Analysis of the California list of Pesticides and Mycotoxins in Edibles

Nathaly Reyes-Garcés; Colton Myers; Ashlee Gerardi

Restek Corporation

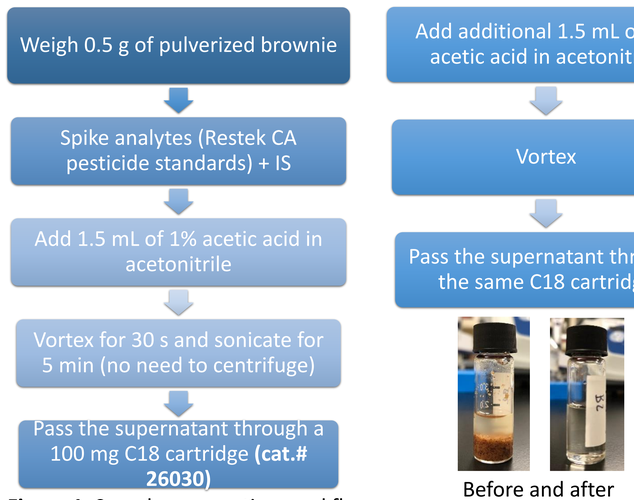
Introduction

- The use of cannabis for medicinal and/or recreational purposes has become legal in several states. Regulations that permit the use of different forms of cannabis demand effective and reliable analytical strategies to ensure the safety of cannabis users.
- Pesticide content is one of the main parameters tested in cannabis and cannabis-derived products due to the risks that these compounds pose for human health.
- The main challenges associated with pesticide testing rely on the broad range of physicochemical properties of these compounds, the low action levels requested by the regulations, and the complexity and diversity of matrices to be analyzed.
- The purpose of this work is to present sample preparation and instrumental strategies for the accurate quantitation of the California list of pesticides and mycotoxins in cannabis products.

Goal

To provide an effective workflow for the simultaneous analysis of the California list of pesticides and mycotoxins in brownies using both LC-MS/MS and GC-MS/MS for instrumental analysis.

Method Development: Sample Preparation



Before and after

Figure 1. Sample preparation workflow

For LC-MS/MS analysis: take 750 µL of extract and mix it with 250 µL of water. Inject.

For GC-MS/MS analysis:

- Transfer the remaining extract to a tube with dSPE sorbents (magnesium sulfate + PSA) **(cat.# 26215)**.
- Vortex and centrifuge. Dilute 500 µL of this extract with 500 µL of 1% acetic acid in acetonitrile. Inject.

Method Development: LC/GC-MS/MS

Table 1. LC-MS/MS conditions (ionization: ESI)

Column	Raptor ARC-18 2.7 µm, 100 mm x 2.1 mm **(Restek Cat.# 9314A12)**			
Guard Column	Raptor ARC-18 EXP Guard Column Cartridge 2.7 µm, 5 x 2.1 mm **(cat.# 9314A0252)**			
Mobile Phase A	Water, 2 mM ammonium formate, 0.1% formic acid			
Mobile Phase B	Methanol, 2 mM ammonium formate, 0.1% formic acid			
Time Program	Time (min.)	%B	Time (min.)	%B
	0	5	10.5	100
	1.5	65	10.6	5
	8.5	95	12.0	5
	9.5	100		
Other parameters	Column T: 40 °C; autosampler T: 10 °C; injection volume:2 µL			
Instrument	Shimadzu LCMS-8060			

Table 2. GC-MS/MS conditions (ionization: EI)

Column	Rxi-5ms **(cat.# 13423)**
Injection	Splitless, 1 µL (0.5 min splitless time, 14 mL/min split flow)
Liner	Topaz 4.0 mm ID Single Taper Inlet Liner w/ Wool **(cat.# 23447)**
Inj. T	250°C
Purge Flow	5 mL/min
Oven	90°C (hold 1 min) to 310°C (hold 10 min) by 25°C/min
Carrier Gas	He, at a constant flow of 1.4 mL/min
Transfer line T	290°C
Source T	330 °C
Instrument	Thermo Trace 1310-TSQ 8000

Results and Discussion

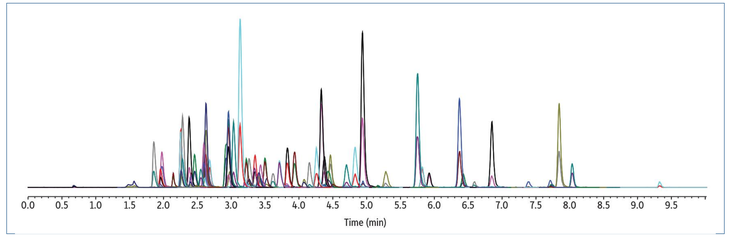


Figure 2. LC-MS/MS amenable pesticides

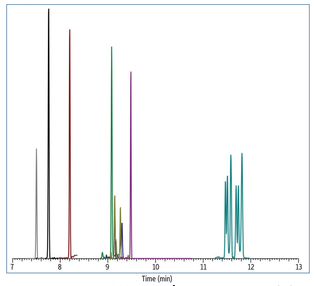


Figure 3. GC-MS/MS amenable pesticides

As seen in Table 3, the proposed methodology showed satisfactory results in the quantification of all the pesticides and mycotoxins regulated by the state of California. The LOQ values obtained were significantly below the action levels established by the state of CA in cannabis goods (not inhalable).

Table 3. Figures of merit corresponding to pesticides and mycotoxins analyzed in brownies.

Compound	LOQ ng/g	R^2	100 ng/g Acc. %	100 ng/g Precision %
Daminozide	25	0.9954	102	12
Acephate	10	0.9944	104	3
Thiamethoxam	5	0.9979	106	1
Methomyl	5	0.9996	104	1
Oxamyl	5	0.9986	104	2
Imidacloprid	10	0.9979	103	2
Dimethoate	5	0.9994	101	3
Acetamiprid	5	0.9991	103	1
Thiacloprid	5	0.9993	106	3
Aldicarb	5	0.9988	99	4
Naled	25	0.9962	105	10
Mevinphos I (79%)	4	0.9991	104	4
Mevinphos II (21%)	2	0.9981	106	6
Carbofuran	5	0.9994	105	2
Carbaryl	5	0.9997	103	4
Dichlorvos	5	0.9949	101	5
Propoxur	5	0.9993	106	2
Chloantraniliprole	10	0.9992	105	5
Imazalil	5	0.9993	100	1
Metalaxyl	5	0.9996	103	4
Azoxystrobin	5	0.9998	103	1
Myclobutanil	5	0.9997	104	4
Phosmet	5	0.9997	103	3
Spiroxamine	5	0.9987	102	5
Fenoxycarb	5	0.9995	103	2
Methiocarb	5	0.9997	104	4
Spiromesifen	25	0.9994	103	5
Boscalid	5	0.9998	106	3
Paclobutrazol	5	0.9996	103	3
Malathion	5	0.9995	102	3
Dimethomorph I (39%)	4	0.9994	101	5
Dimethomorph II (61%)	3	0.9994	103	2
Tebuconazole	5	0.9996	104	2
Bifenazate	5	0.9999	104	2
Fenhexamid	10	0.9992	103	3
Propiconazole	5	0.9997	105	2
Spirotetramat	5	0.9990	104	2
Ethoprophos	5	0.9997	103	2
Kresoxym-methyl	5	0.9993	104	3
Category I pesticides, LOQ < or = to 100 ng/g				

Compound	LOQ ng/g	R^2	100 ng/g Acc. %	100 ng/g Precision %
Spinosyn A (71 %)	3.5	0.9994	102	2
Diazinon	5	0.9995	101	3
Coumaphos	5	0.9997	102	1
Clofentezine	5	0.9997	103	2
Spinosyn D (29%)	1.5	0.999	101	4
Spinosyn J (80%)	4	0.9991	105	2
Spinosyn L (20%)	1	0.9991	100	4
Trifloxystrobin	5	0.9997	102	2
Prallethrin	25	0.9996	98	8
Hexythiazox	5	0.9996	104	3
Cyfluthrin	50	0.9988	107	7
Pyrethrin I (54%)	5.4	0.9998	104	2
Pyrethrin II (34%)	26	0.999	100	11
Etoxazole	5	0.9998	102	1
Piperonyl Butoxide	5	0.9998	103	2
Chlorpyrifos	5	0.9994	101	4
Permethrin-cis (41%)	4.1	0.9994	105	4
Permethrin-trans (59%)	5.9	0.9999	106	4
Fenpyroximate	5	0.9998	103	4
Bifenthrin	5	0.9994	103	5
AbamectinB1a	10	0.9999	105	6
Cypermethrin	25	0.9991	93	7
Etofenprox	5	0.9995	107	2
Pyridaben	10	0.9989	101	5
Acequinocyl	5	0.9987	103	5
Flonicamid	10	0.9993	101	4
Fipronil	10	0.9993	102	5
Fludioxonil	5	0.9995	104	6
Captan (GC)	10	0.9941	103	5
Chlordane (GC)	25	0.9939	106	5
Chlorfenapyr (GC)	25	0.9953	102	3
Methyl parathion (GC)	5	0.9976	103	2
PCNB (GC)	5	0.9975	103	4
Cyfluthrin (GC)	5	0.9983	103	4
Cypermethrin (GC)	10	0.9986	103	2
Aflatoxin G2	5	0.9987	104	3
Aflatoxin G1	5	0.9984	96	1
Aflatoxin B2	5	0.9996	99	2
Ochratoxin A	10	0.9943	112	11
Aflatoxin B1	5	0.999	96	3

Since this methodology only uses 3.5 mL of extraction solvent per sample, a significant reduction in solvent usage/waste is also possible.

Conclusions

A simple analytical workflow involving SPE and dSPE in combination with LC-MS/MS and GC-MS/MS analysis was proven to be effective in the quantitation of CA pesticides and mycotoxins regulated in cannabis. Satisfactory results in terms of linearity, accuracy, and precision were attained for all the target compounds at the three evaluated concentration levels (10, 100 and 500 ng/g).

References

N. Reyes and C. Myers. Analysis of pesticides and mycotoxins in cannabis brownies. Technical article: https://www.restek.com/pdfs/FFAN3149-UNV.pdf