Evaluation of potential improvements in LC-HRMS instruments with the implementation of longer chromatographic columns

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1. Aim and scope

The aim of this study is to assess whether using chromatographic columns longer than 100 mm in high-resolution mass spectrometry (HRMS) enhances compound identification in multi-residue analyses. This investigation will focus on comparing 100 mm and 150 mm columns to determine if extended column lengths can mitigate common challenges in HRMS analysis, such as analyte and matrix component overlap. The findings are intended to offer practical guidance for laboratories looking to improve the accuracy and reliability of their LC-HRMS workflows.

2. Short description

High-resolution mass spectrometry (HRMS) has become a standard tool for multi-residue analysis in various fields, including environmental monitoring and food safety due to its high sensitivity and broad detection capabilities. Despite these advantages, the method faces significant challenges in accurately identifying and quantifying compounds when dealing with complex matrices. Multi-residue methods often involve analyzing samples with a high amount of different analytes, many of which have similar physicochemical properties. Consequently, signal overlaps between analytes and matrix components is a common issue, leading to identification difficulties and a risk of compromised results.

One solution proposed to address this signal overlap is the use of chromatographic columns longer than the conventional 100 mm, as extended columns can offer improved separation of analytes. Increased column length allows for enhanced resolution, giving analytes more time to separate and thereby minimizing the risk of co-elution, where analytes and matrix components might otherwise interfere with each other's detection. Longer columns, such as those extending to 150 mm, are anticipated to provide clearer identification of compounds, especially when dealing with complex samples where numerous analytes and background matrix signals compete within the HRMS system.

In this study, a detailed comparison of 100 mm and 150 mm chromatographic columns will be conducted to evaluate their effectiveness in HRMS. The study was conducted to evaluate the analysis of 182 pesticides in tomato, onion, orange and pineapple matrices at concentration level of 50 µg/kg in matrix.

3. Experimental

3.1. Sample treatment

The samples were extracted using the QuEChERS method. The general experimental procedure was as follows:

1. Weigh 10 g of sample in a 50-mL PTFE centrifuge tube.
2. Add 10 mL acetonitrile.
3. Shake the sample in an axial agitator (Agitax) for 3 minutes.
4. Add 4 g anhydrous magnesium sulphate, 1 g sodium chloride, 1 g trisodium citrate dihydrate and 0.5 g disodium hydrogencitrate sesquihydrate and shake manually (3 sec).
5. Shake the sample in an axial agitator (Agitax) for 3 minutes.
6. Centrifuge the tubes at 4000 rpm for 5 min.

7. Transfer 5 mL of the supernatant to a 15-mL PFTE centrifuge tube containing 750 mg of anhydrous magnesium sulfate and 125 PSA and vortex for 30 sec.
8. Centrifuge the tubes at 4000 rpm for 5 min.
9. Transfer the supernatant to a 4-mL vial and add 10 µL/mL of extract of ACN (5% formic acid)

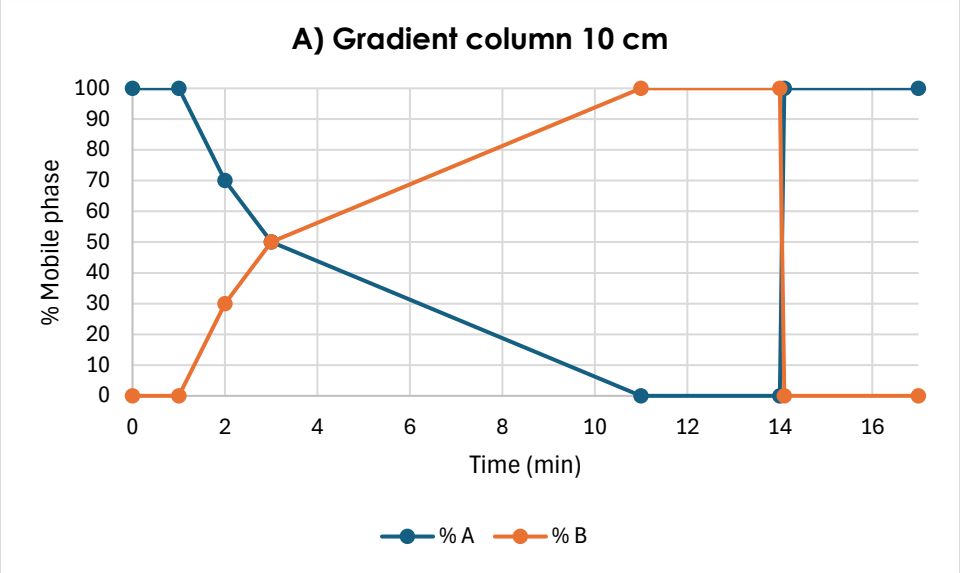
For the experiments, a matrix-matched calibration point corresponding to 50 µg/kg in matrix was injected. It was prepared by mixing 50 µL of the mix of compounds at 100 µg/L in acetonitrile with 400 µL of Optima® water (with dimethoate-d6 as injection standard) and 100 µL of the matrix blank extracted with the previously mentioned method in an injection vial.

3.2. Analysis by LC-QTOF

Instrumentation and analytical conditions for the LC system

- Column:
    1. Kinetex® C8 (100mm x 2.1 mm, 1.7 µm particle size)
    2. Kinetex® C8 (150mm x 2.1 mm, 1.7 µm particle size)
- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)
- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)
- Column temperature: 30 °C
- Flow rate: 0.3 ml/min
- Injection volume: 5 µL
- Autosampler temperature: 12 °C

The gradient used for the 10 cm column (**Figure 1 A**) and the gradient used for the 15 cm column (**Figure 1 B**):



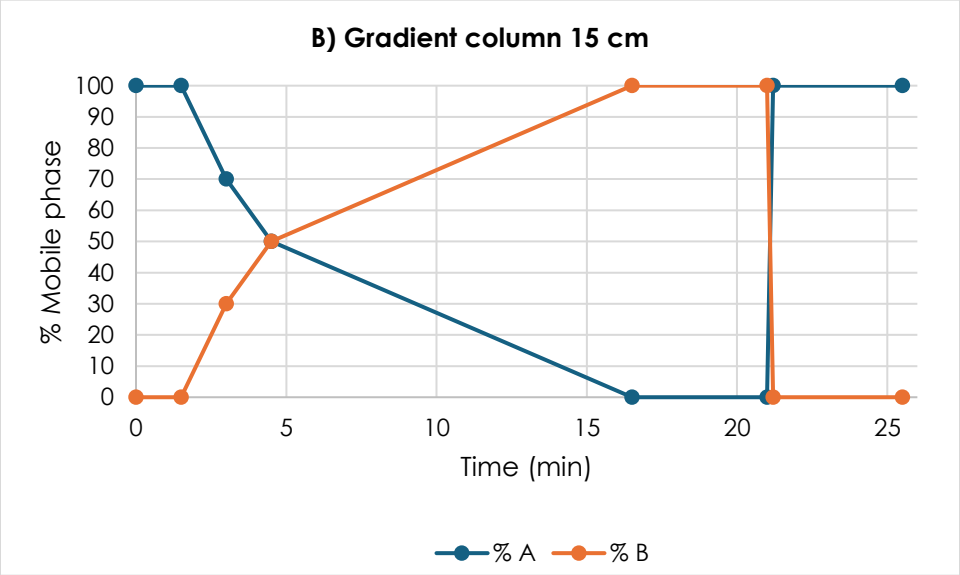


Figure 1: Elution gradient of LC-MS/MS method. Mobile phase gradient used. A (Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)) and B (Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water))

A QTOF X500R (AB SCIEX™) mass spectrometer equipped with a TurboIonSpray ion source was used. The source parameters were operated as follows:

- Polarity: positive mode
- Ion source gas 1: 50 psi
- Ion source gas 2: 50 psi
- Curtain gas: 35 psi
- CAD gas: 7
- Temperature: 350 °C
- Spray voltage: 4500 V

Data acquisition was performed in **FS (MS) and SWATH® (MS/MS)** modes. Parameters used in full scan mode were:

- Accumulation time: 0.08 s
- Declustering potential: 80 V
- TOF start mass: 100 *m/z*
- TOF stop mass: 1000 *m/z*

For the MS/MS mode the parameters were:

- Accumulation time: 0.05 s
- TOF start mass: 50 *m/z*
- TOF stop mass: 100 *m/z*
- Collision energy: 35 ± 15 V

Nine isolation mass windows were optimised *m/z*: 120–180, 179–240, 239–300, 299–360, 359–420, 419–480, 479–540, 539–747.5, 747–1000. The total scan time obtained was 0.651 s. An external TOF mass calibration was carried out daily. For the calibration, a mixture containing 11 compounds with masses in the range of 132.9049–2179.4965 *m/z* was used. Also, this mixture was automatically injected along the batch of every 5 samples to maintain the mass accuracy below 5 ppm.

4. Results and discussion

Figure 2 shows the number of identified and unidentified compounds using different chromatographic columns across the various matrices studied. Identification criteria were those of SANTE 11312/2021v2 (2 ions with mass accuracy ≤ 5 ppm, signal-to-noise ratio ≥ 3, and analyte peaks from precursor and/or product ion(s) in the extracted ion chromatograms must fully overlap).

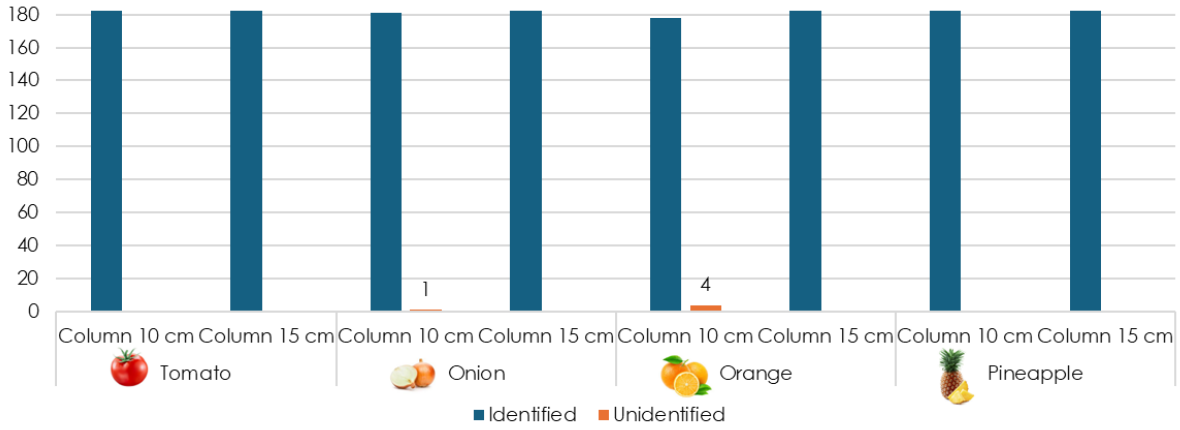


Figure 2: Evaluation of different column lengths in compound identification

For simple matrices like tomato and pineapple, a complete identification of the evaluated compounds was achieved. However, in matrices such as onion and orange, some compounds could not be identified using the 10 cm column, as follows:

Cyantraniliprole in onion matrix

Cyantraniliprole	*m/z*	Column 10 cm ✖		Column 15 cm ✓	
		Area	Mass Error	Area	Mass Error
Precursor	473.0123	5.59E+03	-5.8	3.59E+03	-3.4
Fragment	283.9219	4.33E+03	-8.2	2.29E+04	0.9
Fragment	441.9694	2.14E+03	5.4	7.25E+03	-3.3
Fragment	285.9205	6.01E+03	-4.8	2.96E+04	-6.3
Fragment	287.9178	1.29E+03	-7	6.74E+03	-4.5
Fragment	443.9689	2.79E+03	-6.9	1.07E+04	-2.4

Deltamethrin, chlorpyrifos-methyl, spirodiclofen, and chlorpyrifos in orange matrix

Deltamethrin	*m/z*	Column 10 cm ✖		Column 15 cm ✓	
		Area	Mass Error	Area	Mass Error
Precursor	521.007	6.71E+02	-9.6	7.83E+02	-4.4
Fragment	173.9859	ND		6.42E+02	-6.7

Fragment	181.0656	ND		1.28E+04	-7
Fragment	278.9018	ND		1.59E+03	-16.3
Fragment	280.8997	ND		9.91E+02	-27.8
Fragment	282.8973	ND		1.08E+03	0
Fragment	505.9786	ND		ND	ND
Chlorpyrifos-methyl	***m/z***	**Column 10 cm ✗**		**Column 15 cm ✓**	
		Area	Mass Error	Area	Mass Error
Precursor	321.9023	2.45E+03	-6.3	2.68E+03	0.4
Fragment	289.8761	3.50E+02	90.3	3.95E+03	1.1
Spirodiclofen	***m/z***	**Column 10 cm ✗**		**Column 15 cm ✓**	
		Area	Mass Error	Area	Mass Error
Precursor	411.1124	3.65E+03	-5.8	5.45E+03	-2.2
Fragment	230.961	ND		1.02E+03	-3.5
Fragment	295.0286	ND		8.67E+02	-10.7
Fragment	313.0391	ND		6.85E+03	2.4
Chlopyrifos	***m/z***	**Column 10 cm ✗**		**Column 15 cm ✓**	
		Area	Mass Error	Area	Mass Error
Precursor	349.9336	2.46E+03	-5.4	5.23E+03	-2.2
Fragment	96.9505	1.56E+03	-0.6	2.82E+04	1.8
Fragment	114.9614	1.99E+03	-13.6	1.70E+04	-7.3
Fragment	161.9505	ND	ND	1.48E+03	-5.3
Fragment	197.9276	1.83E+03	-14.9	2.95E+04	-1.7
Fragment	213.9043	ND	ND	1.76E+03	-11.3
Fragment	293.8709	ND	ND	3.29E+03	-1
Fragment	321.9031	ND	ND	2.21E+03	-1.6
Fragment	349.9325	ND	ND	1.90E+03	-0.3

ND: Not detected

In **Figure 3**, The compound spirodiclofen in orange matrix is shown. At the top of the image is the theoretical mass spectrum. When analyzed with the 10 cm column, the precursor ion shows a mass error greater than 5 ppm, and the most abundant fragment ion is not visible in the MS/MS spectrum. Despite using a SWATH mode with 9 windows, the 10 cm column does not allow for the identification of the compound. However, with the 15 cm column, the mass error for the precursor ion is -2.2 ppm and -2.4 ppm for the fragment ion, enabling accurate identification of the compound.

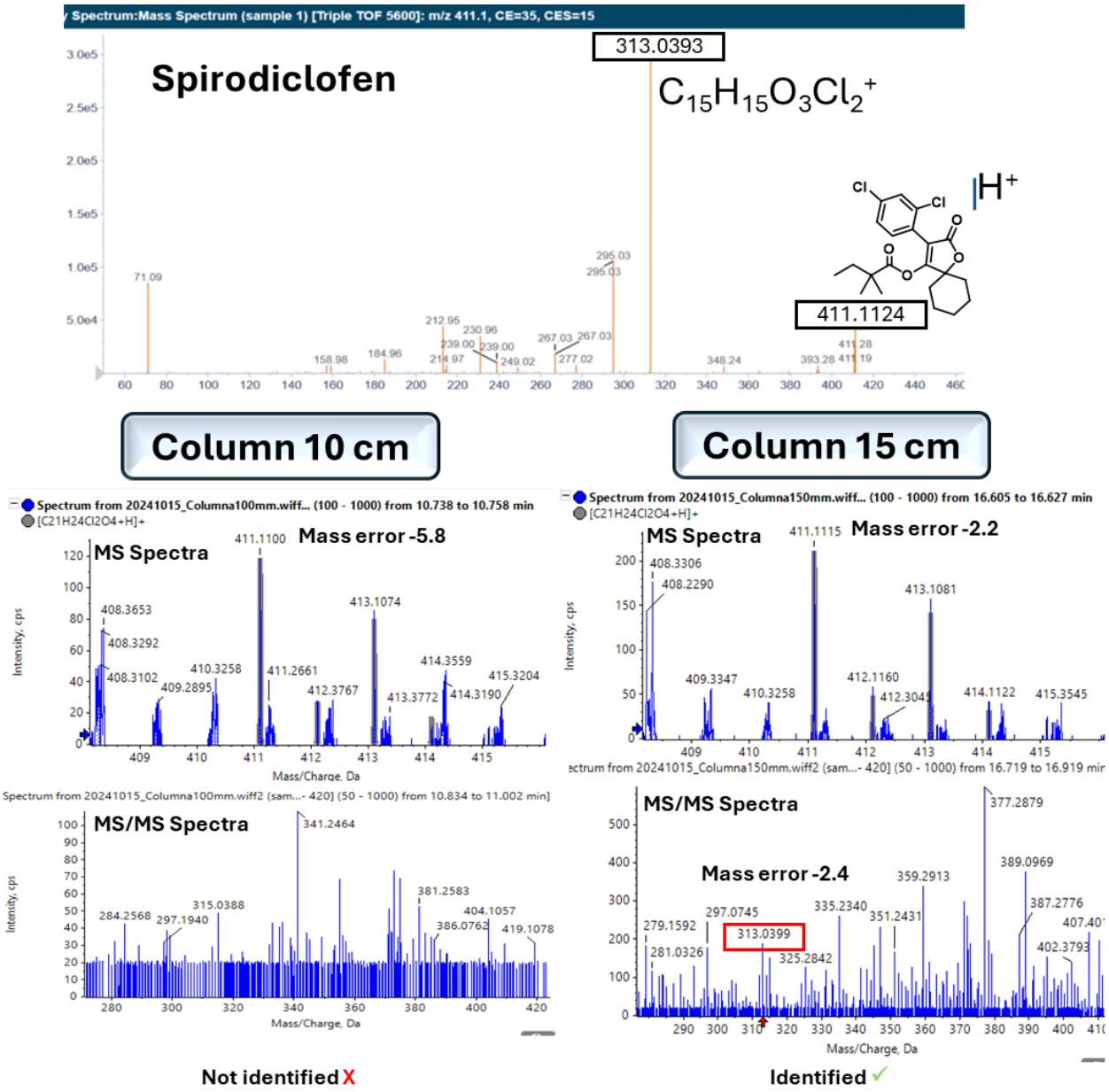


Figure 3: The theoretical spectrum of spirodiclofen is shown at the top; on the left, the experimental MS and MS/MS spectrum with the 10 cm column, and on the right with the 15 cm column. Spirodiclofen can only be accurately identified with the 15 cm column.

5. Conclusions

This study evaluates the performance of 10 cm and 15 cm chromatographic columns for pesticide identification across different matrices—specifically tomato, onion, orange, and pineapple—using high-resolution mass spectrometry (HRMS). The primary objective was to determine whether extending the column length could improve compound identification by minimizing overlaps between analytes and matrix components, a common challenge in HRMS multi-residue analyses.

In simpler matrices, such as tomato and pineapple, both the 10 cm and 15 cm columns facilitated accurate pesticide identification, meeting the mass accuracy criterion (±5 ppm) for at least two ions per compound. However, in more complex matrices like onion and orange, the 15 cm column demonstrated clear advantages. Specific compounds, including cyantraniliprole in onion and deltamethrin, chlorpyrifos-methyl, spirodiclofen, and chlorpyrifos in orange, were reliably identified only when using the 15 cm column.

These findings highlight that while the 10 cm column is generally effective for routine analyses, the 15 cm column offers enhanced reliability for compounds requiring greater sensitivity. Nonetheless, this advantage comes with a trade-off: the analysis time increases to 25.5 minutes with the 15 cm column, which could impact laboratory throughput in high-volume settings. It is important to emphasize that these results are specific to the instrumentation used in this study and should not be generalized to other systems or setups.

APPENDIX I: MASS TRANSITIONS AND VALIDATION RESULTS

Table 1. Detection and chromatographic parameters for the compounds analyzed by LC-QTOF.

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Albendazole	C12H15N3O2S	[M+H]+	266.09577		7.38	11.95
Albendazole	C12H15N3O2S	[M+H]+	266.09577	234.0692	7.38	11.95
Ametoctradin	C15H25N5	[M+H]+	276.21827		9.57	15.02
Ametoctradin	C15H25N5	[M+H]+	276.21827	176.093	9.57	15.02
Amisulbrom	C13H13BrFN5O4S2	[M+H]+	465.96491		9.77	15.38
Amisulbrom	C13H13BrFN5O4S2	[M+H]+	465.96491	226.9738	9.77	15.39
Anilofos	C13H19ClNO3PS2	[M+H]+	368.03053		9.11	14.43
Anilofos	C13H19ClNO3PS2	[M+H]+	368.03053	124.9821	9.11	14.43
Atrazine	C8H14ClN5	[M+H]+	216.10105		7.26	11.71
Atrazine	C8H14ClN5	[M+H]+	216.10105	174.0542	7.27	11.71
Azoxystrobin	C22H17N3O5	[M+H]+	404.1241		7.77	12.41
Azoxystrobin	C22H17N3O5	[M+H]+	404.1241	372.098	7.77	12.41
BAC10	C19H34N	[M]+	276.26858		8.21	13.12
BAC10	C19H34N	[M]+	276.26858	91.0542	8.2	13.12
BAC8	C17H30N	[M]+	248.23728		6.87	11.15
BAC8	C17H30N	[M]+	248.23728	91.0545	6.88	11.15
Bendiocarb	C11H13NO4	[M+H]+	224.09173		6.33	10.24
Bendiocarb	C11H13NO4	[M+H]+	224.09173	109.0284	6.32	10.24
Benzovindiflupyr	C18H15Cl2F2N3O	[M+H]+	398.0633		9.11	14.41
Benzovindiflupyr	C18H15Cl2F2N3O	[M+H]+	398.0633	342.0804	9.1	14.41
Bifenazate	C17H20N2O3	[M+H]+	301.15467		8.39	13.4
Bifenazate	C17H20N2O3	[M+H]+	301.15467	198.0918	8.39	13.39
Bifenthrin	C23H22ClF3O2	[M+NH4]+	440.15987		11.44	17.49
Bifenthrin	C23H22ClF3O2	[M+NH4]+	440.15987	181.10118	11.44	17.49
Bixafen	C18H12Cl2F3N3O	[M+H]+	414.03823		8.81	14
Bixafen	C18H12Cl2F3N3O	[M+H]+	414.03823	265.9941	8.81	14
Boscalid	C18H12Cl2N2O	[M+H]+	343.03994		7.91	12.7
Boscalid	C18H12Cl2N2O	[M+H]+	343.03994	307.0634	7.91	12.7
Bromacil	C9H13BrN2O2	[M+H]+	261.02332		6.43	10.38
Bromacil	C9H13BrN2O2	[M+H]+	261.02332	204.9608	6.43	10.38
Bupirimate	C13H24N4O3S	[M+H]+	317.16419		8.55	13.66
Bupirimate	C13H24N4O3S	[M+H]+	317.16419	166.0978	8.55	13.66
Buprofezin	C16H23N3OS	[M+H]+	306.16346		10.06	15.74

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Buprofezin	C16H23N3OS	[M+H]+	306.16346	201.1058	10.06	15.73
Butoxycarboxim	C7H14N2O4S	[M+H]+	223.0747		4.1	7.88
Butoxycarboxim	C7H14N2O4S	[M+H]+	223.0747	86.06	4.1	7.86
Carbendazim	C9H9N3O2	[M+H]+	192.07675		4.44	6.77
Carbendazim	C9H9N3O2	[M+H]+	192.07675	160.0506	4.44	6.76
Carbendazim-D3	C9(2H)3H6N3O2	[M+H]+	195.09558		4.43	6.74
Carbendazim-D3	C9(2H)3H6N3O2	[M+H]+	195.09558	160.0506	4.44	6.76
Chlorantraniliprole	C18H14BrCl2N5O2	[M+H]+	481.97807		7.41	11.93
Chlorantraniliprole	C18H14BrCl2N5O2	[M+H]+	481.97807	283.9222	7.41	11.93
Chlorbromuron	C9H10BrClN2O2	[M+H]+	292.96869		8.06	13
Chlorbromuron	C9H10BrClN2O2	[M+H]+	292.96869	182.0242	8.06	13
Chlorfenvinphos	C12H14Cl3O4P	[M+H]+	358.97681		9.21	14.53
Chlorfenvinphos	C12H14Cl3O4P	[M+H]+	358.97681	169.9683	9.2	14.53
Chlorfluazuron	C20H9Cl3F5N3O3	[M+H]+	539.97024		10.59	16.39
Chlorfluazuron	C20H9Cl3F5N3O3	[M+H]+	539.97024	382.9362	10.59	16.4
Chloridazon	C10H8ClN3O	[M+H]+	222.04287		5.18	8.05
Chloridazon	C10H8ClN3O	[M+H]+	222.04287	104.0495	5.19	8.05
Chlorotoluron	C10H13ClN2O	[M+H]+	213.07892		6.97	11.28
Chlorotoluron	C10H13ClN2O	[M+H]+	213.07892	140.0261	6.97	11.28
Chloroxuron	C15H15ClN2O2	[M+H]+	291.08948		8.33	13.34
Chloroxuron	C15H15ClN2O2	[M+H]+	291.08948	72.0444	8.34	13.34
Chlorpyrifos	C9H11Cl3NO3PS	[M+H]+	349.93356		10.23	15.98
Chlorpyrifos	C9H11Cl3NO3PS	[M+H]+	349.93356	197.9276	10.23	15.98
Chlorpyrifos-methyl	C7H7Cl3NO3PS	[M+H]+	321.90226		9.49	15.02
Chlorpyrifos-methyl	C7H7Cl3NO3PS	[M+H]+	321.90226	127.0155	9.5	14.97
Chromafenozide	C24H30N2O3	[M+H]+	395.23292		8.65	13.71
Chromafenozide	C24H30N2O3	[M+H]+	395.23292	175.0758	8.65	13.71
Clofentezine	C14H8Cl2N4	[M+H]+	303.01988		9.35	14.83
Clofentezine	C14H8Cl2N4	[M+H]+	303.01988	138.0105	9.36	14.83
Clomazone	C12H14ClNO2	[M+H]+	240.07858		7.63	12.31
Clomazone	C12H14ClNO2	[M+H]+	240.07858	125.0155	7.63	12.31
Coumaphos	C14H16ClO5PS	[M+H]+	363.02174		9.13	14.44
Coumaphos	C14H16ClO5PS	[M+H]+	363.02174	306.9593	9.13	14.44
Cyantraniliprole	C19H14BrClN6O2	[M+H]+	473.01229		6.48	10.46
Cyantraniliprole	C19H14BrClN6O2	[M+H]+	473.01229	285.9205	6.48	10.46
Cyflufenamid	C20H17F5N2O2	[M+H]+	413.1283		9.45	14.85
Cyflufenamid	C20H17F5N2O2	[M+H]+	413.1283	241.0395	9.45	14.85
Cyflumetofen	C24H24F3NO4	[M+NH4]+	465.19957		9.9	15.43
Cyflumetofen	C24H24F3NO4	[M+NH4]+	465.19957	173.0209	9.89	15.43

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Cyhalofop-butyl	C20H20FNO4	[M+NH4]+	375.17146		9.58	15.03
Cyhalofop-butyl	C20H20FNO4	[M+NH4]+	375.17146	256.0768	9.58	15.03
Cymoxanil	C7H10N4O3	[M+H]+	199.08257		5.47	8.61
Cymoxanil	C7H10N4O3	[M+H]+	199.08257	156.077	5.47	8.61
Cyproconazole	C15H18ClN3O	[M+H]+	292.12112		8.19	13.47
Cyproconazole	C15H18ClN3O	[M+H]+	292.12112	70.0402	8.16	13.47
Cyprodinil	C14H15N3	[M+H]+	226.13387		8.68	13.9
Cyprodinil	C14H15N3	[M+H]+	226.13387	210.1025	8.69	13.9
Deltamethrin	C22H19Br2NO3	[M+NH4]+	521.00699		10.8	16.67
Deltamethrin	C22H19Br2NO3	[M+NH4]+	521.00699	280.8997	10.8	16.66
Demeton-S-methylsulfone	C6H15O5PS2	[M+H]+	263.01713		4.45	6.28
Demeton-S-methylsulfone	C6H15O5PS2	[M+H]+	263.01713	121.0322	4.44	6.27
Demeton-S-methylsulfoxide (Oxydemeton-methyl)	C6H15O4PS2	[M+H]+	247.02221		4.34	5.82
Demeton-S-methylsulfoxide (Oxydemeton-methyl)	C6H15O4PS2	[M+H]+	247.02221	105.037	4.34	5.82
Desethylterbuthylazine	C7H12ClN5	[M+H]+	202.0854		6.65	10.45
Desethylterbuthylazine	C7H12ClN5	[M+H]+	202.0854	146.0229	6.66	10.76
Diazinon	C12H21N2O3PS	[M+H]+	305.10833		9.26	14.63
Diazinon	C12H21N2O3PS	[M+H]+	305.10833	169.0797	9.26	14.63
Dichlorvos	C4H7Cl2O4P	[M+H]+	220.95318		6.31	10.2
Dichlorvos	C4H7Cl2O4P	[M+H]+	220.95318	109.0051	6.32	10.19
Dicrotophos	C8H16NO5P	[M+H]+	238.08389		4.72	6.98
Dicrotophos	C8H16NO5P	[M+H]+	238.08389	72.0445	4.72	6.98
Diethofencarb	C14H21NO4	[M+H]+	268.15433		7.67	12.35
Diethofencarb	C14H21NO4	[M+H]+	268.15433	152.0706	7.67	12.34
Difenoconazole	C19H17Cl2N3O3	[M+H]+	406.07197		9.39	14.8
Difenoconazole	C19H17Cl2N3O3	[M+H]+	406.07197	251.0026	9.42	14.81
Difenoxuron	C16H18N2O3	[M+H]+	287.13902		7.27	11.7
Difenoxuron	C16H18N2O3	[M+H]+	287.13902	123.0441	7.27	11.7
Dimethoate	C5H12NO3PS2	[M+H]+	230.0069		5.15	8.04
Dimethoate	C5H12NO3PS2	[M+H]+	230.0069	170.9699	5.15	8.04
Dimethoate-d6	C5(2H)6H6NO3PS2	[M+H]+	236.04456	131.0197	5.12	7.99
Dimethoate-d6	C5(2H)6H6NO3PS2	[M+H]+	236.04456	177.0076	5.12	7.99
Dimethylvinphos	C10H10Cl3O4P	[M+H]+	330.94551		8.31	13.3
Dimethylvinphos	C10H10Cl3O4P	[M+H]+	330.94551	127.0152	8.31	13.3
Diuron	C9H10Cl2N2O	[M+H]+	233.02429		7.39	11.96

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Diuron	C9H10Cl2N2O	[M+H]+	233.02429	161.9689	7.39	11.96
Dodine	C13H29N3	[M+H]+	228.24342		9.15	14.45
Dodine	C13H29N3	[M+H]+	228.24342	60.0559	9.15	14.45
Edifenphos	C14H15O2PS2	[M+H]+	311.03239		9.07	14.35
Edifenphos	C14H15O2PS2	[M+H]+	311.03239	283.0011	9.07	14.35
Emamectin B1a	C49H75NO13	[M+H]+	886.53112		9.77	15.2
Emamectin B1a	C49H75NO13	[M+H]+	886.53112	158.1178	9.77	15.2
Epoxiconazole	C17H13ClFN3O	[M+H]+	330.08039		8.55	13.58
Epoxiconazole	C17H13ClFN3O	[M+H]+	330.08039	121.0449	8.52	13.58
Ethion	C9H22O4P2S4	[M+H]+	384.99489		10.21	15.92
Ethion	C9H22O4P2S4	[M+H]+	384.99489	170.9699	10.21	15.92
Ethiprole	C13H9Cl2F3N4OS	[M+H]+	396.9899		7.86	12.65
Ethiprole	C13H9Cl2F3N4OS	[M+H]+	396.9899	350.9483	7.86	12.65
Ethirimol	C11H19N3O	[M+H]+	210.16009		5.58	8.97
Ethirimol	C11H19N3O	[M+H]+	210.16009	140.107	5.58	8.97
Ethoprophos	C8H19O2PS2	[M+H]+	243.06369		8.66	13.79
Ethoprophos	C8H19O2PS2	[M+H]+	243.06369	130.9385	8.65	13.79
Etofenprox	C25H28O3	[M+NH4]+	394.23767		11.15	17.16
Etofenprox	C25H28O3	[M+NH4]+	394.23767	177.1274	11.15	17.16
Fenamidone	C17H17N3OS	[M+H]+	312.11651		7.94	12.75
Fenamidone	C17H17N3OS	[M+H]+	312.11651	236.1183	7.94	12.75
Fenamiphos	C13H22NO3PS	[M+H]+	304.11308		8.81	13.99
Fenamiphos	C13H22NO3PS	[M+H]+	304.11308	217.0084	8.81	13.99
Fenamiphos-sulfone	C13H22NO5PS	[M+H]+	336.10291		6.37	10.22
Fenamiphos-sulfone	C13H22NO5PS	[M+H]+	336.10291	266.0249	6.37	10.22
Fenamiphos-sulfoxide	C13H22NO4PS	[M+H]+	320.10799		6.26	9.98
Fenamiphos-sulfoxide	C13H22NO4PS	[M+H]+	320.10799	233.0031	6.26	9.98
Fenazaquin	C20H22N2O	[M+H]+	307.18049		10.85	16.73
Fenazaquin	C20H22N2O	[M+H]+	307.18049	161.1325	10.85	16.73
Fenbendazole	C15H13N3O2S	[M+H]+	300.08012		8.21	13.16
Fenbendazole	C15H13N3O2S	[M+H]+	300.08012	268.0536	8.21	13.16
Fenbuconazole	C19H17ClN4	[M+H]+	337.12145		8.63	13.74
Fenbuconazole	C19H17ClN4	[M+H]+	337.12145	70.04	8.63	13.74
Fenhexamid	C14H17Cl2NO2	[M+H]+	302.07091		8.37	13.4
Fenhexamid	C14H17Cl2NO2	[M+H]+	302.07091	170.0963	8.39	13.39
Fenobucarb	C12H17NO2	[M+H]+	208.13321		7.84	12.63
Fenobucarb	C12H17NO2	[M+H]+	208.13321	152.0708	7.55	12.63
Fenoxycarb	C17H19NO4	[M+H]+	302.13868		8.82	14.02
Fenoxycarb	C17H19NO4	[M+H]+	302.13868	88.0393	8.82	14.02

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Fenpicoxamid	C31H38N2O11	[M+H]+	615.25484		9.76	15.21
Fenpicoxamid	C31H38N2O11	[M+H]+	615.25484	239.0677	9.76	15.21
Fenpropidin	C19H31N	[M+H]+	274.25293		7.27	11.79
Fenpropidin	C19H31N	[M+H]+	274.25293	147.1169	7.27	11.79
Fenpropimorph	C20H33NO	[M+H]+	304.26349		7.46	12.07
Fenpropimorph	C20H33NO	[M+H]+	304.26349	147.117	7.46	12.07
Fenpyrazamine	C17H21N3O2S	[M+H]+	332.14272		8.22	13.4
Fenpyrazamine	C17H21N3O2S	[M+H]+	332.14272	230.1289	8.41	13.4
Fensulfothion	C11H17O4PS2	[M+H]+	309.03786		7.22	11.62
Fensulfothion	C11H17O4PS2	[M+H]+	309.03786	234.9648	7.22	11.62
Fenthion	C10H15O3PS2	[M+H]+	279.0273		9.05	14.41
Fenthion	C10H15O3PS2	[M+H]+	279.0273	247.0011	9.06	14.41
Fenthion-sulfone	C10H15O5PS2	[M+H]+	311.01713		6.69	10.82
Fenthion-sulfone	C10H15O5PS2	[M+H]+	311.01713	278.9909	6.69	10.82
Fenthion-sulfoxide	C10H15O4PS2	[M+H]+	295.02221		6.54	10.51
Fenthion-sulfoxide	C10H15O4PS2	[M+H]+	295.02221	279.9987	6.54	10.51
Fenuron	C9H12N2O	[M+H]+	165.10224		5.07	7.84
Fenuron	C9H12N2O	[M+H]+	165.10224	72.0444	5.07	7.85
Flazasulfuron	C13H12F3N5O5S	[M+H]+	408.0584		7.47	12.04
Flazasulfuron	C13H12F3N5O5S	[M+H]+	408.0584	182.0562	7.47	12.04
Flonicamid	C9H6F3N3O	[M+H]+	230.05357		4.49	6.59
Flonicamid	C9H6F3N3O	[M+H]+	230.05357	203.043	4.49	6.59
Florpyrauxifen-benzyl	C20H14Cl2F2N2O3	[M+H]+	439.04223		9.4	14.78
Florpyrauxifen-benzyl	C20H14Cl2F2N2O3	[M+H]+	439.04223	91.0549	9.4	14.78
Fluacrypyrim	C20H21F3N2O5	[M+H]+	427.14753		9.63	15.1
Fluacrypyrim	C20H21F3N2O5	[M+H]+	427.14753	205.0866	9.63	15.1
Flubendiamide	C23H22F7IN2O4S	[M+H]+	683.0306		9.03	14.24
Flubendiamide	C23H22F7IN2O4S	[M+H]+	683.0306	408.9803	9.03	14.24
Flufenacet	C14H13F4N3O2S	[M+H]+	364.07374		8.61	13.73
Flufenacet	C14H13F4N3O2S	[M+H]+	364.07374	152.0507	8.61	13.73
Fluometuron	C10H11F3N2O	[M+H]+	233.08962		6.95	11.26
Fluometuron	C10H11F3N2O	[M+H]+	233.08962	72.0445	6.68	11.27
Fluopicolide	C14H8Cl3F3N2O	[M+H]+	382.97271		8.19	13.11
Fluopicolide	C14H8Cl3F3N2O	[M+H]+	382.97271	172.9558	8.19	13.11
Fluopyram	C16H11ClF6N2O	[M+H]+	397.05369		8.51	13.56
Fluopyram	C16H11ClF6N2O	[M+H]+	397.05369	208.0137	8.51	13.56
Flupyradifurone	C12H11ClF2N2O2	[M+H]+	289.05499		5.05	7.79
Flupyradifurone	C12H11ClF2N2O2	[M+H]+	289.05499	90.0337	5.07	7.84
Flusilazole	C16H15F2N3Si	[M+H]+	316.10761		8.7	13.99

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Flusilazole	C16H15F2N3Si	[M+H]+	316.10761	247.0751	8.62	13.99
Flutianil	C19H14F4N2OS2	[M+H]+	427.05564		9.19	14.48
Flutianil	C19H14F4N2OS2	[M+H]+	427.05564	193.0513	9.19	14.48
Flutriafol	C16H13F2N3O	[M+H]+	302.10994		7.02	11.36
Flutriafol	C16H13F2N3O	[M+H]+	302.10994	70.0401	7.02	11.36
Fluxapyroxad	C18H12F5N3O	[M+H]+	382.09733		8.14	13.04
Fluxapyroxad	C18H12F5N3O	[M+H]+	382.09733	362.0913	8.14	13.04
Forchlorfenuron	C12H10ClN3O	[M+H]+	248.05852		6.92	11.64
Forchlorfenuron	C12H10ClN3O	[M+H]+	248.05852	129.0214	6.95	11.63
Formetanate	C11H15N3O2	[M+H]+	222.1237		3.78	1.88
Formetanate	C11H15N3O2	[M+H]+	222.1237	165.1024	3.78	1.88
Fosthiazate	C9H18NO3PS2	[M+H]+	284.05385		6.81	11
Fosthiazate	C9H18NO3PS2	[M+H]+	284.05385	227.9915	6.81	11.01
Haloxyfop	C15H11ClF3NO4	[M+H]+	362.04015		8.8	14.01
Haloxyfop	C15H11ClF3NO4	[M+H]+	362.04015	316.0342	8.8	14
Hexaflumuron	C16H8Cl2F6N2O3	[M+H]+	460.98889		9.64	15.11
Hexaflumuron	C16H8Cl2F6N2O3	[M+H]+	460.98889	158.0413	9.64	15.11
Hexythiazox	C17H21ClN2O2S	[M+H]+	353.1085		10.3	16.07
Hexythiazox	C17H21ClN2O2S	[M+H]+	353.1085	228.0246	10.31	16.07
Imazalil	C14H14Cl2N2O	[M+H]+	297.05559		6.62	10.77
Imazalil	C14H14Cl2N2O	[M+H]+	297.05559	158.9764	6.63	10.76
Imidacloprid	C9H10ClN5O2	[M+H]+	256.05958		4.83	7.3
Imidacloprid	C9H10ClN5O2	[M+H]+	256.05958	209.0588	4.83	7.3
Indoxacarb	C22H17ClF3N3O7	[M+H]+	528.07799		9.59	15.04
Indoxacarb	C22H17ClF3N3O7	[M+H]+	528.07799	218.0428	9.73	15.03
Iprovalicarb	C18H28N2O3	[M+H]+	321.21727		8.65	13.74
Iprovalicarb	C18H28N2O3	[M+H]+	321.21727	119.0856	8.65	13.74
Isofetamid	C20H25NO3S	[M+H]+	360.16279		8.45	13.46
Isofetamid	C20H25NO3S	[M+H]+	360.16279	210.059	8.49	13.46
Isoprothiolane	C12H18O4S2	[M+H]+	291.07193		8.22	13.14
Isoprothiolane	C12H18O4S2	[M+H]+	291.07193	144.9777	8.22	13.14
Isoxaflutole	C15H12F3NO4S	[M+H]+	360.05119		7.27	11.76
Isoxaflutole	C15H12F3NO4S	[M+H]+	360.05119	250.9985	7.27	11.76
Linuron	C9H10Cl2N2O2	[M+H]+	249.01921		7.91	12.76
Linuron	C9H10Cl2N2O2	[M+H]+	249.01921	159.9719	7.91	12.76
Lufenuron	C17H8Cl2F8N2O3	[M+H]+	510.9857		10.38	15.8
Lufenuron	C17H8Cl2F8N2O3	[M+H]+	510.9857	158.0413	10.37	15.8
Malathion	C10H19O6PS2	[M+H]+	331.04334		8.22	13.17
Malathion	C10H19O6PS2	[M+H]+	331.04334	210.9648	8.2	13.15

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Malathion-D10	C10(2H)10H9O6PS2	[M+H]+	341.10611		8.17	13.11
Malathion-D10	C10(2H)10H9O6PS2	[M+H]+	341.10611	132.0702	8.17	13.11
Mandipropamid	C23H22ClNO4	[M+H]+	412.13101		8.02	12.79
Mandipropamid	C23H22ClNO4	[M+H]+	412.13101	328.1101	8.02	12.8
Mepanipyrim	C14H13N3	[M+H]+	224.11822		8.53	13.61
Mepanipyrim	C14H13N3	[M+H]+	224.11822	106.0649	8.53	13.61
Metaflumizone (E)	C24H16F6N4O2	[M+H]+	507.12502		9.73	15.68
Metaflumizone (E)	C24H16F6N4O2	[M+H]+	507.12502	116.0494	9.72	15.68
Metaflumizone (Z)	C24H16F6N4O2	[M+H]+	507.12502		10.1	15.68
Metaflumizone (Z)	C24H16F6N4O2	[M+H]+	507.12502	287.0794	10.1	15.68
Metalaxyl	C15H21NO4	[M+H]+	280.15433		7.19	11.59
Metalaxyl	C15H21NO4	[M+H]+	280.15433	192.1383	7.19	11.59
Metconazole	C17H22ClN3O	[M+H]+	320.15242		9.23	14.62
Metconazole	C17H22ClN3O	[M+H]+	320.15242	177.0466	9.12	14.61
Methidathion	C6H11N2O4PS3	[M+H]+	302.96913		7.5	12.15
Methidathion	C6H11N2O4PS3	[M+H]+	302.96913	145.0067	7.5	12.15
Methoxyfenozide	C22H28N2O3	[M+H]+	369.21727		8.41	13.37
Methoxyfenozide	C22H28N2O3	[M+H]+	369.21727	149.0597	8.41	13.37
Metobromuron	C9H11BrN2O2	[M+H]+	259.00767		7.04	11.42
Metobromuron	C9H11BrN2O2	[M+H]+	259.00767	169.96	7.04	11.42
Metrafenone	C19H21BrO5	[M+H]+	409.06451		9.36	14.8
Metrafenone	C19H21BrO5	[M+H]+	409.06451	209.081	9.37	14.81
Monocrotophos	C7H14NO5P	[M+H]+	224.06824		4.6	6.7
Monocrotophos	C7H14NO5P	[M+H]+	224.06824	98.0601	4.6	6.69
Myclobutanil	C15H17ClN4	[M+H]+	289.12145		8.3	13.28
Myclobutanil	C15H17ClN4	[M+H]+	289.12145	70.04	8.3	13.28
Novaluron	C17H9ClF8N2O4	[M+H]+	493.01959		9.75	15.23
Novaluron	C17H9ClF8N2O4	[M+H]+	493.01959	158.0413	9.75	15.23
Omethoate	C5H12NO4PS	[M+H]+	214.02974		3.91	2.03
Omethoate	C5H12NO4PS	[M+H]+	214.02974	154.9926	3.91	2.03
Oxadiargyl	C15H14Cl2N2O3	[M+H]+	341.04542		9.27	14.66
Oxadiargyl	C15H14Cl2N2O3	[M+H]+	341.04542	229.976	9.28	14.66
Oxadixyl	C14H18N2O4	[M+H]+	279.13393		5.78	9.19
Oxadixyl	C14H18N2O4	[M+H]+	279.13393	219.1129	5.78	9.19
Oxasulfuron	C17H18N4O6S	[M+H]+	407.10198		6.03	9.6
Oxasulfuron	C17H18N4O6S	[M+H]+	407.10198	150.0664	6.03	9.6
Oxathiapiprolin	C24H22F5N5O2S	[M+H]+	540.14871		8.11	12.9
Oxathiapiprolin	C24H22F5N5O2S	[M+H]+	540.14871	500.1363	8.11	12.9
Paclobutrazol	C15H20ClN3O	[M+H]+	294.13677		8.15	13.06

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Paclobutrazol	C15H20ClN3O	[M+H]+	294.13677	70.04	8.16	13.07
Penconazole	C13H15Cl2N3	[M+H]+	284.07158		9.04	14.37
Penconazole	C13H15Cl2N3	[M+H]+	284.07158	70.0401	9.04	14.37
Pencycuron	C19H21ClN2O	[M+H]+	329.14152		9.51	14.97
Pencycuron	C19H21ClN2O	[M+H]+	329.14152	125.0153	9.5	14.97
Penflufen	C18H24FN3O	[M+H]+	318.19762		8.99	14.24
Penflufen	C18H24FN3O	[M+H]+	318.19762	234.1038	8.99	14.24
Phenthoate	C12H17O4PS2	[M+H]+	321.03786		8.97	14.25
Phenthoate	C12H17O4PS2	[M+H]+	321.03786	135.0442	8.97	14.26
Phosmet	C11H12NO4PS2	[M+H]+	318.00181		7.62	12.33
Phosmet	C11H12NO4PS2	[M+H]+	318.00181	160.0395	7.63	12.33
Pirimicarb	C11H18N4O2	[M+H]+	239.15025		5.82	9.41
Pirimicarb	C11H18N4O2	[M+H]+	239.15025	182.1291	5.82	9.41
Pirimiphos-methyl	C11H20N3O3PS	[M+H]+	306.10358		9.27	14.7
Pirimiphos-methyl	C11H20N3O3PS	[M+H]+	306.10358	136.0872	9.27	14.7
Profenofos	C11H15BrClO3PS	[M+H]+	372.94242		9.89	15.5
Profenofos	C11H15(81Br)ClO3PS	[M+H]+	374.94037	304.862	9.89	15.5
Propamocarb	C9H20N2O2	[M+H]+	189.15975		3.91	1.91
Propamocarb	C9H20N2O2	[M+H]+	189.15975	74.0236	3.91	1.91
Propaquizafop	C22H22ClN3O5	[M+H]+	444.13207		9.86	15.43
Propaquizafop	C22H22ClN3O5	[M+H]+	444.13207	100.0757	9.86	15.43
Propiconazole	C15H17Cl2N3O2	[M+H]+	342.07706		9.2	14.42
Propiconazole	C15H17Cl2N3O2	[M+H]+	342.07706	186.9714	9.07	14.6
Propyzamide	C12H11Cl2NO	[M+H]+	256.02905		8.25	13.26
Propyzamide	C12H11Cl2NO	[M+H]+	256.02905	189.9822	8.24	13.26
Proquinazid	C14H17IN2O2	[M+H]+	373.04075		10.54	16.41
Proquinazid	C14H17IN2O2	[M+H]+	373.04075	271.9204	10.54	16.4
Prosulfocarb	C14H21NOS	[M+H]+	252.14166		9.78	15.37
Prosulfocarb	C14H21NOS	[M+H]+	252.14166	128.1072	9.78	15.38
Pyraclostrobin	C19H18ClN3O4	[M+H]+	388.10586		9.21	14.53
Pyraclostrobin	C19H18ClN3O4	[M+H]+	388.10586	163.0628	9.21	14.53
Pyridaben	C19H25ClN2OS	[M+H]+	365.14489		10.77	16.63
Pyridaben	C19H25ClN2OS	[M+H]+	365.14489	309.0826	10.77	16.63
Pyridalyl	C18H14(37Cl)Cl3F3NO3	[M+H]+	491.97231		11.42	17.49
Pyridalyl	C18H14(37Cl)Cl3F3NO3	[M+H]+	491.97231	108.9607	11.43	17.49
Pyridate	C19H23ClN2O2S	[M+H]+	379.12415		11.21	16.94
Pyridate	C19H23ClN2O2S	[M+H]+	379.12415	207.0321	11.22	16.94
Pyrimethanil	C12H13N3	[M+H]+	200.11822		7.55	12.24
Pyrimethanil	C12H13N3	[M+H]+	200.11822	168.068	7.55	12.24

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Pyriofenone	C18H20ClNO5	[M+H]+	366.11028		9.37	14.84
Pyriofenone	C18H20ClNO5	[M+H]+	366.11028	184.0165	9.37	14.84
Pyriproxyfen	C20H19NO3	[M+H]+	322.14377		10.05	15.73
Pyriproxyfen	C20H19NO3	[M+H]+	322.14377	185.0598	10.05	15.73
Quinalphos	C12H15N2O3PS	[M+H]+	299.06138		8.87	14.28
Quinalphos	C12H15N2O3PS	[M+H]+	299.06138	242.9988	8.98	14.28
Quinoclamine	C10H6ClNO2	[M+H]+	208.01598		6.21	9.97
Quinoclamine	C10H6ClNO2	[M+H]+	208.01598	172.0392	6.21	9.97
Quinoxyfen	C15H8Cl2FNO	[M+H]+	308.00397		10.16	15.88
Quinoxyfen	C15H8Cl2FNO	[M+H]+	308.00397	272.0272	10.15	15.88
Quizalofop	C17H13ClN2O4	[M+H]+	345.06366		8.56	13.65
Quizalofop	C17H13ClN2O4	[M+H]+	345.06366	299.0583	8.56	13.65
Quizalofop-ethyl	C19H17ClN2O4	[M+H]+	373.09496		9.72	15.26
Quizalofop-ethyl	C19H17ClN2O4	[M+H]+	373.09496	299.0584	9.72	15.26
Rotenone	C23H22O6	[M+H]+	395.14891		8.65	13.76
Rotenone	C23H22O6	[M+H]+	395.14891	175.0755	8.65	13.71
Spinetoram J	C42H69NO10	[M+H]+	748.49942		9.34	14.68
Spinetoram J	C42H69NO10	[M+H]+	748.49942	142.1227	9.34	14.68
Spinetoram L	C43H69NO10	[M+H]+	760.49942		9.66	15.12
Spinetoram L	C43H69NO10	[M+H]+	760.49942	142.1227	9.66	15.12
Spinosyn A	C41H65NO10	[M+H]+	732.46812		8.93	14.13
Spinosyn A	C41H65NO10	[M+H]+	732.46812	142.1226	8.93	14.13
Spinosyn D	C42H67NO10	[M+H]+	746.48377		9.28	14.61
Spinosyn D	C42H67NO10	[M+H]+	746.48377	142.1227	9.33	14.67
Spirodiclofen	C21H24Cl2O4	[M+H]+	411.11244		11.04	16.54
Spirodiclofen	C21H24Cl2O4	[M+H]+	411.11244	313.0393	11.06	16.54
Spirotetramat	C21H27NO5	[M+H]+	374.1962		8.48	13.48
Spirotetramat	C21H27NO5	[M+H]+	374.1962	302.1752	8.48	13.48
Tebuconazole	C16H22ClN3O	[M+H]+	308.15242		9.02	14.32
Tebuconazole	C16H22ClN3O	[M+H]+	308.15242	70.0402	9	14.3
Tebufenozide	C22H28N2O2	[M+H]+	353.22235		8.86	14.26
Tebufenozide	C22H28N2O2	[M+H]+	353.22235	133.065	8.88	14.27
Tebufenpyrad	C18H24ClN3O	[M+H]+	334.16807		9.96	15.55
Tebufenpyrad	C18H24ClN3O	[M+H]+	334.16807	147.1169	9.96	15.55
Terbuthylazine	C9H16ClN5	[M+H]+	230.1167		8.16	12.81
Terbuthylazine	C9H16ClN5	[M+H]+	230.1167	174.0542	8.16	13.06
Thiabendazole	C10H7N3S	[M+H]+	202.04334		4.88	7.58
Thiabendazole	C10H7N3S	[M+H]+	202.04334	175.0324	4.88	7.58
Thiacloprid	C10H9ClN4S	[M+H]+	253.03092		5.43	8.47

Compound	Chemical Formula	Adduct	Precursor (m/z)	Fragment (m/z)	Retention time (min) 10 cm column	Retention time (min) 15 cm column
Thiacloprid	C10H9ClN4S	[M+H]+	253.03092	126.0106	5.43	8.47
Thiamethoxam	C8H10ClN5O3S	[M+H]+	292.02656		4.5	6.47
Thiamethoxam	C8H10ClN5O3S	[M+H]+	292.02656	211.065	4.5	6.47
Tolfenpyrad	C21H22ClN3O2	[M+H]+	384.14733		10.1	15.53
Tolfenpyrad	C21H22ClN3O2	[M+H]+	384.14733	197.0965	9.98	15.59
Triadimefon	C14H16ClN3O2	[M+H]+	294.10038		8.28	13.25
Triadimefon	C14H16ClN3O2	[M+H]+	294.10038	171.1381	8.18	13.14
Triallate	C10H16Cl3NOS	[M+H]+	304.00909		10.33	16.13
Triallate	C10H16Cl3NOS	[M+H]+	304.00909	142.9217	10.34	16.13
Triazophos	C12H16N3O3PS	[M+H]+	314.07228		8.44	13.44
Triazophos	C12H16N3O3PS	[M+H]+	314.07228	162.0662	8.44	13.45
Tricyclazole	C9H7N3S	[M+H]+	190.04334		5.67	8.89
Tricyclazole	C9H7N3S	[M+H]+	190.04334	136.0216	5.67	8.9
Trifloxystrobin	C20H19F3N2O4	[M+H]+	409.13697		9.69	15.19
Trifloxystrobin	C20H19F3N2O4	[M+H]+	409.13697	186.0527	9.69	15.19
Triflumizole	C15H15ClF3N3O	[M+H]+	346.09285		9.81	15.39
Triflumizole	C15H15ClF3N3O	[M+H]+	346.09285	278.0557	9.81	15.39
Triflumuron	C15H10ClF3N2O3	[M+H]+	359.04048		9.21	14.61
Triflumuron	C15H10ClF3N2O3	[M+H]+	359.04048	156.0212	9.25	14.61
Triticonazole	C17H20ClN3O	[M+H]+	318.13677		8.52	13.5
Triticonazole	C17H20ClN3O	[M+H]+	318.13677	70.0401	8.3	13.5
Zoxamide	C14H16Cl3NO2	[M+H]+	336.03194		9.19	14.6
Zoxamide	C14H16Cl3NO2	[M+H]+	336.03194	186.9715	9.2	14.6