

APPLICATIONS

Determination of Pesticide Residues in Cannabis by LC-MS/MS

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Scott enjoys surfing and eating. He is crazy about chromatography, because his mom is really into CSI and thinks that is what he does.

Introduction

While legalization of medical and recreational marijuana is proliferating through more and more states throughout the United States, the use of cannabis remains illegal on a federal level. As such, there are no nationally approved pesticides for use, leaving growers without guidance for suitable pesticides and limits. As cannabis consumption increases, so are the risk of pesticides being consumed at harmful levels.

Oregon has the most comprehensive guide/list for pesticides, and many labs outside of Oregon are also adopting these in anticipation of upcoming regulation. The current Oregon pesticides guide/list covers a range of pesticides with diverse chemical properties. When a suitable analytical method is developed using this list, it would be easy to include additional pesticides that may be necessary in different regions. The LC-MS/MS method detailed here makes use of sample prep dilution with reversed phase HPLC column chemistries with resolving power for the multiresidue pesticides of interest. Orthogonal Kinetex[®] and Luna[®] Omega column chemistries provide a complimentary selectivity as well as sensitivity for both standards in solvent and cannabis matrix. Sensitivity is achieved on two different triple quadrupole mass spectrometer platforms: SCIEX QTRAP[®] 4500 and 6500+. The chromatography is demonstrated here on a SCIEX Triple Quad 3500[™] on abbreviated 50 mm length columns.

Experimental Conditions

Equipment and materials

SCIEX ExionLC[™] AC pumps and autosampler were used along with a SCIEX QTRAP 4500 and 6500+, positive polarity, with Turbo V[™] and electrospray (ESI) for detection, here on a SCIEX Triple Quad 3500[™].

Sample Preparation:

Sonicate 200 mg of homogenized sample in 5 mL acetonitrile for 15 minutes. Vortex and centrifuge extracted samples. The extracts are then subjected to dilution with a methanol solution and filtered through a Phenex[™] 0.2 μm polyethersulfone (PES) membrane syringe filter (p/n: AF0-8208-52) into an LC autosampler vial for LC-MS/MS analysis.

LC-MS/MS Method Parameters

Column: Kinetex 2.6 μm Biphenyl 50 x 4.6 mm or
Luna Omega 3 μm Polar C18 50 x 4.6 mm

Recommended Guard: SecurityGuard[™] ULTRA Cartridges

Part No.: AJO-9502

Mobile Phase: A: 5mM Ammonium formate + 0.1% Formic acid in Water
B: 5mM Ammonium formate + 0.1% Formic acid in 98:2
Methanol:Water

Gradient:	Time (min)	B (%)
	0	10
	1	100
	4.3	80
	8.7	95
	10.5	95
	10.6	10
	16	10

Flow Rate: 0.4 mL/min

Inj. Volume: 10 μL

Temperature: 40 °C

Detection: MS/MS (ESI+)

Detector: SCIEX 3500 Triple Quad

The 16 minute LC gradient chromatographically separates all pesticide residues of interest as well as observed endogenous cannabis flower interferences, and the same gradient and run-time can be used on 150 mm length columns for greater capacity and lifetime.

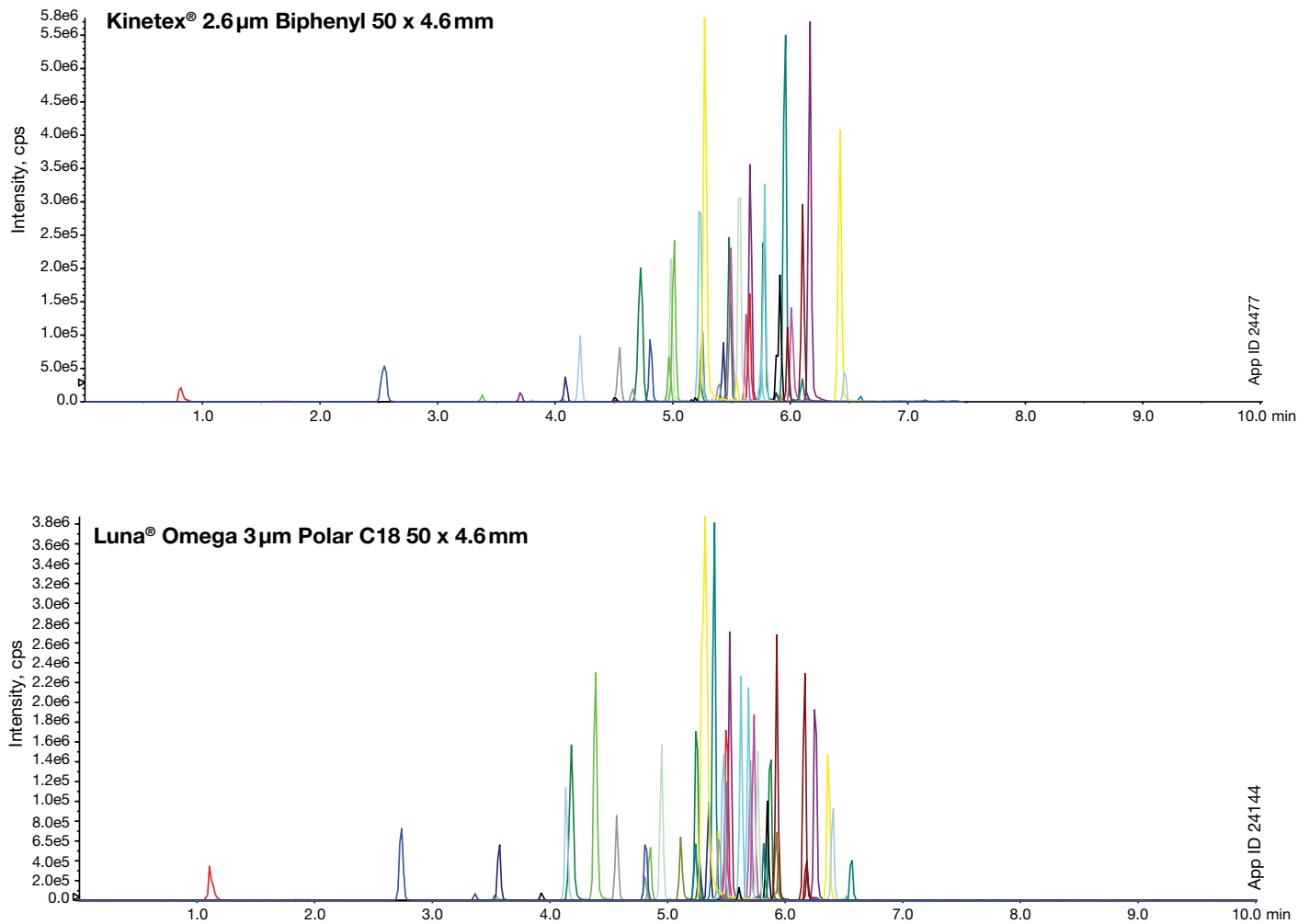


Table 1. Mass Transitions and Retention Times

Name	Q1	Q3	Expected RT (min) Kinetex [®] Biphenyl	Expected RT (min) Luna [®] Omega Polar C18
Acephate 1	184.1	142.9	1.3	2.8
Acequinocyl 1	402.2	343.2	9.7	7.2
Acetamidrid 1	223.2	126.1	4.9	4.3
Aldicarb 1	208.1	116	5.3	4.6
Avermectin B1a 1	890.5	305	9	6.5
Avermectin B1b 1	876.5	291.2	8.9	-
Azoxystrobin 1	404.1	372.1	7.1	5.4
Bifenazate 1	301.1	198.1	7.4	5.6
Bifenthrin 1	440.2	181.1	9.2	6.6
Boscalid 1	343	307	7.2	5.5
Carbaryl 1	202.1	145	6.1	5
Carbofuran 1	222.1	123	6	4.9
Chlorantraniliprole 1	483.9	285.9	6.9	5.3
Chlorpyrifos 1	350	96.9	8.5	6.2
Clofentezine 1	303	138	7.9	6
Cyfluthrin 1	451.1	191	8.7	6.3
Cypermethrin 1	433.1	191	8.8	6.3
Daminozide 1	161.2	143.1	0.3	1.1
Diazinon 1	305.1	169.1	7.8	5.9
Dichlorvos 1	220.9	109.1	5.8	4.9
Dimethoate 1	230	199.1	4.5	4.2
Ethoprophos 1	243	131	7.5	5.8
Etofenprox 1	394	177.3	9.1	6.6
Etoxazole 1	360.2	141	8.6	6.3
Fenoxycarb 1	302.2	87.9	7.7	5.7
Fenpyroximate 1	422.2	366.1	8.8	6.41
Fipronil 1	436.8	367.9	7.6	5.7
Fonicamid 1	230	203.2	3.3	3.6
Fludioxinil 1	266	229	7.1	5.5
Hexythiazox 1	353.1	228	8.5	6.2
Imazalil 1	296.9	158.9	6.5	5.1
Imidacloprid 1	255.9	209.1	4.4	4

Name	Q1	Q3	Expected RT (min) Kinetex Biphenyl	Expected RT (min) Luna Omega Polar C18
Kresoxim-methyl 1	314	116	7.7	5.8
Malathion A 1	331.1	127.1	7.2	5.6
Metalaxyl 1	280.2	192.3	6.7	5.3
Methiocarb 1	226.1	169.2	7	5.5
Methomyl 1	163.1	88.1	3.5	3.6
Myclobutanil 1	289.1	70.1	7.3	5.5
Naled 1	382.8	127.1	6.8	5.3
Oxamyl 1	220.2	72	3.5	3.4
Paclobutrazol 1	294.1	70.1	7.2	5.5
Parathion-methyl 1	264	124.9	7	-
Permethrin, cis- 1	408.1	355.1	9.1	6.4
Permethrin, trans- 1	408.1	355.1	9.1	6.5
Phosmet 1	318	160	6.9	5.4
Piperonyl butoxide 1	356.2	177.1	8.4	6.2
Prallethrin 1	301.3	123	8.1	6
Propiconazole 1	342.1	159	7.9	5.9
Propoxure 1	210.1	111.1	5.9	4.9
Pyrethrins Cinerin 1	361.2	149.1	8.2	6
Pyrethrins Jasmolin 1	375.2	163.2	8.4	6.2
Pyrethrins Pyrethrin 1	329.3	133.2	8.7	6.3
Pyridaben 1	365.1	309.1	8.9	6.4
Spinosyn A 1	732.4	142.2	8.1	5.8
Spinosyn D 1	746.4	142.2	8.2	5.9
Spiromesifen 1	371.3	273.3	8.7	6.3
Spirotetramat 1	374.2	302.2	7.5	5.7
Spiroxamine 1	298.3	144.2	7.2	5.4
Tebuconazole 1	308.1	70.1	7.7	5.8
Thiacloprid 1	253	126	5.2	4.5
Thiamethoxam 1	292	211	3.8	3.7
Trifloxystrobin 1	409.1	186.1	8.1	6
Uniconazole 1	292.1	70.1	7.3	5.5
Fipronil NH4 1	454	368	7.6	5.5

Figure 2. Representative Chromatograms



Results and Discussion

Described is a dependable LC-MS/MS method covering 59 pesticides in the Oregon guide/list plus 5 representative internal standards that are run routinely on the Kinetex Biphenyl core-shell column chemistry, where the enhanced polar and aromatic selectivity from the Biphenyl column chemistry concurrent with aliphatic selectivity from the carbon skeleton has proven to be an excellent column chemistry for multi-residue screening methods.

In addition, the Luna Omega Polar C18 column chemistry also works very well for multiresidue screening methods, with the polar functionality enhancing polar retention through dipole-dipole and hydrogen bonding interactions, while the C18 ligand maintains the range of hydrophobic selectivity.

Conclusion

Kinetex Biphenyl and Luna Omega Polar C18 column chemistries are excellent as a complimentary pair for multi-residue pesticide LC-MS/MS screening, each working well independently for the Oregon pesticide target list in Cannabis, and both available across UHPLC and HPLC dimensions. With the diverse range of samples that could require testing, from dry flowers and concentrated oils to lotions and edibles, having the option of complimentary column chemistries that are each suitable can be advantageous when different ion-suppressing matrix interferences arise from different samples.



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Luna[®] Omega Polar C18 LC Column Ordering Information

1.6 µm Minibore Columns (mm)

Phases	30 x 2.1	50 x 2.1	100 x 2.1	150 x 2.1	SecurityGuard [™] ULTRA Cartridges [‡]
Polar C18	00A-4748-AN	00B-4748-AN	00D-4748-AN	00F-4748-AN	AJO-9505 for 2.1 mm ID

3 µm Minibore and Midbore[™] Columns (mm)

Phases	30 x 2.1	50 x 2.1	100 x 2.1	150 x 2.1	50 x 3.0	100 x 3.0	150 x 3.0	SecurityGuard [™] Cartridges (mm)
Polar C18	00A-4760-AN	00B-4760-AN	00D-4760-AN	00F-4760-AN	00B-4760-YO	00D-4760-YO	00F-4760-YO	4 x 2.0* AJ0-7600 for ID: 2.0 - 3.0 mm

3 µm Analytical Columns (mm)

Phases	50 x 4.6	100 x 4.6	150 x 4.6	250 x 4.6	SecurityGuard [™] Cartridges (mm)
Polar C18	00B-4760-E0	00D-4760-E0	00F-4760-E0	00G-4760-E0	4 x 3.0* AJ0-7601 for ID: 3.1-8.0 mm

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Kinetex Core-Shell Column Ordering Information

1.7 µm Minibore Columns (mm)

Phases	50 x 2.1	100 x 2.1	150 x 2.1	SecurityGuard [™] ULTRA Cartridges [‡]
Biphenyl	00B-4628-AN	00D-4628-AN	00F-4628-AN	3/pk AJ0-9209 for 2.1 mm ID

[‡]SecurityGuard ULTRA Cartridges require holder, Part No.: AJ0-9000

2.6 µm Minibore Columns (mm)

Phases	30 x 2.1	50 x 2.1	100 x 2.1	150 x 2.1	SecurityGuard [™] ULTRA Cartridges [‡]
Biphenyl	00A-4622-AN	00B-4622-AN	00D-4622-AN	00F-4622-AN	3/pk AJ0-9209 for 2.1 mm ID

2.6 µm MidBore Columns (mm)

Phases	50 x 3.0	100 x 3.0	150 x 3.0	SecurityGuard [™] ULTRA Cartridges [‡]
Biphenyl	00B-4622-Y0	00D-4622-Y0	00F-4622-Y0	3/pk AJ0-9208 for 3.0 mm ID

2.6 µm Analytical Columns (mm)

Phases	50 x 4.6	100 x 4.6	150 x 4.6	SecurityGuard [™] ULTRA Cartridges [‡]
Biphenyl	00B-4622-E0	00D-4622-E0	00F-4622-E0	3/pk AJ0-9207 for 4.6 mm ID

[‡]SecurityGuard ULTRA Cartridges require holder, Part No.: AJ0-9000

* SecurityGuard Analytical Cartridges require holder, Part No.: KJ0-4282



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