighing 10 ± 0.1 mg and dissolution in 10 mL acetonitrile. The solutions were stored in amber colored glass vials at -20°C. A total of ten intermediate mixtures (containing 15-20 compounds each) of 10 mg/L concentration were prepared by diluting adequate quantity of each compound in acetonitrile. A working standard solution (1 mg/L) was prepared by mixing adequate quantity of intermediate standard solution and dilution with acetonitrile and stored at -20°C. The calibration standards ranging from 1 µg/L to 250 µg/Lwere freshly prepared for measurement of the calibration curves. The calibration graphs for all the compounds were obtained by plotting the individual peak areas against the concentration of the corresponding calibration standards.

Instrument and Method Setup

The analytical method comprised of the sample handling using the Thermo Scientific Triplus™ RSH liquid auto sampler, Thermo Scientific TRACE™ 1300 Series gas chromatograph equipped with a spilt/splitlessinjector(SSL), and the Thermo Scientific TSQ™ 8000 Evo triple quadrupole GC-MS/MS system.

The Thermo Scientific TraceFinder™ software was used for method setup, data acquisition and data processing. For all pesticides, due to the complex spice matrix,three SRM transitions were chosen for the MRM acquisition method. The first transition was used for quantitationand the other two transitions for confirmation by checking the ion intensity ratio.

TRACE™ 1310 Gas Chromatograph Parameter

Carrier gas	Helium
Injector	SSL
Mode	Splitless
Inlet liner	single tapered liner with glass wool, 5 mm ID (p/n453A1925)
Splitless time	1 min, split flow: 30 mL/min
Oven program	65 °C, 1.5 min 30 °C/min to 320 °C 320 °C, 1 min
Column	TraceGOLD™ TG-5SilMS, 15m x 0.25mm x 0.25µm (p/n 26096-1300)
Column flow	1.2 mL/min, constant flo
Injection	2 µL by TriPlus RSH Autosampler, fast liquid band injection

TSQ 8000 MS/MS Parameter

Ion source temperature	280 °C
Interface temperature	310 °C
Acquisition mode	EI, 70 eV
MRM detection	timed SRM mode
MRM parameter	seeTable 1

The timed-SRM acquisition method used with the TSQ 8000 avoids laborious and time consuming process of segment creation and method maintenance.The scan times are automatically calculated based upon the specified cycle time so that uniform cycle times are obtained for each mass transition, thus reducing the extensive optimization process for scan times and data points across a peak. The dwell times for data acquisition are maximized independent on the number of compounds in the MRM method. The data processing and reporting was done using the TraceFinder™ software suite. All SRM transitions were directly imported from the TraceFinder™ compound database.

Results

The multi-residue pesticide analysis of Cardamom powder for routine target analytes detection and quantitationis described using QuEChERS and GC-MS/MS detection with the TSQ 8000 Evo GC-MS/MS system. All standards and samples were processed using the TraceFinder software with high speed and throughput. All compounds included into this method had acceptable calibration with correlation coefficients of > 0.99. The obtained recoveries were within 70-125% with < 20 % associated RSDs. Limit of quantification of 105 compounds was less than 1 µg/kg. For 35 compounds the limit of quantification was less than 2.5 µg/kg and 45 compounds limit of quantification was less than 5 µg/kg. Due to the high target compound selectivity of the TSQ 8000 Evo timed-MRM acquisition mode the automated TraceFinder peak integration works very reliable with high precision. No manual baseline rework or adjustments has been necessary. Selected examples are shown in Figure 2.

Sample Analysis

A total of200 pesticide compounds with three SRM transitions each (total 600 SRMs per run) were included into a routine screening method with only 11 min total run time. The method setup as described above was applied for analyzing samples bought from the local market.The results from analysis of market samples with found traces of Malathion and Chlorpyrifos ethyl are presented in Figure 3. All other tested pesticides of Table 2 were not detected.

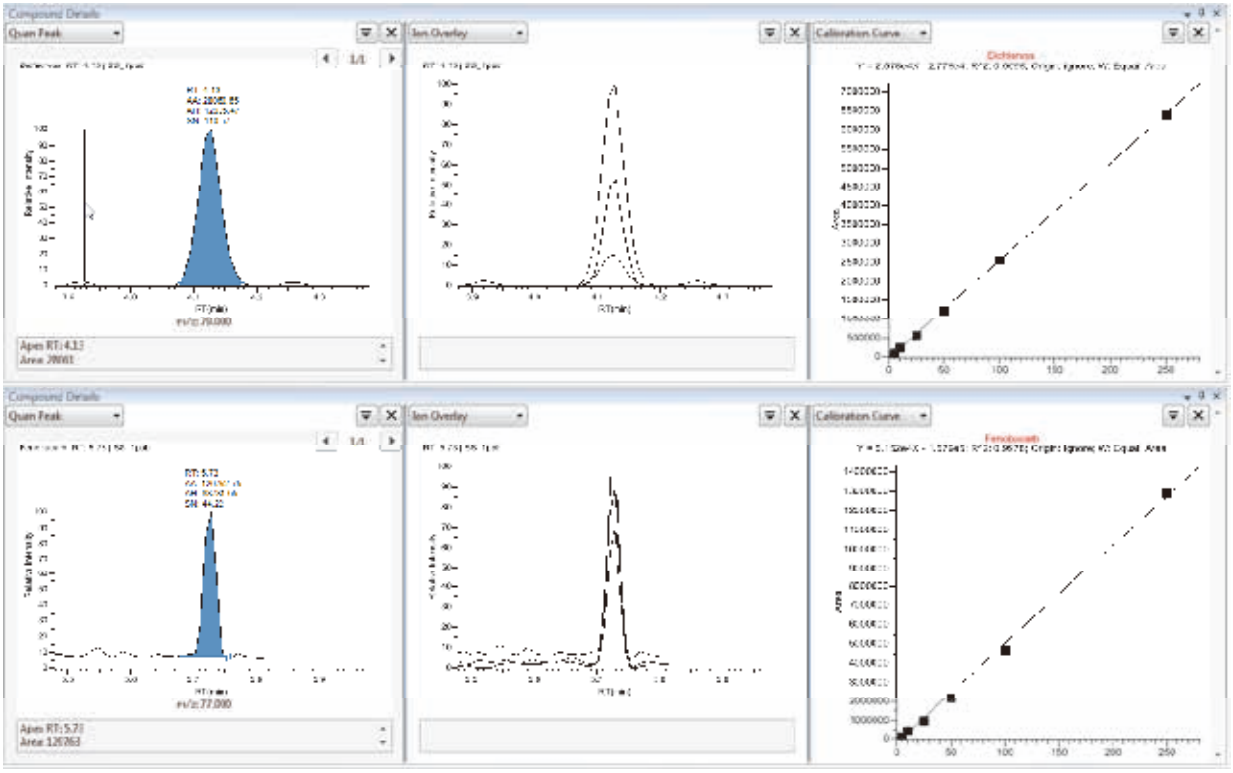

Figure 2.Selected pesticide chromatograms at 1µg/kg spike in Cardamom powder showing the reliable peak integration in matrix, the ion ratio check with overlaid ion profiles, and the resulting quantitative calibrations.

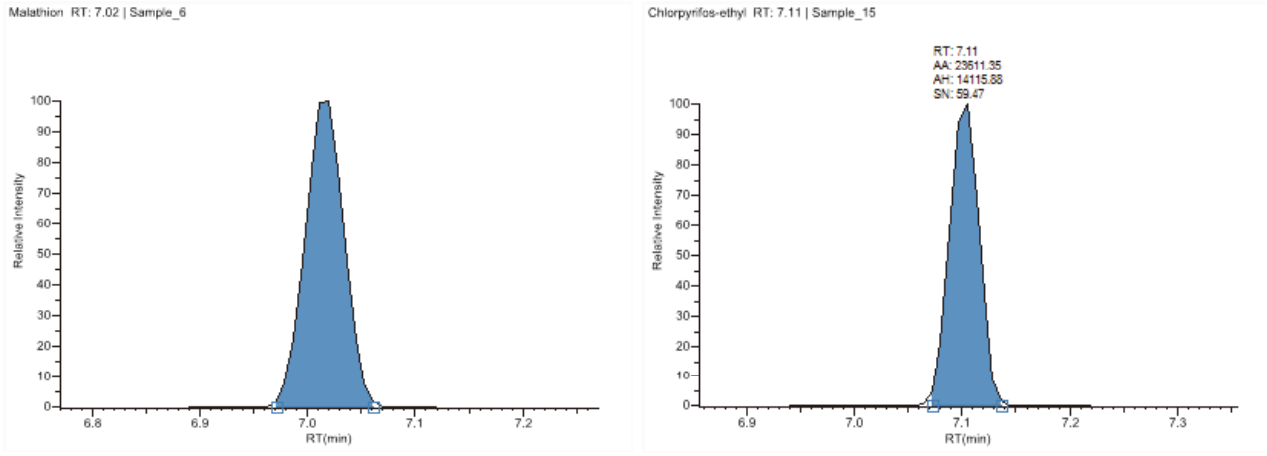

Figure 3. Traces of Malathion and Chlorpyrifos ethyl were detected at 5.93 and 2.95 µg/kg respectively in market samples.

Conclusion

A rapid and sensitive quantitative method for a large number of compounds is a major goal for analytical laboratories involved in pesticide analysis. Within 11 minutes cycle time200 pesticides were quantitatively determined using the described pesticides analysis method.

Triple quadrupole mass analyzer TSQ™ 8000 Evo GC-MS/MS system with TraceFinder™ was used for data processing to reduce the processing time thereby resulting in a high throughput method.

This method is recommended to be utilized for detection and confirmation of trace amounts of pesticides in complicated matrices such as cardamom and other spices. The method has potential to detect trace level compounds at concentration as low as 1-2 µg/kg compliant with international maximum pesticide residue regulations.

References

1. Cardamom nutrition facts, accessed May 2015,http://www.nutrition-and-you.com/cardamom.html

2. EU Pesticides database, accessed May 2015, http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=homepage&language=EN

Table 1.MRM transitions and optimized collision energy (CE) of target pesticides (as of TraceFinder pesticide compound data base)

	Compound Name	RT [min]	Quantitation *m/z*			CE[V]	Qualifier 1 *m/z*			CE[V]	Qualifier 2 *m/z*			CE[V]
1.	3, 5-Dichloroaniline	4.99	161.0	>	98.9	22	161.0	>	90.0	20	161.0	>	125.5	14
2.	3-Chloroaniline	3.50	127.0	>	65.0	22	127.0	>	91.9	12	127.0	>	100.0	10
3.	Acephate	4.97	136.0	>	42.1	8	95.5	>	65.4	8	136.0	>	94.0	12
4.	Acetochlor	6.75	146.0	>	131.1	12	131.8	>	117.0	14	146.0	>	117.7	8
5.	Acrinathrin	8.86	181.0	>	152.0	22	208.1	>	180.9	8	289.0	>	93.1	8
6.	Alachlor	6.82	188.1	>	160.1	8	160.1	>	131.7	10	188.1	>	130.0	32
7.	Aldrin	7.08	330.0	>	298.9	10	262.7	>	191.0	30	262.7	>	192.9	32
8.	Allethrin (Bioallethrin)	7.34	123.1	>	81.1	8	123.1	>	41.1	24	136.1	>	93.1	12
9.	Ametryne	6.90	227.1	>	58.1	12	227.1	>	170.0	10	227.1	>	212.1	8
10.	Amitraz	8.80	121.0	>	106.1	10	131.9	>	117.1	16	161.9	>	132.0	8
11.	Anilofos	8.64	225.9	>	157.0	14	183.7	>	157.0	8	225.9	>	184.0	6
12.	Atrazine	6.24	215.1	>	58.1	12	200.0	>	122.1	8	200.0	>	132.0	8
13.	Azinphos-ethyl	8.96	132.0	>	77.0	12	132.0	>	51.0	26	160.0	>	77.0	16
14.	Azinphos-methyl	8.76	160.0	>	77.0	16	132.0	>	77.0	12	160.0	>	50.9	34
15.	Azoxystrobin	10.04	344.1	>	329.0	14	344.1	>	156.0	34	344.1	>	171.9	36
16.	Benalaxyl	8.15	148.1	>	77.0	30	91.0	>	65.0	12	148.1	>	79.0	22
17.	Bendiocarb	5.98	166.1	>	151.1	10	126.0	>	51.9	16	151.0	>	43.0	20
18.	Benfluralin	5.97	292.0	>	264.0	8	292.0	>	159.7	20	292.0	>	206.1	10
19.	Benfuracarb	6.93	163.1	>	107.1	14	163.1	>	135.1	6	135.1	>	107.1	8
20.	Bentazon	7.17	198.0	>	118.8	12	118.8	>	63.7	20	118.8	>	91.8	12
21.	BHC, Alpha	6.11	218.8	>	183.0	8	182.8	>	146.7	12	218.8	>	146.6	20
22.	BHC, Beta	6.27	180.9	>	145.0	14	218.7	>	146.6	18	218.7	>	183.0	8
23.	BHC, delta	6.31	218.8	>	182.9	8	182.8	>	146.7	14	218.8	>	146.5	20
24.	BHC, gamma	6.35	180.9	>	145.0	14	180.9	>	109.0	26	218.7	>	183.0	8
25.	Bifenazate	8.52	258.0	>	196.1	12	198.9	>	184.1	12	258.0	>	199.1	12
26.	Bifenthrin	8.49	181.0	>	165.9	10	165.1	>	163.6	24	181.0	>	179.0	12
27.	Bitertanol	9.07	170.0	>	141.1	20	170.0	>	115.1	34	170.0	>	169.1	16
28.	Bromophos-ethyl	7.48	96.9	>	65.0	16	302.7	>	284.8	14	96.9	>	78.9	12
29.	Bromopropylate	8.51	184.9	>	156.9	12	184.9	>	75.5	30	340.8	>	185.0	14
30.	Buprofezin	7.76	105.1	>	77.0	18	105.1	>	50.9	32	175.0	>	132.1	12
31.	Butachlor	7.56	176.1	>	146.9	12	160.0	>	131.7	12	188.1	>	160.1	10
32.	Cadusafos	6.00	159.0	>	130.9	8	159.0	>	96.9	16	213.0	>	89.1	12
33.	Captafol	8.36	150.1	>	79.0	6	150.1	>	77.2	24	183.1	>	79.1	8
34.	Captan	7.39	149.0	>	105.0	6	149.0	>	70.0	20	149.0	>	78.8	14
35.	Carbaryl	6.81	144.0	>	115.1	22	144.0	>	116.1	10	115.0	>	89.0	16
36.	Carbofuran	6.23	164.0	>	149.1	8	149.1	>	77.0	24	149.1	>	121.1	8
37.	Carbofuran, 3-Hydroxy	6.77	180.1	>	137.0	10	137.0	>	81.0	14	137.0	>	109.0	8
38.	Carfentrazon-ethyl	8.13	340.1	>	312.1	10	290.0	>	99.9	36	311.9	>	150.7	18
39.	Chlordane alpha-cis	7.5.0	374.7	>	265.8	20	372.8	>	265.8	20	376.6	>	268.0	20
40.	Chlordane gamma-trans	7.59	271.7	>	236.8	12	372.7	>	263.7	20	374.7	>	265.9	22
41.	Chlorfenapyr	7.86	136.9	>	102.0	12	248.9	>	112.0	24	248.9	>	137.1	18
42.	Chlorfenvinphos-E-trans	7.28	266.9	>	159.0	14	268.8	>	161.0	12	322.9	>	267.0	12
43.	Chlorfenvinphos-Z-cis	7.36	294.9	>	267.0	8	266.9	>	159.0	14	323.0	>	267.0	12
44.	Chlorobenzylate	8.57	139.0	>	111.0	12	111.0	>	75.1	14	139.0	>	74.9	26
45.	Chlorothalonil	6.53	265.8	>	133.0	36	228.8	>	168.0	8	265.8	>	170.0	24
46.	Chlorpyrifos-ethyl	7.09	196.7	>	168.9	12	196.7	>	107.0	36	313.9	>	257.9	12

	Compound Name	RT [min]	Quantitation *m/z*			CE[V]	Qualifier 1 *m/z*			CE[V]	Qualifier 2 *m/z*			CE[V]
47.	Chlorpyrifos-methyl	6.77	125.0	>	79.0	6	125.0	>	47.0	12	285.9	>	93.0	20
48.	Chlorthiamid	6.71	204.9	>	170	10	170.0	>	135.1	12	170.0	>	143.0	10
49.	Clethodim	8.04	164.1	>	108.1	8	164.1	>	80.8	16	204.9	>	176.1	12
50.	Clomazone	6.28	125.0	>	89.0	16	138.0	>	74.9	24	138.0	>	111.0	12
51.	Cyazofamid	8.23	108.0	>	44.0	6	216.0	>	103.1	16	324.0	>	108.1	10
52.	Cyfluthrin peak 1	9.26	163.0	>	127.1	6	163.0	>	65.1	26	163.0	>	91.1	12
53.	Cyfluthrin peak 2	9.30	163.0	>	127.0	6	163.0	>	91.1	12	206.0	>	151.1	18
54.	Cyfluthrin peak 3	9.32	163.0	>	127.0	6	163.0	>	91.1	12	226.0	>	206.1	12
55.	Cyfluthrin peak 4	9.34	163.0	>	127.0	6	163.0	>	91.1	12	226.0	>	206.1	10
56.	Cyhalofop butyl	8.76	256.0	>	120.0	10	256.0	>	91.1	24	256.0	>	157.8	30
57.	Cyhalothrin-λ	8.77	180.9	>	151.9	22	197.0	>	141.1	10	208.1	>	180.9	8
58.	Cymoxanil	5.70	110.9	>	53.0	12	128.2	>	83.0	12	128.2	>	111.0	6
59.	Cypermethrin peak 1	9.38	163.0	>	127.1	6	163.0	>	91.1	12	180.9	>	152.1	20
60.	Cypermethrin peak 2	9.41	163.0	>	127.0	6	163.0	>	91.1	12	180.9	>	151.9	18
61.	Cypermethrin peak 3	9.46	163.0	>	127.0	6	180.9	>	152.2	20	163.0	>	91.0	12
62.	Cypermethrin peak 4	9.48	163.0	>	127.1	6	163.0	>	91.1	12	180.9	>	152.2	20
63.	Cyprazine	6.70	212.1	>	170.1	10	170.0	>	109.1	12	212.1	>	109.1	20
64.	Cyproconazole	7.86	222.0	>	125.0	20	222.0	>	82.1	10	222.0	>	89.3	38
65.	DDD p,p	7.98	235.0	>	165.1	20	235.0	>	199.0	14	236.8	>	165.0	20
66.	DDD, o, p	7.98	235.0	>	165.1	20	235.0	>	199.0	14	236.8	>	165.0	20
67.	DDE o,p	7.71	246.0	>	176.1	28	317.8	>	246.0	20	317.8	>	248.0	18
68.	DDE p, p	7.52	246.0	>	176.1	28	317.8	>	246.0	20	317.8	>	248.0	18
69.	DDT o,p	8.01	235.0	>	165.1	22	235.0	>	199.5	10	236.8	>	165.0	22
70.	DDT p,p	8.21	235.0	>	165.1	22	235.0	>	199.5	10	236.8	>	165.0	22
71.	Deltamethrin	9.94	181.0	>	152.1	22	252.8	>	92.9	16	252.8	>	172.0	8
72.	Dialifos	8.99	208.0	>	180.9	10	209.7	>	182.9	10	208.0	>	89.1	26
73.	Diazinon	6.43	137.1	>	84.1	12	137.1	>	54.1	20	179.1	>	121.5	26
74.	Diazinonoxon	6.31	273.1	>	137.1	12	137.0	>	54.1	20	137.0	>	84.1	12
75.	Dichlobenil	4.60	170.9	>	99.9	24	170.9	>	136.0	14	172.8	>	99.8	24
76.	Dichlofluanid	7.02	123.0	>	77.0	18	123.0	>	51.0	32	223.9	>	123.0	10
77.	Dichlorobenzophenone, 4, 4	7.12	139.0	>	111.0	12	111.0	>	74.9	12	139.0	>	74.9	26
78.	Dichlorvos	4.12	109.0	>	79.0	6	185.0	>	93.0	12	186.9	>	93.0	12
79.	Diclofop methyl	8.30	252.9	>	161.9	16	252.9	>	126.9	36	340.0	>	253.0	10
80.	Dicofol	8.58	139.0	>	111.0	12	111.0	>	74.9	12	250.9	>	139.0	12
81.	Dieldrin	7.75	262.8	>	192.9	30	262.8	>	190.9	30	262.8	>	227.8	16
82.	Difenoconazole peak 1	9.84	323.0	>	265.0	14	265.0	>	139.0	36	265.0	>	202.1	16
83.	Difenoconazole peak 2	9.85	323.0	>	265.0	16	265.0	>	138.9	36	265.0	>	202.0	18
84.	Diflubenzuron	4.30	141.0	>	113.0	12	113.0	>	63.0	12	141.0	>	63.0	26
85.	Diflufenican	8.29	266.0	>	246.1	10	394.0	>	266.1	12	266.0	>	238.1	12
86.	Dimethoate	6.19	87.0	>	42.1	10	93.0	>	63.0	8	125.0	>	79.0	8
87.	Dimethomorph peak 1	10.04	301.0	>	165.1	12	165.0	>	77.0	18	165.0	>	137.0	10
88.	Dimethomorph peak 2	10.14	301.0	>	165.1	10	301.0	>	139.0	14	387.1	>	301.1	10
89.	Diniconazole	7.95	268.0	>	232.0	10	232.0	>	149.0	14	268.0	>	136.0	34
90.	Edifenphos	8.17	172.9	>	109.0	8	172.9	>	65.1	30	310.0	>	109.0	26
91.	Endosulfan peak 1	7.59	240.6	>	205.9	14	194.7	>	125.0	22	194.7	>	159.4	8
92.	Endosulfan peak 2	7.95	158.9	>	123.0	12	194.7	>	159.0	8	240.6	>	205.8	12
93.	Endosulfan sulfate	8.21	271.7	>	236.8	12	238.7	>	203.9	12	271.7	>	234.9	12

	Compound Name	RT [min]	Quantitation *m/z*			CE[V]	Qualifier 1 *m/z*			CE[V]	Qualifier 2 *m/z*			CE[V]
94.	Endrin	7.89	262.8	>	192.9	30	280.8	>	245.3	8	245.0	>	173.0	22
95.	Epoxiconazole	8.40	192.0	>	138.0	12	165.0	>	138.0	8	192.0	>	111.0	22
96.	Esfenvalerate	9.78	167.0	>	125.0	10	125.0	>	89.3	20	225.1	>	119.1	18
97.	Ethiofencarb	6.59	107.0	>	77.0	16	168.0	>	77.0	30	168.0	>	107.0	8
98.	Ethion	7.99	230.9	>	128.9	22	153.0	>	97.0	10	230.9	>	174.9	12
99.	Ethoprophos	5.81	157.9	>	96.9	16	157.9	>	113.9	6	200.0	>	158.0	6
100.	Ethoxyquin	6.19	202.1	>	174.1	14	174.1	>	131.2	18	174.1	>	146.1	12
101.	Etofenprox	9.48	163.1	>	135.1	10	163.1	>	77.1	32	163.1	>	107.1	16
102.	Etrimfos	6.54	153.1	>	56.0	16	153.1	>	98.0	10	167.9	>	153.1	6
103.	Famoxadone	10.05	224.1	>	196.1	8	224.1	>	167.2	18	329.8	>	224.1	8
104.	Fenamidone	8.59	268.0	>	180.1	18	238.1	>	103.1	22	268.0	>	77.1	34
105.	Fenamiphos	7.60	154.0	>	139.0	10	216.9	>	202.0	12	303.1	>	195.2	8
106.	Fenarimol	8.92	139.0	>	111.0	14	139.0	>	74.9	26	219.0	>	107.0	10
107.	Fenazaquin	8.61	145.1	>	117.1	12	145.1	>	91.0	24	160.1	>	145.1	8
108.	Fenbuconazol	9.30	129.0	>	77.8	18	198.1	>	129.1	8	129.0	>	102.0	14
109.	Fenchlorfos	6.87	124.9	>	79.0	6	124.9	>	47.0	12	169.0	>	110.4	6
110.	Fenitrothion	6.96	277.0	>	260.0	6	125.0	>	79.0	8	277.0	>	109.0	16
111.	Fenobucarb	5.71	121.1	>	77.0	20	121.1	>	103.1	12	150.1	>	121.1	8
112.	Fenoxycarb	8.49	116.0	>	88.0	8	116.0	>	44.1	16	255.1	>	186.1	10
113.	Fenpropathrin	8.55	97.1	>	55.1	6	181.0	>	126.8	28	181.0	>	151.9	22
114.	Fenthion	7.09	278.0	>	109.0	18	245.3	>	125.0	12	278.0	>	169.0	14
115.	Fenvalerate	9.70	167.0	>	125.0	10	125.0	>	89.0	18	167.0	>	89.0	32
116.	Flonicamid	5.70	174.0	>	146.0	10	146.0	>	126.0	8	174.0	>	69.0	36
117.	Fluchloralin	6.45	306.0	>	264.0	8	264.0	>	159.5	14	264.0	>	206.1	8
118.	Flucythrinate peak 1	9.45	199.1	>	157.1	8	157.0	>	107.1	12	199.1	>	107.1	22
119.	Flucythrinate peak 2	9.51	157.0	>	107.0	12	199.0	>	157.1	8	199.0	>	107.0	22
120.	Flufenacet	7.10	151.1	>	136.1	10	122.7	>	122.0	8	151.1	>	95.0	24
121.	Flufenoxuron	6.53	267.9	>	241.0	12	267.9	>	135.0	34	267.9	>	169.9	24
122.	Flusilazole	7.77	233.0	>	164.9	16	206.0	>	151.3	14	233.0	>	151.9	14
123.	Fluvalinate peak 1	9.74	250.0	>	55.1	16	180.8	>	152.1	22	250.0	>	199.9	18
124.	Fluvalinate peak 2	9.76	180.8	>	152.1	20	250.0	>	55.1	16	250.0	>	200.0	16
125.	Folpet	7.43	104.0	>	76.0	10	130.0	>	102.0	12	259.9	>	130.1	14
126.	Heptachlor	6.85	271.8	>	236.9	12	99.8	>	39.0	26	99.8	>	65.0	12
127.	Heptachlor epoxide	7.35	352.8	>	262.9	16	262.9	>	192.9	30	354.7	>	264.9	12
128.	Hexaconazole	7.64	231.0	>	175.0	10	213.9	>	123.5	28	213.9	>	159.0	18
129.	Hexazinone	8.27	171.1	>	71.1	14	127.7	>	83.0	10	171.1	>	85.1	12
130.	Imazalil	7.65	215.0	>	173.0	8	172.8	>	109.0	26	174.7	>	147.0	16
131.	Imiprothrin	8.03	123.0	>	81.0	8	123.0	>	41.1	22	123.0	>	55.9	12
132.	Iprobenfos	6.58	203.9	>	91.9	8	203.9	>	121.0	28	91.1	>	65.0	16
133.	Iprodione	8.44	314.0	>	245.0	10	315.7	>	247.0	10	315.7	>	273.0	8
134.	Iprovalicarb peak 1	7.76	134.1	>	42.0	20	118.9	>	91.0	12	118.9	>	117.1	8
135.	Iprovalicarb peak 2	7.79	118.9	>	91.1	12	118.9	>	117.1	8	134.1	>	42.0	20
136.	Isazophos	6.55	161.0	>	119.0	8	118.9	>	76.0	18	161.0	>	146.0	6
137.	Isodrin	7.29	192.9	>	123.0	28	146.8	>	111.1	10	192.9	>	157.2	20
138.	Isoprothiolane	7.66	204.0	>	118.0	8	204.0	>	85.0	28	290.0	>	118.0	12
139.	Isoproturon	6.90	146.1	>	128.0	10	191.1	>	146.1	8	206.1	>	72.1	18
140.	Kresoxim-methyl	7.77	116.0	>	89.0	14	116.0	>	62.9	24	130.9	>	130.1	10

	Compound Name	RT [min]	Quantitation *m/z*			CE[V]	Qualifier 1 *m/z*			CE[V]	Qualifier 2 *m/z*			CE[V]
141.	Malathion	7.02	173.1	>	99.0	12	92.8	>	63.0	8	125.0	>	79.0	8
142.	Metalaxyl	6.84	131.9	>	117.0	12	160.1	>	130.0	18	160.1	>	144.8	10
143.	Methidathion	7.49	145.0	>	85.0	6	145.0	>	58.0	14	302.6	>	284.9	14
144.	Methiocarb	6.95	168.1	>	153.0	10	153.0	>	45.0	12	153.0	>	109.1	6
145.	Methomyl	5.60	104.7	>	88.0	6	87.8	>	44.0	10	104.7	>	58.0	10
146.	Methoxychlor	8.55	227.1	>	169.1	22	227.1	>	141.1	32	227.1	>	212.1	12
147.	Metolachlor	7.07	162.1	>	132.9	14	238.1	>	132.8	26	238.1	>	162.2	10
148.	Metoxuron	7.49	183.0	>	167.9	10	167.9	>	140.0	8	228.2	>	183.0	6
149.	Metribuzin	6.70	198.0	>	82.1	16	198.0	>	55.0	26	198.0	>	110.0	10
150.	Mevinphos	4.96	127.0	>	109.0	10	127.0	>	95.0	14	192.0	>	127.0	10
151.	Myclobutanil	7.75	179.0	>	125.0	14	179.0	>	90.0	28	179.0	>	151.7	8
152.	Ortho-phenylphenol	5.35	141.1	>	115.1	14	170.1	>	141.1	22	170.1	>	115.0	34
153.	Oxadiazon	7.71	174.9	>	112.0	12	174.9	>	76.0	28	174.9	>	147.2	6
154.	Oxamyl	5.40	162.0	>	115.0	10	145.1	>	61.0	8	145.1	>	72.0	16
155.	Oxyfluorfen	7.74	252.0	>	146.0	30	252.0	>	169.8	28	252.0	>	224.0	10
156.	Paraoxon-ethyl	6.89	109.0	>	81.0	10	149.0	>	91.1	10	149.0	>	102.0	16
157.	Paraoxon-methyl	6.47	109.0	>	79.0	6	95.9	>	65.0	12	230.0	>	105.9	16
158.	Parathion (ethyl)	7.09	109.0	>	81.0	10	124.9	>	97.0	6	291.0	>	109.0	12
159.	Parathion-methyl	6.77	124.9	>	79.0	6	124.9	>	47.0	12	263.0	>	109.0	12
160.	Penconazole	7.32	248.0	>	157.0	22	158.9	>	89.0	28	248.0	>	192.0	12
161.	Pendimethalin	7.31	252.1	>	162.0	8	252.1	>	161.0	14	252.1	>	191.3	8
162.	Pentachlorophenol	6.32	263.9	>	164.9	26	267.8	>	166.9	26	267.8	>	168.9	28
163.	Permethrin peak 1	9.08	183.1	>	168.0	12	183.1	>	153.0	12	163.0	>	91.1	12
164.	Permethrin peak 2	9.13	183.0	>	168.1	10	183.0	>	153.0	14	183.0	>	165.1	10
165.	Phenothrin	8.66	123.1	>	81.1	8	123.1	>	41.1	24	123.1	>	79.1	14
166.	Phenthoate	7.38	274.0	>	121.0	10	121.0	>	77.0	22	246.0	>	121.0	8
167.	Phorate	6.05	75.0	>	47.0	8	121.0	>	65.0	8	260.0	>	75.0	8
168.	Phosalone	8.74	182.0	>	111.0	14	121.1	>	65.0	10	182.0	>	74.8	30
169.	Phosmet	8.51	160.0	>	76.9	22	160.0	>	50.9	38	160.0	>	133.0	10
170.	Phosphamidon	6.70	127.0	>	109.0	12	127.0	>	94.9	16	264.1	>	127.0	12
171.	Pirimicarb	6.62	238.1	>	166.1	10	166.1	>	55.0	18	166.1	>	96.0	12
172.	Pirimiphos-ethyl	7.18	304.0	>	168.1	12	318.1	>	166.1	12	318.1	>	182.1	10
173.	Pirimiphos-methyl	6.95	290.1	>	125.0	20	290.1	>	233.0	8	305.1	>	180.1	8
174.	Pretilachlor	7.69	202.1	>	174.2	8	202.1	>	145.5	14	238.1	>	146.1	10
175.	Prochloraz	9.20	180.1	>	138.1	12	69.9	>	42.0	8	308.0	>	147.1	12
176.	Procymidone	7.44	95.9	>	67.1	8	95.9	>	53.0	16	283.0	>	96.1	8
177.	Profenofos	7.67	336.9	>	266.9	12	296.7	>	268.9	10	336.9	>	308.9	8
178.	Propanil	6.70	217.0	>	161.0	8	160.9	>	99.0	24	160.9	>	125.7	16
179.	Propargite	8.29	135.1	>	107.1	12	135.1	>	77.1	26	150.1	>	135.1	8
180.	Propetamphos	6.34	138.0	>	110.0	10	138.0	>	64.0	15	193.9	>	165.9	10
181.	Propiconazole peak 1	8.18	172.9	>	145.0	16	172.9	>	74.0	38	172.9	>	109.0	26
182.	Propiconazole peak 2	8.23	172.9	>	145.0	14	172.9	>	74.0	38	172.9	>	109.0	24
183.	Propoxur	5.72	110.0	>	62.9	24	110.0	>	64.1	16	152.1	>	110.0	8
184.	Pyrimethanil	6.41	198.1	>	182.9	14	198.1	>	117.9	30	198.1	>	157.6	18
185.	Pyriproxyfen	8.74	136.1	>	78.0	20	136.1	>	96.0	10	226.1	>	186.1	12
186.	Quinalphos	7.39	146.0	>	118.1	10	157.1	>	102.0	22	157.1	>	129.0	14
187.	Quintozene	6.35	213.8	>	178.9	14	213.8	>	141.9	28	294.8	>	236.9	14

	Compound Name	RT [min]	Quantitation *m/z*			CE[V]	Qualifier 1 *m/z*			CE[V]	Qualifier 2 *m/z*			CE[V]
188.	Tebuconazole	8.29	250.0	>	125.0	20	125.0	>	89.0	16	125.0	>	99.0	16
189.	Tetraconazole	7.14	100.9	>	51.0	10	336.0	>	204.0	28	159.0	>	123.4	16
190.	Tetradifon	8.69	159.0	>	131.0	10	159.0	>	74.8	32	159.0	>	111.0	20
191.	Tralkoxydim	8.82	137.0	>	57.0	10	109.0	>	57.1	6	137.0	>	109.1	6
192.	Transfluthrin	6.77	163.0	>	143.0	14	127.0	>	91.1	8	163.0	>	91.1	12
193.	Triadimefon	7.11	208.0	>	180.8	8	208.0	>	111.0	20	208.0	>	126.7	12
194.	Triadimenol	7.43	168.2	>	70.0	10	112.0	>	57.6	8	128.0	>	65.0	18
195.	Triallate	6.54	86.1	>	43.3	6	268.0	>	183.9	18	268.0	>	226.0	12
196.	Triazophos	6.53	91.0	>	65.0	12	161.0	>	105.7	12	161.0	>	134.1	8
197.	Trichlorfon	7.11	109.0	>	81.0	6	92.9	>	65.0	6	109.0	>	63.0	10
198.	Trifloxystrobin	8.16	116.1	>	89.0	14	116.1	>	63.0	24	145.0	>	95.0	14
199.	Trifluralin	5.96	306.1	>	264.1	8	306.1	>	206.0	10	306.1	>	159.7	20
200.	Triticonazole	8.72	235.1	>	217.1	8	217.0	>	167.0	18	235.1	>	181.9	12

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