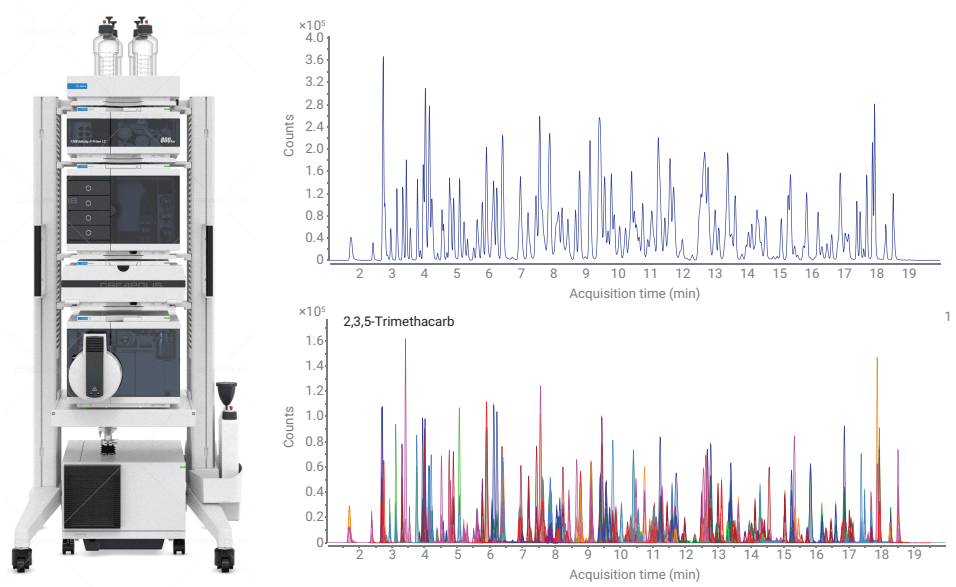
Application Note

Food & Agriculture

Multimethod Pesticide Analysis with the Agilent 1260 Infinity II Prime LC System and Agilent Ultivo Triple Quadrupole LC/MS



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Abstract

This application note demonstrates the advantages of the Agilent 1260 Infinity II Prime LC system to act as a front end for MS instruments. The 1260 Infinity II Prime LC system has a pressure range up to 800 bar, which enables the use of modern 2.1 mm id columns packed with 1.9 µm solid phase material. These columns are typically used for high-end LC/MS analysis. An example of a multiresidue pesticide analysis in a complex matrix is shown. Some critical pesticide analyses, such as the separation of isomers or very polar samples, are discussed in more detail.

Introduction

Many different pesticides are used for plants grown for food, drinks, and spices. Pesticides protect plants from insects, fungi, and weeds. The use of all these pesticides is highly regulated to protect the environment and the consumer of these food products. Therefore, the food products must be controlled to meet legal requirements that there will be no banned pesticides present. The requirement that the permitted pesticides are kept below the allowed threshold must be observed or, in best case, no pesticide residues are present at all.[1]

For that purpose, modern multiresidue pesticide methods were established, which are capable to quantify hundreds of pesticides in one analysis. These techniques are typically based on HPLC triple quadrupole mass spectrometry. Modern HPLC instruments and sub-2 µm columns can separate these compounds to a degree, but modern MS instruments can measure even remaining coeluting compounds. Here, excellent chromatographic separation is not only necessary to separate the pesticide compounds, they must be separated from a complicated matrix originating from the plants. These matrix compounds are often present in a large excess and could lead to ionization suppression of pesticide compounds in small amounts. Matrix compounds can also adulterate the final quantitative result.

This application note describes the use of the 1260 Infinity II Prime LC system as an MS front end for a multiresidue pesticide analysis with a modern Agilent Poroshell sub-2 µm column. This is supported by the capability of the 1260 Infinity II Prime LC system to deliver a pressure range up to 800 bar. For the pesticide compounds, the limit of quantification (LOQ), linearity, and matrix recovery are shown.

Experimental

Instrument

- Agilent 1260 Infinity II Flexible Pump (G7104C)
- Agilent 1260 Infinity II Multisampler (G7167A)
- Agilent 1260 Infinity II Multicolumn Thermostat (G7116A)
- Agilent Ultivo LC/TQ (G6465B)

Software

- Agilent MassHunter workstation
  - LC/MS data acquisition for Ultivo LC/TQ, V1.1
  - Optimizer for LC/TQ, V1.1
  - Source Optimizer for LC/TQ, V1.1
- MassHunter qualitative software, V10.0
- MassHunter quantitative software, V10.0

Column

Agilent InfinityLab Poroshell 120 EC-C18, 2.1 × 100 mm, 1.9 µm (p/n 695675-902)

HPLC method

Parameter	Value
Flow rate	0.35 mL/min
Solvent A	Water + 2.5 mM ammonium formate + 0.05% formic acid
Solvent B	Methanol + 2.5 mM ammonium formate + 0.05% formic acid
Solvent C	Acetonitrile + 0.1% formic acid
Gradient 1	0 min – 5% B, 2 min – 45% B, 15 min – 80% B, 16 min – 95% B, stop time: 20 min, post time: 5 min.
Gradient 2	0 min – 5% B, 2 min – 45% B, 15 min – 80% B, 16 min – 95% B, 20 min – 95% B, 20.1 min – 0% B, 95% C. stop time: 25 min, post time: 5 min.
Column Temperature	30 °C
Injection Volume	1 µL
Needle Wash	3 second, methanol

MS method

Parameter	Value
Agilent Jet Stream Source	
Gas Temperature	120 °C
Gas Flow	12 L/min
Sheath Gas Temperature	325 °C
Sheath Gas Flow	12 L/min
Nebulizer Pressure	45 psi
Capillary Voltage, Positive	3,500 V, nozzle, positive: 300 V
Capillary Voltage, Negative	3,500 V, nozzle, negative: 0 V
Time Filter	0.02 min
MRM and dMRM Conditions	See appendix, Table A1

Sample preparation for green tea[2]

1. Weigh 1.00 ±0.01 g green tea sample into a 50 mL centrifuge tube.
2. Spike as required and add 10 mL water, cap, and shake for 1 minute.
3. Add 10 mL acetonitrile, cap, shake for 1 minute, and sonicate 15 minutes.
4. Add Bond Elute QuEChERS Original (10 g) extraction salt (p/n 5982-5550) and shake for 1 minute.
5. Centrifuge at 4000 rpm for 5 minutes.
6. Transfer 6 mL supernatant to a 15 mL Bond Elute QuEChERS Dispersive Universal SPE tube (p/n 5190-5088).
7. Vortex for 1 minute and centrifuge at 4000 rpm for 3 minutes.
8. Transfer 2 mL of supernatant to a clean test tube and dry under nitrogen.
9. Reconstitute with 0.7 mL water + 0.1% formic acid and add 0.3 mL acetonitrile.
10. Filter with a Captiva premium syringe filter into an autosampler vial.

Standards

Agilent LC/MS pesticides test mixture, comprising eight sub mixtures (p/n 5190-0551), 100 mg/L each compound in acetonitrile

Calibration

The LC/MS test mixtures were diluted to a stock solution of 1 mg/L (1 ppm) in methanol. The calibration curves were created for 100, 20, 10, 2, 1, 0.2, and 0.1 µg/L (ppb)

Solvent and Chemicals

- All solvents were purchased from Merck, Germany.
- Chemicals were purchased from Merck, Germany.
- Fresh ultrapure water was obtained from a Milli-Q integral system equipped with LC-Pak polisher and a 0.22 µm membrane pointofuse cartridge (Millipak).

Results and discussion

To separate more than 250 pesticide compounds in one run with as little coelution as possible, a modern sub-2 µm Poroshell column was used for high resolution. An organic gradient eluent methanol was used. Methanol has the advantage of less elution power than the typically applied acetonitrile and allows a broader elution pattern over the run time (Figure 1). To maximize the run time for separation, an initial steep increase of the organic content has been applied. The lower number of polar pesticides are sufficiently separated with excellent peak shape. This is followed by a longer, shallower increase for best separation of most of the pesticides between 2 and 15 minutes run time (see gradient in experimental). A final steep ramp up to 95% methanol elutes late nonpolar pesticides.

The drawback of using methanol is the higher backpressure occurring during the gradient from aqueous to organic phase. This drawback is intensified by the low

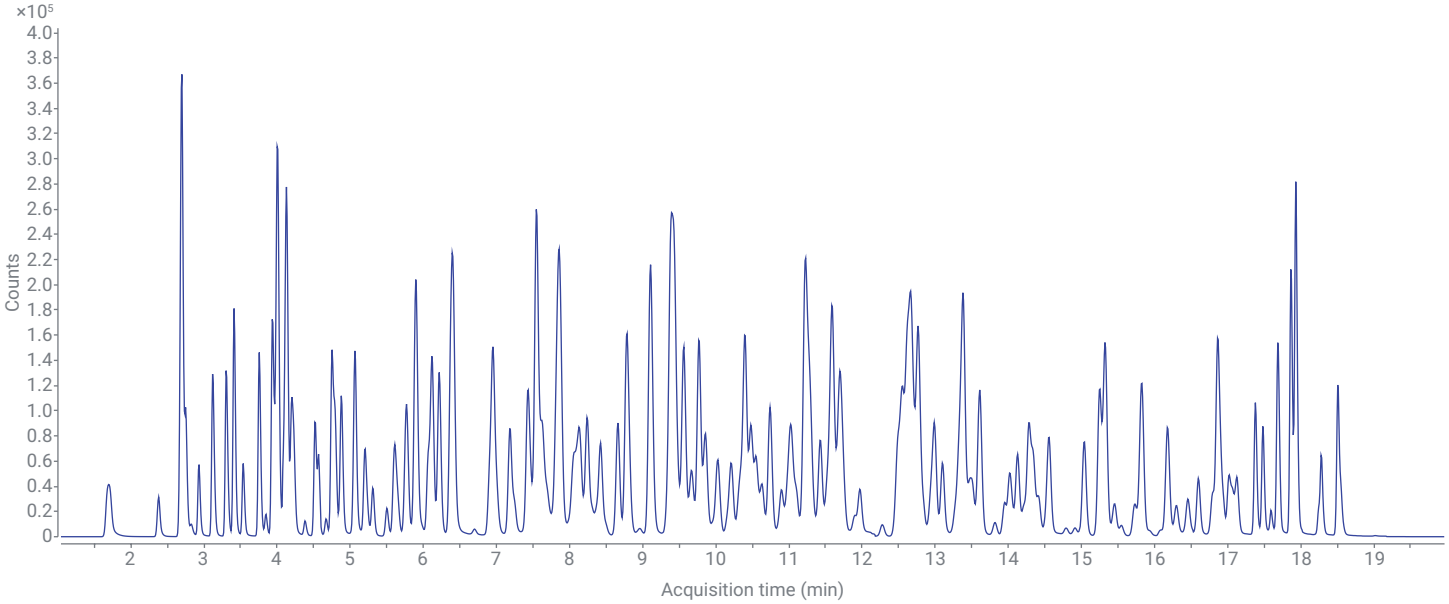

Figure 1. Separation of more than 250 pesticides in the described gradient at a concentration of 100 ppb each.

column temperature of 30 °C. To cope with these conditions, the 1260 Infinity II Flexible Pump can be applied and can provide up to 800 bar pressure.

The achieved resolution allows easy detection of all pesticides by dynamic MRM (dMRM) with the connected triple quadrupole, the Agilent Ultivo LC/TQ. The complete detection requires more than 500 transitions (quantifier and qualifier). In the time range with the highest number of coeluting pesticides (10 to 18 minutes) more than 50 transitions must be acquired with a minimum dwell time of approximately 5.6 ms per transition (Figure 2).

Since some pesticides occur as isomeric compounds, the chromatographic resolution is also a critical parameter to detect their presence. Sometimes, they elute close together as do phosphamidone I and II, which are *cis-trans* isomers (Figure 3). The developed chromatographic method allows their separation with a resolution of 0.66. Some other examples with larger differences in retention times can be found in Table A2.

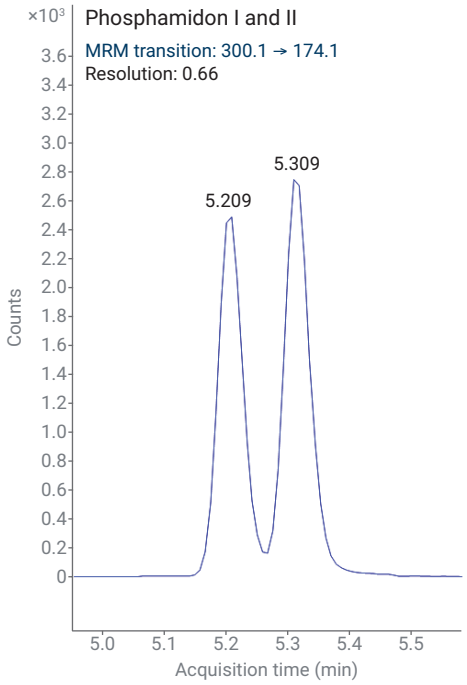

Figure 3. Chromatographic resolution of separated phosphamidone I and II isomers with a chromatographic resolution of 0.66.

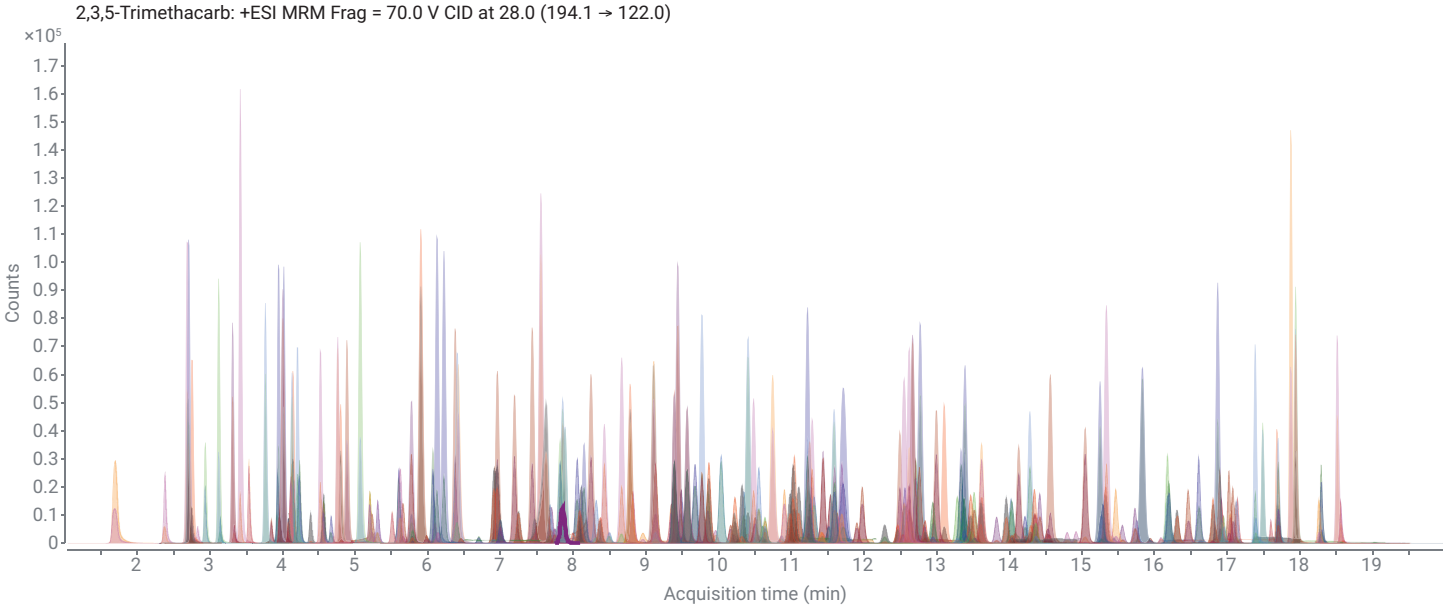

Figure 2. Detection of more than 250 pesticides by dMRM, more than 500 individual transitions.

For the determination the mass spectrometric detection performance, calibration curves between 100 ppb and 100 ppt were created for all compounds. All compounds showed excellent linearity in the chosen range with R^2 values greater than 0.9990 (Table A2). The lower limit of quantification (LLOQ) was calculated based on a signal-to-noise ratio of 10 for the quantifier transition by the lowest reasonable calibration point. Most compounds showed an LLOQ below 100 ppt and only 14 compounds showed an LLOQ above 200 ppt (Figure 4).

The superior resolution of the column enables the separation of the pesticide compounds from each other, and also the separation of matrix compounds and pesticides. This separation is crucial for the detection of pesticides in the mass spectrometer, because, typically the matrix compounds are present in large excess. The matrix compounds compete for ionization in the ion source of the mass spectrometer. Ultimately, the presence of matrix compounds could have a large influence on the recovery of the pesticide compounds due to ion suppression. To judge the ion suppression and the quality of sample preparation as well, the recovery of the pesticide compounds was measured for spikes of 10 and 100 ppb in a matrix of green tea (see Experimental, QuEChERS sample preparation for green tea). The distribution of recovery is shown in Figure 5 and outlined in detail in Table A2. In accordance to the SANTE guidelines, SANTE/12682/2019, an apparent recovery of 80 to 120% is acceptable.[3] For the 10 ppb and the 100 ppb spike, a recovery in the required range could be seen for 82.6 and 85.8% of the compounds, respectively.

To prevent carryover from matrix compounds from one run into the next, a column cleaning flush with a solvent of higher elution strength could be programmed into the gradient (see gradient 1 and gradient 2 in Experimental). Since the 1260 Infinity II Flexible Pump has quaternary solvent selection, it can be done easily in one gradient without solvent exchange or extra valve hardware.

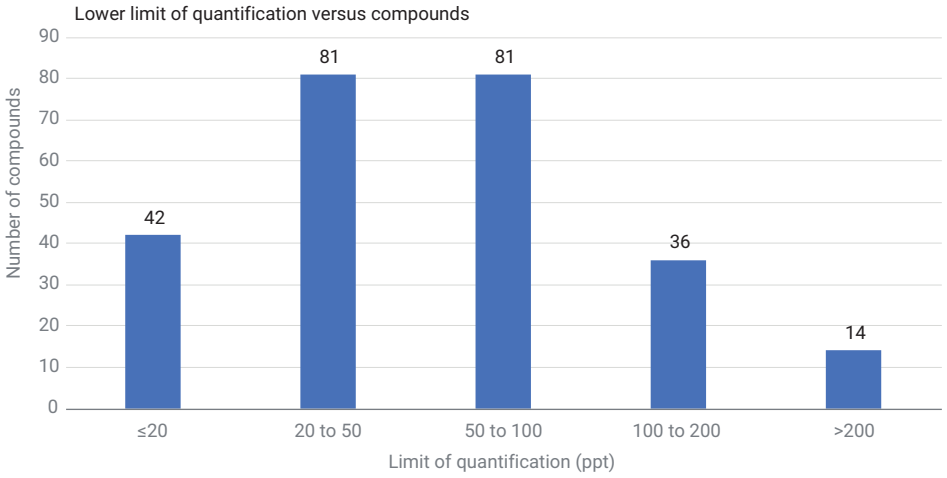

Figure 4. Distribution of the lower limit-of-quantitation at signal-to-noise of 10 in the range of the measured compounds.

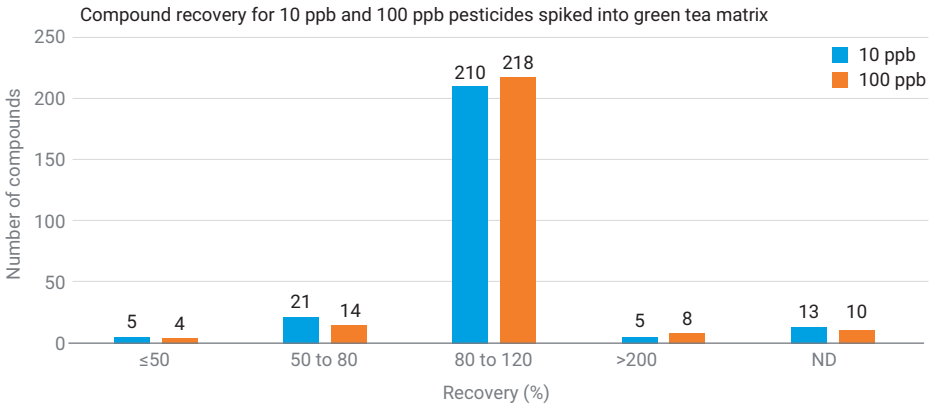

Figure 5. Distribution of recoveries for the 10 ppb and 100 pb spikes in green tea matrix.

Conclusion

This application note demonstrates the use of an Agilent 1260 Infinity II Prime LC for its use as an MS front end for multiresidue pesticide residue analysis. With the capability of 800 bar pressure, it is possible to use modern sub-2 µm columns. Methods using viscous solvents such as methanol with lower column temperatures can achieve excellent chromatographic resolution. The quantification of the pesticides with an Agilent Ultivo LC/TQ showed excellent linearities between 100 ppb and 100 ppt. The LLOQs were typically below 100 ppt, and recoveries met the requirements for pesticide residue analysis in more than 86% of samples.

References

1. Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin (including amendments as of 18 March 2008) and complying with regulation (EC) 1107, **2009**.
2. Optimizing Sample Preparation for LC/MS/MS of Pesticides Residues in Herbal Teas, *Agilent Technologies application note*, publication number 5991-3728EN.
3. European Commission: Health & Consumer Protection Directorate – Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, SANTE/12682/2019.

Appendix

Table A1. MRM conditions (fragmentor voltage and collison energy) for transition 1 and transition 2, retention time was used to create the dMRM method.

Compound Name	Retention Time (min)	Precursor Ion (*m/z*)	Fragmentor (V)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Polarity
Methamidophos	1.714	142.0	88	93.9	12	124.9	12	+
Acephate	2.394	184.0	60	143.0	4	49.1	20	+
Aminocarb	2.705	209.1	101	137.0	24	122.0	48	+
Omethoate	2.711	214.0	88	125.0	20	155.0	12	+
Propamocarb	2.726	189.2	106	102.0	16	74.0	28	+
Pymetrozine	2.771	218.1	106	78.0	48	105.1	24	+
Dinotefuran	2.943	203.1	78	129.1	8	157.0	4	+
Oxamyl	3.132	237.1	70	72.0	16	90.0	4	+
Nitenpyram	3.148	271.1	101	225.1	8	126.1	36	+
Methomyl	3.321	163.1	60	88.0	4	106.0	8	+
Flonicamid	3.340	230.1	144	203.1	16	174.1	16	+
Carbendazim	3.431	192.1	126	160.0	16	132.0	36	+
Monocrotophos	3.548	224.1	70	192.9	4	127.0	12	+
Thiabendazole	3.774	202.0	162	175.1	28	131.1	36	+
Imidacloprid	3.856	256.1	88	209.1	16	175.0	28	+
Ethidimuron	3.940	265.0	98	208.0	12	114.0	16	+
Fuberidazole	3.956	185.1	144	157.0	24	65.1	48	+
Flumetsulam	3.967	326.1	150	129.1	36	109.1	64	+
Fenuron	4.020	165.1	98	72.0	16	46.1	12	+
Mexacarbate	4.040	223.1	106	151.0	24	166.0	12	+
Mevinphos I	4.096	225.1	70	127.0	12	192.9	4	+
Metamitron	4.119	203.1	83	175.0	16	42.0	44	+
Dioxacarb	4.125	224.1	70	167.0	4	122.9	12	+
Cymiazole	4.134	219.1	159	77.0	60	144.0	36	+
Dimethoate	4.136	230.0	78	198.9	4	125.0	20	+
Acetamiprid	4.149	223.1	106	126.0	20	56.0	16	+
Quinmerac	4.211	222.0	83	204.0	12	141.0	40	+
Chloridazon	4.250	222.0	139	77.0	40	104.1	24	+
Cymoxanil	4.405	199.1	68	127.8	4	157.1	24	+
Thiacloprid	4.530	253.0	111	125.9	24	90.1	44	+
Mevinphos II	4.580	225.1	70	127.0	12	192.9	4	+
Cyazofamid	4.686	325.1	167	231.1	32	217.0	32	+
Tricyclazole	4.768	190.0	144	163.0	24	136.0	32	+
Butocarboxim	4.820	213.1	121	75.1	12	47.1	48	+
Ethirimol	4.820	210.2	139	140.1	24	98.0	28	+
Aldicarb	4.894	208.1	73	116.0	0	89.1	12	+
Pirimicarb	5.093	239.2	103	182.0	12	72.0	24	+
Phosphamidon I	5.216	300.1	116	174.1	12	127.0	20	+
Oxadixyl	5.248	279.1	78	219.1	8	132.0	32	+
Phosphamidon II	5.323	300.1	116	174.1	12	127.0	20	+

Compound Name	Retention Time (min)	Precursor Ion (*m/z*)	Fragmentor (V)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Polarity
Quinoclamine	5.511	208.0	121	105.1	28	77.1	40	+
Azamethiphos	5.614	325.0	103	76.0	60	112.0	40	+
Oxasulfuron	5.625	407.1	116	150.0	16	106.9	56	+
Dichlorvos	5.675	221.0	106	109.0	16	79.9	28	+
Propoxur	5.782	210.1	65	111.0	12	168.0	4	+
Metribuzin	5.784	215.1	121	187.0	16	84.0	20	+
Triasulfuron	5.801	402.1	111	166.9	30	141.1	30	+
Thifensulfuron-methyl	5.802	388.0	111	167.0	12	204.9	28	+
Carbofuran	5.908	222.1	98	165.0	8	123.0	24	+
Nicosulfuron	5.986	411.1	111	182.1	28	106.1	44	+
Malaoxon	6.077	315.1	88	99.0	24	126.9	8	+
Metsulfuron-methyl	6.109	382.1	111	167.1	12	77.1	60	+
Pyracarbolid	6.129	218.1	100	125.1	20	97.1	28	+
Thidiazuron	6.150	221.0	100	101.9	12	93.9	8	+
Tebuthiuron	6.228	229.1	106	172.1	16	116.0	28	+
Carboxin	6.382	236.1	98	143.0	12	43.0	44	+
Secbumeton	6.428	226.2	121	170.1	16	113.9	24	+
Prometon	6.441	226.2	134	142.0	24	184.1	16	+
Sulfentrazone	6.462	385.0	162	306.9	28	199.0	40	negativ
Carbaryl	6.481	202.1	65	145.1	8	127.0	32	+
Chlorsulfuron	6.703	358.0	131	141.1	20	167.0	16	+
Thiofanox	6.919	241.0	103	184.0	8	98.0	8	+
Amidosulfuron	6.931	370.0	103	261.1	12	218.1	24	+
Fosthiazate	6.943	284.1	88	104.0	24	227.9	8	+
Fluometuron	6.958	233.1	111	72.0	20	46.1	20	+
Imazalil	7.010	297.1	139	201.0	16	158.9	24	+
Vamidothion	7.010	299.0	139	41.1	36	161.1	24	+
Foramsulfuron	7.023	453.1	126	182.1	24	83.1	64	+
Chlorotoluron	7.192	213.1	101	72.0	24	46.1	16	+
Metobromuron	7.255	259.0	106	169.9	16	91.1	40	+
Methabenzthiazuron	7.438	222.1	88	165.0	16	149.9	36	+
Ethoxyquin	7.508	218.2	154	174.1	32	160.1	40	+
Deet	7.561	192.1	116	119.0	16	91.0	32	+
Metazachlor	7.631	278.1	83	134.0	20	210.0	4	+
Lenacil	7.677	235.1	93	153.0	12	136.0	36	+
Flutriafol	7.710	302.1	101	70.1	12	123.1	32	+
Tribenuron-methyl	7.752	396.1	106	155.1	28	181.1	28	+
Methoprotryne	7.839	272.2	139	198.1	24	240.1	20	+
2,3,5-Trimethacarb	7.861	194.1	70	137.1	8	122.1	28	+
Metalaxyl	7.863	280.2	103	220.0	12	192.1	16	+
Cycluron	7.891	199.2	116	89.0	12	72.0	28	+
Isoxaflutole	8.002	360.1	126	250.9	12	220.1	44	+
Diuron	8.059	233.0	98	72.0	24	46.1	16	+
Azaconazole	8.113	300.0	103	159.0	32	231.0	16	+

Compound Name	Retention Time (min)	Precursor Ion (*m/z*)	Fragmentor (V)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Polarity
Pyrimethanil	8.117	200.0	139	107.2	24	82.0	28	+
Isocarbofos	8.158	231.0	100	121.0	20	65.0	40	+
Dimethachlor	8.246	256.1	93	224.1	12	148.1	28	+
Forchlorfenuron	8.313	246.0	88	127.0	8	91.0	32	negativ
Methidathion	8.373	303.0	75	145.1	8	85.1	24	+
Fenpropidin	8.421	274.3	162	147.2	32	86.1	32	+
Methacrifos	8.501	241.0	73	124.9	20	208.9	4	+
Clomazone	8.669	240.1	106	125.0	20	89.0	60	+
Desmedipham	8.784	318.1	83	182.0	8	136.1	28	+
Guthion	8.814	318.0	65	132.0	12	77.0	40	+
Phosmet	8.996	318.0	106	159.9	16	133.0	40	+
Flumioxazin	9.000	355.1	100	299.1	32	107.1	36	+
Phenmedipham	9.103	318.1	83	167.9	8	136.0	24	+
Flazasulfuron	9.132	408.1	116	182.1	16	83.1	60	+
Fenobucarb	9.135	208.1	78	95.1	12	77.1	48	+
Linuron	9.345	249.0	101	160.1	16	182.9	12	+
Spiroxamine I	9.384	298.3	131	144.1	20	100.0	36	+
Diethofencarb	9.394	268.2	78	226.1	4	124.0	36	+
Furalaxyl	9.435	302.1	101	95.0	32	242.1	12	+
Ethofumesate	9.487	304.1	93	287.1	4	120.9	20	+
Spiroxamine II	9.563	298.3	131	144.1	20	100.0	36	+
Methiocarb	9.665	226.1	131	169.2	6	121.0	16	+
Thiodicarb	9.765	372.1	182	344.1	20	329.1	28	+
Azoxystrobin	9.771	404.1	111	372.1	12	344.1	24	+
Fenamidone	9.851	312.1	111	236.0	12	92.0	28	+
Halofenozide	9.862	331.1	83	275.1	0	104.9	16	+
Dimethomorph I	9.959	388.1	145	301.0	24	165.1	36	+
Promecarb	10.030	208.1	75	151.1	4	109.0	12	+
Fludioxonil	10.167	266.1	78	228.9	4	158.1	40	+
Boscalid	10.209	343.0	116	307.1	20	271.1	36	+
Molinate	10.218	188.1	98	126.1	12	55.2	28	+
Pronamide	10.226	256.0	93	190.0	16	173.0	28	+
Paclobutrazol	10.321	294.1	106	70.0	20	125.0	48	+
Fluopicolide	10.364	383.0	116	172.9	24	144.9	60	+
Bispyribac-sodium	10.390	431.1	121	275.1	12	413.1	16	+
Isoprothiolane	10.402	291.1	88	231.0	8	188.9	20	+
Isoxaben	10.481	333.2	111	164.9	16	106.9	60	+
Malathion	10.503	331.0	78	127.0	8	98.9	20	+
Diflubenzuron	10.549	328.1	187	124.9	32	89.0	60	+
Mandipropamid	10.556	412.1	131	328.1	12	124.9	48	+
Cyproconazole I	10.602	292.1	98	70.0	16	124.9	40	+
Triadimefon	10.631	294.1	106	69.0	20	196.9	12	+
Propham	10.634	197.1	167	69.1	8	41.1	24	+
Dimethomorph II	10.639	388.1	145	301.0	24	165.1	36	+

Compound Name	Retention Time (min)	Precursor Ion (*m/z*)	Fragmentor (V)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Polarity
Methoxyfenozide	10.737	369.2	83	149.1	12	313.1	0	+
Bromuconazole I	10.859	378.0	106	70.0	22	158.9	42	+
Propetamphos	10.904	282.1	106	138.1	20	156.1	8	+
Trietazine	10.985	230.1	144	99.0	24	132.0	20	+
Mepanipyrim	11.021	224.1	144	77.1	48	106.0	28	+
Bupirimate	11.105	317.2	154	166.1	24	210.1	24	+
Chloroxuron	11.211	291.1	131	72.1	24	46.1	20	+
Cyproconazole II	11.235	292.1	98	70.0	16	124.9	40	+
Iprovalicarb	11.249	321.2	98	119.0	24	91.0	60	+
Triazophos	11.261	314.1	111	162.0	16	119.0	40	+
Bifenazate	11.281	301.2	88	198.1	4	170.1	24	+
Cyprodinil	11.329	226.1	154	93.1	44	77.0	56	+
Triadimenol	11.404	296.1	88	70.2	8	99.1	12	+
Fluquinconazole	11.421	376.0	116	107.9	52	307.0	28	+
Ethoprop	11.433	243.1	98	96.9	36	131.0	20	+
Fenhexamid	11.512	302.1	126	97.1	28	55.1	48	+
Azinphos-ethyl	11.534	346.0	75	132.0	12	77.1	52	+
Fenarimol	11.583	331.0	134	80.9	32	139.1	36	+
Tolylfluanid	11.586	347.0	88	330.0	0	227.0	8	+
Mecarbam	11.588	330.1	70	227.0	4	96.9	48	+
Flufenacet	11.591	364.1	98	194.1	8	152.0	16	+
Spirotetramat	11.627	374.2	126	216.1	36	330.2	12	+
Fluoxastrobin	11.689	459.1	134	427.0	16	188.0	40	+
Triticonazole	11.693	318.1	136	70.0	16	125.0	40	+
Metolachlor	11.707	284.1	106	134.1	32	176.1	28	+
Procymidone	11.707	284.0	106	252.1	12	70.1	16	+
Tetraconazole	11.901	372.0	154	158.9	40	70.0	24	+
Epoxiconazole	11.973	330.1	126	121.0	24	101.0	60	+
Uniconazole	12.276	292.1 294.1	126	70.1	20	70.1	20	+
Fenbuconazole	12.451	337.1	134	69.9	32	125.0	40	+
Fenamiphos	12.489	304.0	131	216.9	24	201.9	40	+
Rotenone	12.522	395.1	154	213.0	24	192.1	24	+
Flusilazole	12.556	316.1	139	247.1	16	165.0	28	+
Silthiofam	12.556	268.1	103	252.1	4	73.0	32	+
Bromuconazole II	12.578	378.0	106	70.0	22	158.9	42	+
Quinalphos	12.607	299.1	106	96.9	40	163.0	24	+
Tebufenozide	12.615	353.2	103	133.1	20	105.1	52	+
Picoxystrobin	12.666	368.1	78	205.0	4	145.0	20	+
Fenoxycarb	12.706	302.1	106	88.0	20	116.1	8	+
Fipronil	12.768	434.9	126	330.0	16	250.1	28	negativ
Dimoxystrobin	12.773	327.2	88	205.1	8	116.0	20	+
Phenthoate	12.828	321.0	70	247.1	8	163.1	12	+
Kresoxim-methyl	12.829	314.1	85	223.0	15	116.0	32	+
Penconazole	12.937	284.1	106	70.1	24	123.1	52	+

Compound Name	Retention Time (min)	Precursor Ion (*m/z*)	Fragmentor (V)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Polarity
Carfentrazone-ethyl	12.956	412.0	150	366.1	16	346.1	24	+
Isofenphos-methyl	12.995	332.1	93	230.9	12	121.0	36	+
Beflubutamid	13.098	356.1	126	91.0	40	65.0	60	+
Tebuconazole	13.272	308.2	134	70.0	24	125.0	48	+
Diazinon	13.330	305.1	131	169.1	20	96.9	40	+
Flubendiamide	13.368	681.0	157	254.0	32	274.1	12	negativ
Alanycarb	13.371	400.1	98	238.1	4	91.0	56	+
Benalaxyl	13.379	326.2	106	148.1	20	91.0	52	+
Propiconazole	13.391	342.1	111	159.1	44	69.1	20	+
Prochloraz	13.468	376.0	103	307.9	8	70.0	28	+
Zoxamide	13.510	336.0	121	186.9	20	158.9	48	+
Coumaphos	13.588	363.0	126	227.0	28	307.0	16	+
Chlorfenvinphos	13.608	359.0	111	98.9	32	155.1	8	+
Pirimiphos-methyl	13.613	306.1	139	164.1	20	108.0	32	+
Hexaconazole	13.815	314.1	121	70.0	20	158.9	40	+
Phoxim	13.959	299.1	75	77.0	36	128.9	12	+
Clofentezine	14.024	303.0	93	138.0	12	102.0	44	+
Metconazole	14.025	320.2	111	70.0	28	125.0	48	+
Tolclofos-methyl	14.030	301.0	116	124.9	16	268.9	16	+
Famoxadone	14.076	392.2	98	331.0	4	93.0	48	+
Pyraclostrobin	14.122	388.1	106	194.1	8	163.0	24	+
Phosalone	14.201	368.0	103	182.1	12	110.9	44	+
Spinosad A	14.261	732.5	195	142.1	32	98.0	60	+
Benzoximate	14.269	364.1	78	199.0	4	77.0	60	+
Bitertanol	14.338	338.2	88	70.3	4	269.3	4	+
Disulfoton	14.342	275.0	73	89.0	4	61.0	44	+
Triflumuron	14.351	359.0	106	155.9	12	139.0	36	+
Cycloate	14.352	216.1	98	83.1	16	55.1	32	+
Metrafenone	14.415	409.1	106	209.0	12	227.0	20	+
Diniconazole	14.510	326.0 8328.1	106	70.1	36	70.1	36	+
Chlorpyriphos-methyl	14.536	321.9	110	47.1	48	124.9	20	+
Pencycuron	14.562	329.1	134	125.0	32	89.0	60	+
Difenoconazole	14.907	406.1	121	251.0	20	188.0	40	+
Triflumizole	15.035	346.1	88	278.0	4	43.0	24	+
Spinosad D	15.230	746.5	195	142.5	32	98.5	60	+
Trifloxystrobin	15.248	409.1	103	186.1	20	145.0	56	+
Hydramethylnon	15.281	495.2	220	151.1	60	323.1	36	+
Diflufenican	15.287	395.1	139	266.1	24	246.1	40	+
Prosulfocarb	15.340	252.1	116	91.0	32	65.0	60	+
Indoxacarb	15.420	528.1	126	202.9	44	249.1	12	+
Ipconazole	15.449	334.2	131	70.0	28	125.0	52	+
Clethodim	15.548	360.1	126	164.1	20	268.0	8	+
Profenophos	15.721	372.9	116	302.9	16	344.9	8	+
Hexaflumuron	15.742	459.0	106	438.9	8	174.9	40	negativ

Compound Name	Retention Time (min)	Precursor Ion (*m/z*)	Fragmentor (V)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Product Ion 1 (*m/z*)	Collision Energy (eV)	Polarity
Buprofezin	15.838	306.2	106	201.1	8	57.1	24	+
Benfuracarb	15.927	411.2	111	195.1	36	252.1	12	+
Novaluron	16.079	493.0	111	158.1	20	141.0	52	+
Furathiocarb	16.172	383.2	106	195.0	16	252.0	8	+
Terbufos	16.181	289.1	78	103.1	4	57.0	20	+
Tebufenpyrad	16.295	334.2	167	117.1	44	144.9	28	+
Propaquizafop	16.452	444.1	131	100.1	16	56.0	40	+
Picolinafen	16.593	377.1	126	238.1	28	145.1	64	+
Oxadiazon	16.614	345.1	90	220.1	20	185.1	28	+
Teflubenzuron	16.773	381.0	116	141.0	48	158.0	16	+
Quinoxyphen	16.790	308.0	167	196.9	36	161.9	56	+
Pyriproxyfen	16.856	322.1	106	96.0	12	78.1	60	+
Ethion	16.898	385.0	83	97.0	56	142.9	24	+
Temephos	16.953	467.0	167	124.9	36	418.9	16	+
Metaflumizone	17.009	505.1	154	302.1	16	285.1	60	negativ
Chlorpyriphos	17.021	349.9	101	96.9	32	197.9	16	+
Tralkoxydim	17.071	330.2	116	284.1	8	95.9	32	+
Pendimethalin	17.102	282.1	78	212.0	8	194.0	16	+
Hexythiazox	17.124	353.1	111	227.9	12	168.1	24	+
Lufenuron	17.153	511.0	159	158.1	26	141.1	44	+
Trichlorfon	17.367	274.0	152	256.1	12	67.1	36	+
Spiromesifen	17.372	388.1	100	273.0	8	255.0	28	+
Propargite	17.485	368.2	98	175.1	16	57.1	24	+
Flufenoxuron	17.591	489.0	136	158.0	16	141.1	60	+
Fenpyroximate	17.676	422.2	167	366.2	16	135.1	36	+
Proquinazid	17.692	373.0	106	331.0	12	289.0	24	+
Spirodiclofen	17.692	411.1	111	71.0	16	313.2	8	+
Myclobutanil	17.695	289.1	200	272.0	20	89.0	64	+
Fenazaquin	17.867	307.2	116	57.1	24	161.1	16	+
Pyridaben	17.937	365.1	106	147.1	28	309.1	8	+
Thiamethoxam	17.938	309.0	162	147.0	16	116.9	60	+
Pyridate	18.247	379.1	106	207.0	16	351.1	4	+
Carbosulfan	18.286	381.2	126	118.1	16	160.1	12	+
Mesosulfuron-methyl	18.286	382.2	121	118.0	16	76.0	40	+
Etofenprox	18.511	394.2	98	177.1	12	107.0	52	+
Bifenthrin	18.553	440.2	98	181.2	8	166.2	56	+
Moxidectin	18.581	640.4	126	528.3	4	199.1	28	+
Ivermectine B1a	19.016	892.5	159	307.2	24	569.3	12	+

Table A2. Measured linearity of individual calibration curves, LLOQ, and recoveries at 10 and 100 ppb.

Compound Name	Retention Time (min)	LLOQ (ppt)	Recovery 10 ppb	Recovery 100 ppb	R^2
Methamidophos	1.714	50	98.2	103.8	0.9992
Acephate	2.394	50	101.5	98.7	0.9992
Aminocarb	2.705	20	90.8	98.9	0.9997
Omethoate	2.711	30	101.0	103.5	0.9996
Propamocarb	2.726	30	110.0	106.5	0.9994
Pymetrozine	2.771	30	100.2	95.8	0.9994
Dinotefuran	2.943	70	100.0	96.3	0.9994
Oxamyl	3.132	20	ND	ND	0.9992
Nitenpyram	3.148	100	ND	ND	0.9998
Methomyl	3.321	50	111.5	115.0	0.9997
Flonicamid	3.340	100	85.0	87.0	0.9998
Carbendazim	3.431	40	85.0	83.0	0.9997
Monocrotophos	3.548	20	45.0	32.0	0.9996
Thiabendazole	3.774	10	75.0	65.0	0.9998
Imidacloprid	3.856	30	95.0	65.0	0.9998
Ethidimuron	3.940	80	95.5	90.0	0.9998
Fuberidazole	3.956	60	82.5	82.5	0.9998
Flumetsulam	3.967	100	195.0	190.0	0.9997
Fenuron	4.020	10	93.0	89.5	0.9995
Mexacarbate	4.040	20	85.0	90.0	0.9997
Mevinphos I	4.096	200	110.0	80.0	0.9992
Metamitron	4.119	10	40.0	45.0	0.9997
Dioxacarb	4.125	30	ND	ND	0.9992
Cymiazole	4.134	60	70.0	75.0	0.9998
Dimethoate	4.136	10	110.0	111.0	0.9998
Acetamiprid	4.149	10	80.0	80.0	0.9996
Quinmerac	4.211	20	65.0	70.0	0.9997
Chloridazon	4.250	80	60.0	65.0	0.9997
Cymoxanil	4.405	120	50.0	85.0	0.9995
Thiacloprid	4.530	40	ND	ND	0.9997
Mevinphos II	4.580	200	95.0	80.0	0.9994
Cyazofamid	4.686	100	110.0	80.0	0.9991
Tricyclazole	4.768	10	90.0	90.0	0.9997
Ethirimol	4.820	20	87.5	80.0	0.9993
Butocarboxim	4.820	100	112.0	115.0	0.9993
Aldicarb	4.894	70	103.5	95.0	0.9992
Pirimicarb	5.093	30	98.5	90.0	0.9960
Phosphamidon I	5.216	40	98.0	94.0	0.9990
Oxadixyl	5.248	100	104.0	85.0	0.9991
Phosphamidon II	5.323	30	108.0	97.3	0.9990
Quinoclamine	5.511	200	93.0	75.0	0.9997
Azamethiphos	5.614	20	115.0	125.0	0.9996
Oxasulfuron	5.625	50	102.0	101.2	0.9996
Dichlorvos	5.675	200	89.0	80.0	0.9996

Compound Name	Retention Time (min)	LLOQ (ppt)	Recovery 10 ppb	Recovery 100 ppb	R^2
Propoxur	5.782	30	99.5	91.5	0.9998
Metribuzin	5.784	200	74.0	88.3	0.9997
Triasulfuron	5.801	20	96.5	113.0	0.9991
Thifensulfuron-methyl	5.802	200	95.5	99.5	0.9996
Carbofuran	5.908	10	127.5	125.0	0.9997
Nicosulfuron	5.986	200	96.5	80.0	0.9992
Malaoxon	6.077	30	95.5	88.0	0.9992
Metsulfuron-methyl	6.109	100	98.0	98.6	0.9994
Pyracarbolid	6.129	20	94.5	88.7	0.9996
Thidiazuron	6.150	130	85.5	91.5	0.9998
Tebuthiuron	6.228	20	92.0	93.4	0.9997
Carboxin	6.382	35	96.5	97.6	0.9996
Secbumeton	6.428	30	99.5	101.1	0.9996
Prometon	6.441	20	89.0	95.6	0.9996
Sulfentrazone	6.462	200	95.5	112.2	0.9991
Carbaryl	6.481	1000	69.5	72.4	0.9992
Chlorsulfuron	6.703	200	106.0	93.9	0.9994
Thiofanox	6.919	250	142.0	145.0	0.9990
Amidosulfuron	6.931	100	84.6	86.1	0.9997
Fosthiazate	6.943	50	83.0	80.1	0.9990
Fluometuron	6.958	30	102.5	102.0	0.9997
Imazalil	7.010	100	95.5	95.0	0.9991
Vamidothion	7.010	100	109.5	102.4	0.9997
Foramsulfuron	7.023	200	94.0	96.2	0.9995
Chlorotoluron	7.192	30	102.1	103.0	0.9997
Metobromuron	7.255	100	110.5	98.5	0.9997
Methabenzthiazuron	7.438	20	90.0	89.6	0.9995
Ethoxyquin	7.508	200	67.5	69.4	0.9992
Deet	7.561	5	101.5	101.3	0.9997
Metazachlor	7.631	30	93.5	98.0	0.9995
Lenacil	7.677	100	88.0	83.5	0.9994
Flutriafol	7.710	100	95.0	87.0	0.9996
Tribenuron-methyl	7.752	100	ND	ND	0.9998
Methoprotryne	7.839	30	101.8	101.5	0.9996
2,3,5-Trimethacarb	7.861	20	95.0	95.5	0.9999
Metalaxyl	7.863	15	89.1	95.6	0.9992
Cycluron	7.891	50	100.5	100.5	0.9995
Isoxaflutole	8.002	75	91.5	86.8	0.9991
Diuron	8.059	20	103.5	100.4	0.9996
Azaconazole	8.113	20	85.5	88.8	0.9997
Pyrimethanil	8.117	100	105.0	99.6	0.9996
Isocarbofos	8.158	30	91.5	89.5	0.9997
Dimethachlor	8.246	50	83.5	90.7	0.9993
Forchlorfenuron	8.313	50	93.0	103.3	0.9999

Compound Name	Retention Time (min)	LLOQ (ppt)	Recovery 10 ppb	Recovery 100 ppb	R^2
Methidathion	8.373	100	96.5	92.7	0.9996
Fenpropidin	8.421	25	113.0	104.3	0.9996
Methacrifos	8.501	50	97.0	99.2	0.9997
Clomazone	8.669	20	101.5	98.3	0.9997
Desmedipham	8.784	10	105.0	101.1	0.9996
Guthion	8.814	35	84.5	86.3	0.9998
Phosmet	8.996	100	ND	ND	0.9990
Flumioxazin	9.000	1000	75.8	76.0	0.9995
Phenmedipham	9.103	10	104.0	99.3	0.9997
Flazasulfuron	9.132	100	47.5	42.7	0.9997
Fenobucarb	9.135	60	102.5	94.2	0.9996
Linuron	9.345	40	99.0	95.8	0.9998
Spiroxamine I	9.384	20	97.5	98.6	0.9996
Diethofencarb	9.394	20	92.0	87.4	0.9997
Furalaxyl	9.435	25	102.0	100.5	0.9997
Ethofumesate	9.487	50	106.5	99.2	0.9997
Spiroxamine II	9.563	30	101.4	99.4	0.9995
Methiocarb	9.665	70	115.5	107.5	0.9997
Thiodicarb	9.765	50	83.5	93.6	0.9993
Azoxystrobin	9.771	20	82.5	94.3	0.9993
Fenamidone	9.851	30	97.4	95.5	0.9996
Halofenozide	9.862	60	104.5	97.9	0.9997
Dimethomorph I	9.959	100	90.5	83.8	0.9990
Promecarb	10.030	50	96.0	96.7	0.9997
Fludioxonil	10.167	100	88.0	83.4	0.9995
Boscalid	10.209	200	95.0	93.0	0.9998
Molinate	10.218	100	99.0	92.5	0.9992
Pronamide	10.226	35	95.5	90.9	0.9997
Paclobutrazol	10.321	75	91.5	92.5	0.9998
Fluopicolide	10.364	100	94.5	99.5	0.9998
Bispyribac-sodium	10.390	100	87.5	92.6	0.9996
Isoprothiolane	10.402	60	98.5	94.5	0.9997
Isoxaben	10.481	10	91.0	97.6	0.9998
Malathion	10.503	100	93.5	98.5	0.9998
Diflubenzuron	10.549	80	90.5	91.0	0.9997
Mandipropamid	10.556	100	92.0	94.1	0.9997
Cyproconazole I	10.602	100	96.0	89.2	0.9995
Triadimefon	10.631	200	98.0	93.4	0.9996
Propham	10.634	250	96.5	90.0	0.9995

Compound Name	Retention Time (min)	LLOQ (ppt)	Recovery 10 ppb	Recovery 100 ppb	R^2
Dimethomorph II	10.639	100	93.5	84.9	0.9993
Methoxyfenozide	10.737	25	103.0	99.5	0.9997
Bromuconazole I	10.859	300	94.5	87.5	0.9997
Propetamphos	10.904	75	104.5	100.6	0.9995
Trietazine	10.985	35	93.5	98.5	0.9998
Mepanipyrim	11.021	1000	121.4	103.8	0.9996
Bupirimate	11.105	50	99.0	100.3	0.9996
Chloroxuron	11.211	30	100.5	100.8	0.9980
Cyproconazole II	11.235	100	86.5	88.9	0.9999
Iprovalicarb	11.249	15	93.5	96.2	0.9996
Triazophos	11.261	10	97.5	98.8	0.9997
Bifenazate	11.281	25	93.0	91.7	0.9997
Cyprodinil	11.329	200	114.5	103.6	0.9998
Triadimenol	11.404	200	92.5	89.3	0.9996
Fluquinconazole	11.421	200	90.0	93.3	0.9990
Ethoprop	11.433	100	99.0	98.1	0.9996
Fenhexamid	11.512	200	97.5	90.2	0.9997
Azinphos-ethyl	11.534	100	88.0	86.7	0.9998
Fenarimol	11.583	1000	109.4	95.4	0.9996
Tolylfluanid	11.586	100	130.5	132.7	0.9991
Mecarbam	11.588	30	109.5	104.5	0.9991
Flufenacet	11.591	35	89.5	94.7	0.9998
Spirotetramat	11.627	40	99.0	94.6	0.9993
Fluoxastrobin	11.689	50	102.0	90.8	0.9991
Triticonazole	11.693	100	96.0	94.9	0.9993
Procymidone	11.707	30	85.0	91.2	0.9995
Metolachlor	11.707	40	87.5	97.5	0.9997
Tetraconazole	11.901	100	92.5	91.3	0.9995
Epoxiconazole	11.973	100	97.5	92.9	0.9996
Uniconazole	12.276	90	103.0	83.3	0.9998
Fenbuconazole	12.451	100	96.0	90.5	0.9998
Fenamiphos	12.489	30	90.5	86.3	0.9995
Rotenone	12.522	200	93.5	97.5	0.9997
Flusilazole	12.556	30	85.5	93.0	0.9999
Silthiofam	12.556	30	99.5	96.1	0.9999
Bromuconazole II	12.578	200	80.0	94.5	0.9998
Quinalphos	12.607	100	90.0	99.2	0.9998
Tebufenozide	12.615	15	103.0	102.9	0.9998
Picoxystrobin	12.666	20	87.0	96.3	0.9997

Compound Name	Retention Time (min)	LLOQ (ppt)	Recovery 10 ppb	Recovery 100 ppb	R^2
Fenoxycarb	12.706	20	94.0	94.7	0.9997
Fipronil	12.768	55	ND	105.0	0.9990
Dimoxystrobin	12.773	30	101.0	100.8	0.9998
Phenthoate	12.828	100	92.5	93.4	0.9998
Kresoxim-methyl	12.829	40	95.5	96.8	0.9998
Penconazole	12.937	100	94.5	99.5	0.9998
Carfentrazone-ethyl	12.956	200	94.5	98.5	0.9997
Isofenphos-methyl	12.995	25	94.5	93.8	0.9996
Beflubutamid	13.098	100	92.0	93.2	0.9997
Tebuconazole	13.272	30	93.0	90.1	0.9996
Diazinon	13.330	40	83.5	82.6	0.9997
Flubendiamide	13.368	30	89.5	103.5	0.9997
Alanycarb	13.371	25	ND	ND	0.9997
Benalaxyl	13.379	30	97.5	99.0	0.9998
Propiconazole	13.391	75	100.5	94.7	0.9996
Prochloraz	13.468	100	68.0	86.3	0.9996
Zoxamide	13.510	75	80.0	89.9	0.9997
Coumaphos	13.588	120	93.0	96.8	0.9998
Chlorfenvinphos	13.608	30	99.0	94.8	0.9997
Pirimiphos-methyl	13.613	15	95.0	96.1	0.9998
Hexaconazole	13.815	15	116.0	88.8	0.9997
Phoxim	13.959	100	96.0	93.3	0.9996
Clofentezine	14.024	50	109.0	101.8	0.9993
Metconazole	14.025	75	90.5	92.0	0.9997
Tolclofos-methyl	14.030	200	92.5	91.5	0.9996
Famoxadone	14.076	200	84.0	78.5	0.9995
Pyraclostrobin	14.122	40	99.0	100.5	0.9996
Phosalone	14.201	30	95.5	89.9	0.9998
Spinosad A	14.261	65	ND	90.1	0.9990
Benzoximate	14.269	40	90.0	96.3	0.9997
Bitertanol	14.338	200	95.0	92.4	0.9950
Disulfoton	14.342	60	90.5	93.3	0.9997
Triflumuron	14.351	100	90.5	89.3	0.9997
Cycloate	14.352	200	91.0	94.5	0.9997
Metrafenone	14.415	50	78.5	89.6	0.9995
Diniconazole	14.510	200	88.0	84.6	0.9996
Chlorpyriphos-methyl	14.536	200	85.0	84.8	0.9996
Pencycuron	14.562	30	95.5	99.1	0.9998
Difenoconazole	14.907	200	87.5	87.5	0.9995
Triflumizole	15.035	50	67.6	83.3	0.9996
Spinosad D	15.230	100	115.5	103.6	0.9995
Trifloxystrobin	15.248	15	96.5	99.4	0.9998
Hydramethylnon	15.281	100	65.0	84.5	0.9997
Diflufenican	15.287	30	81.0	87.4	0.9998

Compound Name	Retention Time (min)	LLOQ (ppt)	Recovery 10 ppb	Recovery 100 ppb	R^2
Prosulfocarb	15.340	15	90.0	97.7	0.9999
Indoxacarb	15.420	230	89.0	91.5	0.9999
Ipconazole	15.449	60	89.5	93.8	0.9999
Clethodim	15.548	100	52.0	53.3	0.9997
Profenophos	15.721	50	81.5	92.9	0.9996
Hexaflumuron	15.742	200	ND	120.4	0.9991
Buprofezin	15.838	40	94.5	97.2	0.9997
Benfuracarb	15.927	200	ND	ND	0.9998
Novaluron	16.079	200	84.0	78.5	0.9993
Furathiocarb	16.172	50	79.5	88.1	0.9991
Terbufos	16.181	200	92.2	92.2	0.9995
Tebufenpyrad	16.295	100	92.0	88.4	0.9997
Propaquizafop	16.452	50	95.5	93.9	0.9997
Picolinafen	16.593	100	87.0	89.6	0.9996
Oxadiazon	16.614	1000	90.5	88.5	0.9996
Teflubenzuron	16.773	1000	65.0	75.3	0.9997
Quinoxyphen	16.790	100	94.5	96.1	0.9998
Pyriproxyfen	16.856	20	92.5	98.1	0.9998
Ethion	16.898	100	91.5	90.3	0.9998
Temephos	16.953	100	84.5	97.6	0.9997
Metaflumizone	17.009	50	96.5	144.5	0.9991
Chlorpyriphos	17.021	100	92.5	91.9	0.9998
Tralkoxydim	17.071	100	48.0	48.3	0.9997
Pendimethalin	17.102	100	89.9	86.6	0.9997
Hexythiazox	17.124	100	93.0	87.8	0.9998
Lufenuron	17.153	1000	88.5	85.0	0.9991
Trichlorfon	17.367	1000	92.0	90.0	0.9998
Spiromesifen	17.372	30	67.5	90.0	0.9990
Propargite	17.485	100	97.0	95.5	0.9997
Flufenoxuron	17.591	200	86.5	86.4	0.9992
Fenpyroximate	17.676	50	83.0	84.6	0.9996
Proquinazid	17.692	50	68.0	82.1	0.9998
Spirodiclofen	17.692	100	84.5	97.0	0.9995
Myclobutanil	17.695	100	73.0	81.4	0.9998
Fenazaquin	17.867	100	74.0	69.5	0.9997
Pyridaben	17.937	15	89.0	88.2	0.9998
Thiamethoxam	17.938	30	74.0	82.2	0.9996
Pyridate	18.247	50	90.5	121.2	0.9993
Carbosulfan	18.286	50	ND	ND	0.9996
Mesosulfuron-methyl	18.286	100	ND	ND	0.9997
Etofenprox	18.511	200	86.5	95.5	0.9994
Bifenthrin	18.553	50	107.0	86.1	0.9993
Moxidectin	18.581	1000	76.5	87.2	0.9996
Ivermectine B1a	19.016	2000	82.0	91.6	0.9990

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