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アプリケーションノート

Determination of Pesticide and Mycotoxin Residues in Dried Cannabis Flower: LC-MS/MS and GC-MS/MS Methodology to Meet the Recommended AOAC Regulatory Requirements for US States and Canada

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Abstract

The methodology presented in this application note is used to determine pesticides and mycotoxin residues in cannabis flower currently regulated by any of the US states or Canada at the AOAC-recommended LOQ.

Benefits

- Sensitive method to meet US and Canada requirements for all regulated pesticides and mycotoxins
- Simple sample preparation and cleanup followed by rapid LC-MS/MS and APGC-MS/MS analysis using the same mass spectrometer

Introduction

Although cannabis products are legal for medicinal or recreational use in many US states and in Canada,

there are currently no harmonized guidelines for pesticide and mycotoxin residue tolerances. Consequently, each state or nation with legalized cannabis has its own list of such contaminants with legal residue tolerance limits that may be quite different in each region. Moreover, AOAC has published Standard Method Performance Requirements (SPMRs) to describe the minimum recommended performance characteristics to be used to evaluate methods for determination of pesticides in cannabis.[1] AOAC has used the lowest tolerance level from any of the US states or Canada as the target action level for any proposed method with a recommended LOQ at 50% of the action level. These criteria are used for evaluation of validation study data for methods under consideration for AOAC Official Methods of Analysis; they also are commonly used as acceptance criteria for verification at user laboratories. The methodology presented in this application note is suitable, with a few exceptions, to determine pesticides and mycotoxins currently regulated by any of the US states or Canada at the AOAC-recommended LOQ. In their SMPR document, AOAC has also included twenty-nine pesticides that do not currently have a regulatory requirement in the US or in Canada. For these pesticides, the AOAC Cannabis working group has recommended an arbitrary target LOQ of 0.005 ppm (mg/kg).

Because it is convenient and efficient to determine mycotoxins and pesticides in one analysis from the same extract, sample preparation was developed with this approach in mind. Although most of the target pesticides and mycotoxins are amenable to LC-MS/MS analysis, many compounds have much lower detection limits using GC-MS/MS methods. Consequently, to obtain the low detection limits required, both types of chromatography were employed for this study. APGC (atmospheric pressure ionization for GC-MS) was chosen for the GC amenable compounds due to its greater specificity and selectivity compared with EI (electron ionization) mass spectrometry. Another significant benefit to this approach is that APGC-MS/MS can be performed on the same mass-spectrometer as LC-MS/MS.

Experimental

Materials and reagents

Standard compounds

Pesticide standards (certified reference materials) were obtained from Chem Service Inc. (West Chester, PA) in the form of six prepared mixes for the Canada cannabis pesticide list (95 compounds). Additional individual pesticide standards were obtained from Accustandard (New Haven, CT), Sigma-Aldrich, Inc. (St. Louis, MO), and from Chem Service. Mycotoxin standards were obtained from Sigma-Aldrich.

Reagents

LC-MS grade solvents for sample extractions and LC mobile phases were obtained from Honeywell-Burdick

& Jackson(Muskegon, MI). Formic acid was from Sigma-Aldrich. Reagent water for LC-MS was prepared in house (Milli-Q). Acetone and hexanes (LC-MS grade) were obtained from Thermo Fisher Scientific (Waltham, MA).

Sample preparation

Cannabis samples were obtained from local sources (Massachusetts) and were prepared at ProVerde Laboratories (Milford, MA). 0.5 gm samples were weighed into 50 mL centrifuge tubes. 10 mL of acetonitrile was added along with two stainless steel grinding balls. The samples were then processed with a Geno/Grinder (SPEX, Metuchen, NJ) for three minutes at 1500 RPM. After centrifugation (five minutes at 3000 RCF), aliquots of each sample were taken for passthrough SPE cleanup prior to LC-MS or dispersive SPE (dSPE) cleanup prior to GC-MS.

Fortified (spiked) samples

A mixed spiking solution containing all analytes was prepared at a concentration of 1 µg/mL in acetonitrile (prepared as needed and kept in freezer for 1 week maximum). Fortified samples (six replicates per level), were prepared at 0.010, 0.020, 0.050, and 0.100 ppm by spiking appropriate amounts of diluted mixed standard onto pre-weighed 0.5 gm cannabis samples. The fortified samples were then subjected to the extraction and cleanup procedures described in this section.

SPE cleanup for LC-MS samples with Oasis PRiME HLB (3 cc, 150 mg)

The Oasis PRiME HLB cartridge (p/n: 186008717) was positioned on a vacuum manifold; no conditioning or equilibration steps were employed. Remove 2.25 mL extract, add 0.25 mL water; A 0.75 mL portion of the sample extract was passed through the cartridge and discarded to waste. Then, after collection vessels were installed, a 1.75 mL portion of the extract was passed through the cartridge and collected for transfer to the LC-MS sample vial. To improve the chromatography for early eluting compounds, 100 µL of methanol were added to 1.0 mL of cleaned extract prior to injection.

dSPE cleanup for GC-MS samples

900 µL of 50:50 acetone/hexanes were transferred to a dSPE tube containing 150 mg $MgSO_4$, 50 mg PSA, 50 mg C_{18}, and 7.5 mg graphitized carbon black. 100 µL of sample extract were then added to the tube and the capped tube was vortexed for ten seconds and shaken vigorously for one minute. After centrifugation (one minute at 9400 RCF), a portion of the extract was transferred to the GC-MS sample vial. Note that this protocol involves a 10:1 dilution of the initial acetonitrilebased sample extract.

Calibration

Matrix-matched calibration curves were prepared for each compound covering the range from 0.001 ppm to

2.00 ppm initial sample concentration (LC-MS) and 0.004 to 0.500 ppm initial sample concentration (GC-MS). For LC-MS/MS, the standards were prepared to account for an effective 20:1 dilution of the initial sample concentration (0.5 g sample extracted into 10 mL). For GC-MS/MS, the standards were prepared to account for an effective 200:1 dilution of the initial sample concentration (further 10:1 dilution of the initial sample extract). For each spiking level, four replicate equivalent matrix matched standards were prepared from blank matrix extracts and analyzed as continuing calibration standards.

Instrumentation and software

A Waters ACQUITY UPLC H-Class PLUS System coupled with a Waters Xevo TQ-XS Tandem Quadrupole Mass Spectrometer was used for the LC pesticides and mycotoxins (LC-MS/MS). An Agilent 7890A gas chromatograph coupled with a Waters Xevo TQ-XS Tandem Quadrupole Mass Spectrometer was used for the GC pesticides (APGC-MS/MS). MassLynx MS Software (v4.2) was used for data acquisition and processing.

The APGC compounds were determined using the proton transfer mode (water in source) except for chlordane, pentachloronitrobenzene, and endosulfan sulfate. The latter three compounds were determined in a separate injection using the charge transfer mode (dry source).

LC conditions

Column:	XBridge BEH C_{18} XP (2.5 µm, 2.1 mm × 150 mm) (p/n: 186006709)
Flow rate:	0.400 mL/min
Mobile phase A:	5 mM ammonium formate with 0.10% formic acid in water
Mobile phase B:	Methanol
Injection volume:	10 µL
Column temp.:	50 °C
Weak wash:	50:50 Methanol:water
Strong wash:	Acetonitrile

Seal wash:	10:90 Acetonitrile:water

Time	%A	%B
0	98	2
0.2	98	2
4.0	30	70
10.0	30	70
15.0	5	95
17.0	1	99
18.0	98	2
20.0	98	2

LC-MS conditions

Mode:	MRM, Positive and Negative Ion Electrospray (ESI+/ESI-)
Capillary voltage:	3.0 kV (+), 2.5 kV (-)
Source temp:	150 °C
Desolvation temp.:	600 °C
Desolvation gas flow:	1000 L/hr
Cone gas flow:	150 L/hr

Collision gas flow:	0.15 mL/min
MRM transitions and associated conditions:	Summarized in Appendix A

GC conditions

Column:	Rxi-5MS (30 m × 0.25 mm × 0.25 µm)
Carrier gas:	Helium @ 1 mL/min
Injection volume:	1 µL (2 µL for charge transfer compounds)
Injector temp.:	260 °C
Mode:	Pulsed, splitless
Pulse time:	1.0 min
Pulse pressure:	35 psi
Inlet liner:	Single taper splitless with glass wool
Interface temp.:	320 °C
Temp. program:	Initial temp.: 70 °C Initial time: 1.0 min

Rate (°C/min)	Final temp (°C)	Hold time (min)	Total time (min)
35	180	0.0	
10	200	0.0	
8	320	5.0	26.14

APGC-MS conditions

Mode:	MRM, Positive Ion Atmospheric Pressure

	Ionization (API+) Proton Transfer Mode (water in source) for all compounds except Charge Transfer Mode (dry source) for chlordane, pentachloronitrobenzene, and endosulfan sulfate
Source temp.:	150 °C
Transfer line temp.:	320 °C
Corona:	2.9 µA
Auxiliary gas flow:	200 L/hr
Cone gas flow:	200 L/hr
Collision gas flow:	0.15 mL/min
Solvent delay:	4 min
MRM transitions:	Summarized in Appendix B

Results and Discussion

Sample Preparation

The Oasis PRiME HLB pass-through cleanup protocol removes about 50% of cannabinoids and over 95% of chlorophyll, fats, and phospholipids. The dispersive SPE approach used for the GC-MS analysis would remove 70% or more of cannabis resin with comparable performance for removal of the other substances. Yet, dSPE was not chosen for LC analysis. The dSPE cleanup relies on the anion-exchange behavior of PSA sorbent to remove acidic phospholipids and weakly acidic cannabinoids from the cannabis extract. However, daminozide and any other acidic compound of interest will also be removed from the extract. Therefore, the dSPE approach was not used for the LC compounds.

Pesticides Analysis

Figure 1 shows calibration curves and chromatograms obtained for two representative LC-MS/MS compounds, spirodiclofen and etoxazole, at the 0.010 ppm spiking level. Figure 2 shows typical calibration curves and chromatograms obtained for two representative APGC-MS/MS compounds, azoxystrobin, and fensulfothion at the 0.010 ppm spiking level.

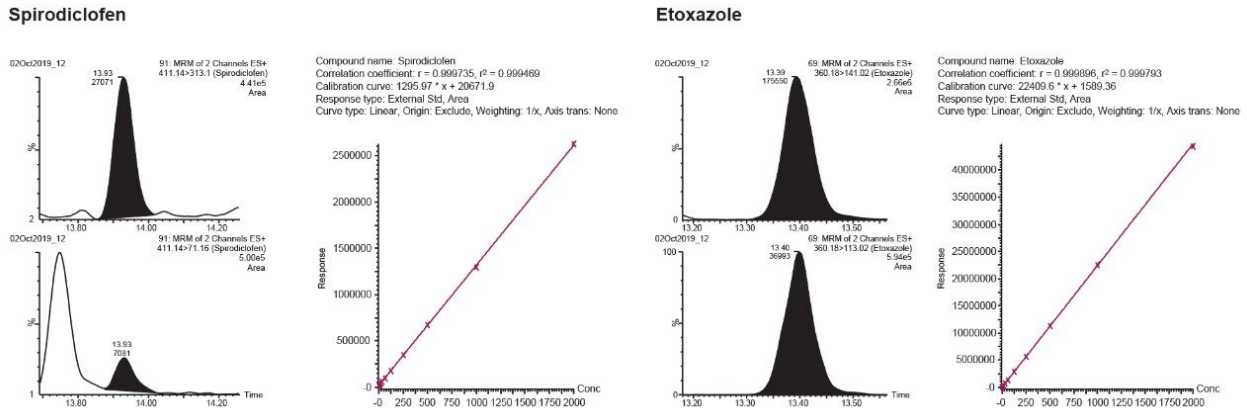

Figure 1. Typical chromatograms (two MRM transitions) and calibration curve obtained for representative LC-MS/MS compounds at the 0.010 ppm spiking level.

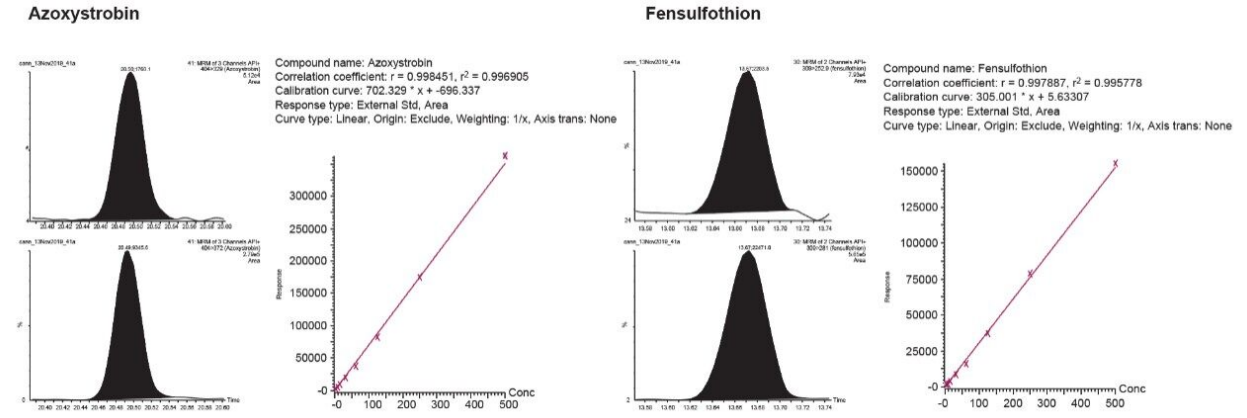

Figure 2. Typical chromatograms (two MRM transitions) and calibration curve obtained for representative APGC-MS/MS compounds at the 0.010 ppm spiking level.

Resmethrin and thiophanate methyl did not show acceptable recovery. In both cases, significant degradation occurred in the initial extracts prior to any cleanup steps. A follow-up experiment indicated that thiophanate methyl was nearly quantitatively transformed to carbendazim and can be determined with high recovery as that degradant. The resmethrin degradant has not yet been identified.

Mycotoxin Analysis

Figure 3 shows typical calibration curves and chromatograms obtained for aflatoxin B2 determined by LC-MS/MS at the 0.010 ppm spiking level.

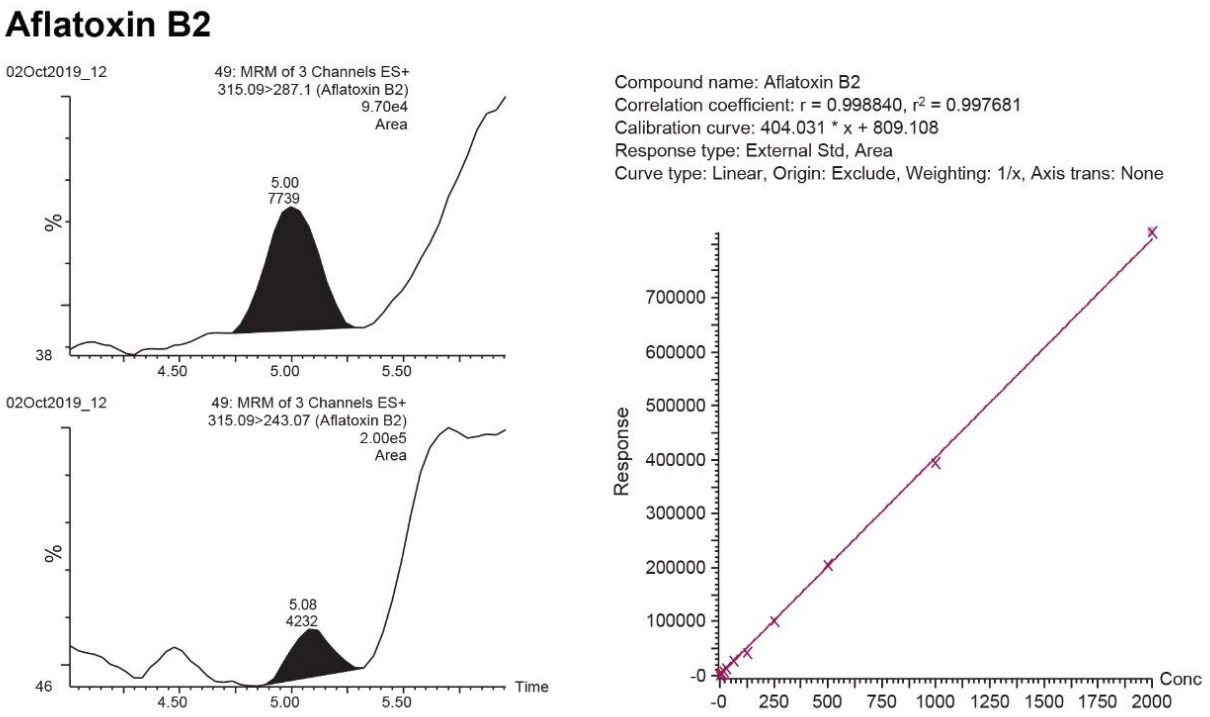

Figure 3. Typical chromatogram (two MRM transitions) and calibration curve obtained for Aflatoxin B2 at the 0.010 ppm spiking level.

Recovery results for pesticides and mycotoxins are presented in Table 1 (LC-MS/MS compounds) and Table 2 (APGC-MS/MS compounds). Recovery for each compound was calculated from data obtained from six replicate samples spiked at four different fortification levels. The observed method LOQ was estimated based on the signal/noise ratio from the lowest spiked recovery samples showing acceptable method performance. Of the one hundred five pesticides listed in the AOAC SMPR, twenty-nine do not currently have a regulatory imposed action limit from any US state or Canada. For these pesticides, AOAC recommends an LOQ of 0.005 ppm.

Table 1

Pesticides	RT	%Recovery (% RSD)				Lowest action level	Method LOQ
		0.01 ppm	0.02 ppm	0.05 ppm	0.100 ppm	ppm	ppm
Abamectin B1a	15.31	100 (11)	90(7)	87(11)	89(4)	0.050	0.010
Abamectin B1b	14.87	74 (11)	89(8)	78(4)	91(4)	0.050	0.010
Acephate	2.93	76(10)	98(7)	83(6)	96(4)	0.100	0.010
Acequinocyl	17.05	94(7)	90(8)	90(5)	87(2)	0.100	0.010
Acetamiprid	4.39	93(18)	82(8)	75(13)	91(18)	0.100	0.010
Aflatoxin B1	5.11	70(11)	90(16)	72(6)	70(4)	N/A	0.010
Aflatoxin B2	4.99	91(10)	85(17)	89(16)	89(9)	N/A	0.010
Aflatoxin G1	4.84	88(17)	84(6)	82(17)	87(6)	N/A	0.010
Aflatoxin G2	4.65	89(18)	78(16)	70(13)	90(5)	N/A	0.010
Aldicarb	4.9	106(7)	88(16)	89(17)	95(16)	0.100	0.010
Allethrin	11.54	LOQ	95(9)	86(7)	93(4)	0.100	0.020
Azadirachtin	5.43	LOQ	LOQ	LOQ	108(17)	0.100	≥0.100
Bifenazate	6.64	85(17)	97(19)	89(3)	87(11)	0.010	0.004
Boscalid	6.25	LOQ	94(20)	81(16)	93(9)	0.100	0.020
Buprofenzin	10.87	74(6)	94(4)	76(3)	90(6)	0.100	0.010
Carbaryl	5.39	113(9)	90(4)	63(12)	102(10)	0.200	0.010
Carbofuran	5.35	88(4)	85(9)	98(11)	95(10)	0.100	0.010
Chlorantraniliprole	5.89	LOQ	LOQ	76(20)	87(12)	0.200	0.050
Chlormequat chloride	1.05	94(14)	102(11)	83(6)	107(6)	N/A	0.004
Clofentezine	8.18	77(19)	69(21)	84(7)	92(10)	0.100	0.010
Clothianidin	4.11	69(10)	110 (6)	113(12)	81(14)	N/A	0.004
Cyantraniliprole	5.47	74(15)	102(16)	101(12)	86(7)	N/A	0.010
Cypermethrin	14.49	86(19)	95(12)	85(4)	95(4)	0.05	0.010
Cyprodinil	7.3	67(10)	67(9)	63(13)	66(6)	N/A	0.010
Daminozide	1.17	85(5)	100(6)	93(11)	101(3)	0.05	0.010
Dimethomorph	6.4	111(14)	104(12)	76(7)	96(10)	2.0	0.010
Dinotefuran	3.18	82(8)	100(5)	84(3)	95(4)	N/A	0.010
Dodemorph	5.86	67(7)	85(10)	68(9)	72(4)	N/A	0.010
Ethephon[1]	ND	ND	ND	ND	ND	N/A	N/A
Ethoprop(hos)	6.99	95(20)	95(18)	95(11)	92(6)	0.100	0.010
Etofenprox	15.59	65(5)	75(5)	68(3)	74(4)	0.100	0.010
Etoxazole	13.4	77(6)	94(6)	80(4)	89(5)	0.01	0.010
Fenhexamid	6.77	LOQ	104(15)	91(15)	94(14)	0.100	0.020
Fenpyroximate	13.82	71(5)	88(3)	76(4)	87(4)	0.100	0.010
Flonicamid	3.7	71(11)	85(6)	78(7)	88(9)	0.100	0.010
Fluopyram	6.67	77(19)	111(12)	82(2)	89(13)	N/A	0.010
Hexythiazox	12.41	69(5)	87(12)	82(4)	83(12)	0.100	0.010
Imazalil	5.61	73(5)	98(15)	93(7)	77(5)	0.01	0.010
Imidacloprid	4.07	112(9)	92(18)	47(15)	105(18)	0.01	0.010
Iprodione	7.13	LOQ	LOQ	LOQ	99(16)	N/A	≥0.100
Malathion	6.34	70(7)	96(10)	96(13)	102(5)	0.05	0.01
Methiocarb	6.2	LOQ)	104(8)	82(16)	90(19)	0.100	0.020
Methomyl	3.64	80(13)	103(9)	92(5)	99(4)	0.400	0.010
Myclobutanil	6.55	LOQ	65(12)	91(15)	92(3)	0.01	0.02
Naled	5.89	118(14)	88(7)	62(9)	93(21)	0.1	0.010
Novaron	10.19	71(13)	85(14)	89(10)	102(10)	N/A	0.004
Orchatoxin A	6.4	99(17)	110(16)	77(7)	98(14)	N/A	0.010
Oxamyl	3.48	79(6)	96(5)	92(5)	96(4)	0.5	0.010
Paclobutrazol	6.37	LOQ	89(16)	76(14)	103(8)	0.05	0.010
Phosmet Oxon	4.91	75(13)	82(7)	103(18)	94(13)	0.2	0.010
Piperonylbutoxide	11.28	79(9)	98(5)	86(4)	96(5)	1.000	0.010
Pirimicarb	5.35	62(18)	75(12)	68(13)	69(3)	N/A	0.010
Prallethrin	9.09	79(5)	90(6)	87(6)	92(4)	0.100	0.010
Propiconazole	7.96	100(16)	116(6)	101(9)	92(5)	0.100	0.010
Propoxur	5.26	106(7)	128(19)	99(13)	96(7)	0.100	0.010
Pyraclostrobin	7.98	93(13)	115(4)	85(16)	102(11)	N/A	0.004
Pyrethrin I	13.81	84(14)	91(7)	77(3)	91(7)	0.500	0.03
Pyrethrin II	9.19	94(19)	92(13)	82(5)	93(5)	0.500	0.010
Pyridaben	14.59	72(7)	83(5)	70(3)	85(5)	0.100	0.010
Spinetoram	9.6	60(6)	66(6)	64(4)	63(4)	0.100	0.010
Spinetoram L	11.66	LOQ	61(4)	60(4)	60(5)	0.100	0.020
Spinosad A	8.1	LOQ	86(8)	60(2)	69(6)	0.06	0.020
Spinosad D	9.38	61(5)	71(5)	67(5)	64(5)	0.06	0.010
Spirodiclofen	13.94	89(2)	92(4)	80(3)	95(4)	N/A	0.004
Spiromesifen	13.28	78(7)	99(3)	82(3)	92(4)	0.01	0.004
Spirotetramat	6.71	63(10)	102(18)	71(10)	109(4)	0.02	0.010
Spiroxamine	6.07	73(8)	90(3)	77(12)	98(14)	0.100	0.010
Tebuconazole	7.59	109(18)	81(18)	82(13)	83(10)	0.01	0.004
Tebufenozide	7.2	LOQ	73(10)	88(9)	98(9)	N/A	0.020
Teflubenzuron	11.29	LOQ	106(20)	80(17)	97(6)	N/A	0.020
Thiacloprid	4.61	73(13)	83(7)	106(10)	105(6)	0.100	0.010
Thiamethoxam	3.72	79(10)	97(4)	88(2)	94(8)	0.050	0.010

NA No current regulatory imposed action level; AOAC Cannabis Working Group recommends LOQ of 0.005 ppm for these compounds.

[1] Ethephon, a highly polar pesticide is not efficiently extracted by this method.

[2] Compound shows significant degradation (primarily to carbendazim) in extracts within a few hours.

Table 2

Pesticides	RT	%Recovery (% RSD)				Lowest action level	Method LOQ
		0.01 ppm	0.02 ppm	0.05 ppm	0.1 ppm	ppm	ppm
Ancymidol	13.05	LOQ	69(20)	89(17)	85(13)	0.100	0.020
Azoxystrobin	20.49	104(19)	73(13)	80(10)	94(6)	0.020	0.003
Benzovindiflupyr	19.21	105(16)	94(14)	97(11)	94(5)	0.100	0.007
Bifenthrin	15.15	93(9)	71(8)	90(11)	103(5)	0.010	0.004
Captan	11.57	LOQ	83(8)	95(12)	90(10)	0.050	0.018
Chlordane	11.30	LOQ	82(5)	90(7)	97(7)	0.100	0.015
Chlorfenapyr	12.80	91(20)	83(9)	99(7)	99(12)	0.100	0.002
Chlorpyrifos	10.47	LOQ	82(19)	89(12)	89(4)	0.100	0.015
Coumaphos	17.48	LOQ	109(12)	84(18)	98(11)	0.100	0.015
Cyfluthrin	17.39	97(14)	102(5)	95(6)	98(5)	0.01	0.010
Deltamethrin[1]	20.32	LOQ	60(13)	98(11)	93(6)	NA	0.015
Diazinon	8.69	LOQ	84(7)	94(10)	95(8)	0.100	0.020
Dichlorvos	5.18	117(12)	82(9)	99(6)	100(3)	0.100	0.005
Dimethoate	8.30	92(13)	79(8)	92(4)	95(5)	0.100	0.003
Endosulfan sulfate[3]	13.56	LOQ	76(7)	89(7)	97(7)	NA	0.015
Endosulfan I	12.20	105(15)	81(8)	91(7)	95(5)	NA	0.010
Endosulfan II	13.40	94(9)	77(17)	99(7)	103(5)	NA	0.008
Etridazole	6.37	100(14)	74(7)	100(7)	96(2)	NA	0.003
Fenoxycarb	15.27	LOQ	86(16)	92(9)	89(6)	0.100	0.015
Fensulfothion	13.23	88(17)	75(14)	85(11)	106(6)	NA	0.005
Fenthion	10.54	72(12)	72(12)	78(10)	86(5)	NA	0.005
Fenvalerate	19.44	95(16)	108(9)	97(12)	97(7)	NA	0.008
Fipronil	11.12	101(17)	78(8)	82(10)	93(13)	0.100	0.005
Fludioxinil	11.05	104(11)	80(13)	86(16)	82(19)	0.020	0.010
Flurprimidol	9.52	76(15)	74(8)	87(10)	96(7)	NA	0.008
Kinoprene	10.41	LOQ	91(12)	85(14)	93(16)	NA	0.015
Kresoxim-methyl	12.59	LOQ	73(8)	106(7)	86(7)	0.100	0.020
Metalaxyl	9.85	110(18)	81(18)	82(5)	98(9)	0.200	0.005
Methoprene	11.52	LOQ	LOQ	89(10)	93(12)	NA	0.025
Methyl Parathion	9.74	94(12)	78(8)	81(14)	89(14)	0.100	0.002
Mevinphos	6.11	95(11)	83(10)	98(5)	96(5)	0.100	0.008
MGK-264	10.93	LOQ	99(14)	89(20)	89(4)	0.200	0.015
Permethrin	17.45	80(6)	81(11)	98(7)	99(2)	0.040	0.010
Phenothrin	15.83	99(19)	102(16)	96(6)	92(14)	NA	0.005
Phosmet	15.21	93(15)	81(11)	84(9)	95(10)	0.020	0.005
Resmethrin[2]	14.60	–	–	–	–	NA	0.015
Pentachloro nitrobenzene[3]	8.33	87(18)	70(5)	88(7)	90(5)	0.200	0.004
Tetrachlorvinphos[1]	11.85	LOQ	94(7)	91(16)	109(26)	0.020	0.020
Tetramethrin	15.39	LOQ	38(21)	108(6)	99(7)	NA	0.030
THPI (Captan)	6.61	93(16)	81(10)	76(19)	76(8)	0.050	0.005

LOQ Result below method LOQ.

NA No current regulatory imposed action level; AOAC Cannabis Working Group recommends LOQ of 0.005 ppm for these compounds.

[1] Compound shows significant degradation in extracts within a few days.

[2] Compound shows significant degradation in extracts within a few hours; compound was detected but recovery could not be calculated.

[3] Results obtained using charge transfer mode.

Conclusion

Simple extraction and cleanup protocols followed by LC-MS/MS and APGC-MS/MS analysis provide rapid, sensitive, and robust workflows for determination of pesticides and mycotoxins in challenging cannabis matrix.

Method detection limits meet or exceed AOAC SMPR requirements for all pesticides with regulatory imposed action levels in any US State or Canada.

The multiresidue analysis of 105 pesticides plus mycotoxins can be accomplished using the same mass spectrometer (Xevo TQ-XS) for both UPLC and APGC analyses.

References

1. Standard Method Performance Requirements (SMPRs) for Quantitation of Cannabinoids in Plant Materials of Hemp (Low THC Varieties Cannabis sp.). *AOAC SMPR* 2019.003.

Appendix Table A

Pesticides	Quan trace	1° trace
	cone (V) collision (eV)	cone (V) collision (eV)
Abamectin B1a	890.8 > 305.3 (24,26)	890.8 > 567.6 (24,14)
Abamectin B1b	876.51 > 291.2 (45,26)	876.51 > 553.32 (45,14)
Acephate	184.02 > 142.99 (20,6)	184.02 > 94.99 (20,21)
Acequinocyl	343.23 > 188.9 (35,20)	343.23 > 115.05 (35,40)
Acetamiprid	223.08 > 126.01 (35,20)	223.08 > 90.03 (35,31)
Aflatoxin B1	313.07 > 241.05 (60,35)	313.07 > 213.06 (60,43)
Aflatoxin B2	315.09 > 287.1 (65,28)	315.09 > 243.07 (65,35)
Aflatoxin G1	329.07 > 311 (55,21)	329.07 > 243.07 (55,25)
Aflatoxin G2	331.08 > 189.06 (60,40)	331.08 > 245.08 (60,28)
Aldicarb	116 > 89.1 (30,11)	116 > 70.1 (30,11)
Allethrin	303.03 > 134.94 (20,10)	303.03 > 90.95(20,40)
Azadirachtin	703.6 > 585.47 (10,15)	703.6 > 567.45 (10,15)
Bifenazate	301.16 > 153.07 (28,28)	301.16 > 170.1 (28,22)
Boscalid	343.04 > 307.06 (25,18)	343.04 > 272.09 (25,29)
Buprofenzin	306.1 > 201 (30,12)	306.1 > 115.9 (30,16)
Carbaryl	202.09 > 145.07 (21,11)	202.09 > 127.05 (21,25)
Carbofuran	222.11 > 165.1 (30,10)	222.11 > 123 (30,20)
Chlorantraniliprole	481.98 > 283.92 (43,18)	481.98 > 450.94 (43,15)
Chlormequat chloride	124.2 > 58.8 (25,10)	122.1 > 59.07 (25,10)
Clofentezine	303.02 > 138.01 (20,15)	303.02 > 102.03 (20,30)
Clothianidin	250 > 169 (30,10)	250 > 132 (30,15)
Cyantraniliprole	475 > 286 (50,13)	473.1 > 283.9 (50,18)
Cypermethrin	433.11 > 191(30,14)	435.11 > 193 (30,14)
Cyprodinil	226 > 93 (30,35)	226 > 108 (30,25)
Daminozide	161.09 > 143.08 (24,8)	161.09 > 61.08 (24,10)
Dimethomorph	388.13 > 301.06 (45,19)	388.13 > 165.06 (45,30)
Dinotefuran	203 > 129 (30,10)	203 > 113 (30,10)
Dodemorph	282.1 > 116 (40,21)	282.1 > 98 (40,28)
Ethephon	145 > 80.79 (35,15)	143.05 > 79 (35,15)
Ethoprop(hos)	243.06 > 130.94 (33,19)	243.06 > 96.95 (33,27)
Etofenprox	394.24 > 177.13 (26,14)	394.24 > 107.05 (26,38)
Etoxazole	360.18 > 141.02 (55,30)	360.18 > 113.02(55,55)
Fenhexamid	302.07 > 97.1 (55,23)	302.07 > 55.05 (55,33)
Fenoxycarb	302.14 > 88.04 (35,20)	302.14 > 116.07 (35,10)
Fenpyroximate	422.21 > 366.15 (42,13)	422.21 > 138.07 (42,33)
Flonicamid	230.05 > 203.04 (50,16)	230.05 > 148.04 (50,25)
Fluopyram	397 > 208.1(30,35)	397 > 173.2 (30,41)
Hexythiazox	353.11 > 228.02 (42,15)	353.11 > 168.06 (42,25)
Imazalil	297.06 > 158.98 (25,20)	297.06 > 69.05(25,20)
Imidacloprid	256.06 > 84.06 (35,15)	256.06 > 175.1 (35,20)
Iprodione	332 > 246.9 (35,15)	330 > 245(35,15)
Malathion	331.04 > 99.01(12,15)	331.04 > 127.04 (12,11)
Methiocarb	226.09 > 169.07(25,10)	226.09 > 77 (25,45)
Methomyl	163.05 > 88.02(20,8)	163.05 > 106.03 (20,8)
Myclobutanil	289.12 > 125.02 (30,38)	289.12 > 70.04 (30,20)
Naled	381 > 127 (30,17)	381 > 109 (30,27)