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The Analysis of 85 Pesticides Commonly Found in Cannabis and Cannabis-Related Products by LC-MS and GC-MS

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Abstract

Residual pesticides in cannabis and cannabis products can pose a major health risk to consumers in both recreational and medicinal applications. The main source of these chemicals comes during the growing process where chemicals are applied to the plants to control insects, mold or fungus growth. Some of those pesticides, such as organophosphates, are known for their toxic effects to both humans and wildlife.

As a result, regulators and standardization bodies such as ASTM and AOAC have published different test methods to analyze for residual pesticides in cannabis and cannabis-related products.

In order to make this screening as efficient as possible, AccuStandard used the target lists from different agencies, and was able to identify and quantify over 80 pesticides commonly used during cannabis cultivation. The analysis was conducted using multiple Certified Reference Materials (CRMs) prepared by AccuStandard and formulated based on the compatibility and the stability of those chemicals. Using both GC-MS and LC-MS we were able to offer a comprehensive and robust analysis for those compounds, most of which are in the target list of compounds in ASTM test method D8399 and AOAC SMPR 2018.011. The results illustrate the proper methods for handling the CRM samples and the appropriate analytical technique used to evaluate every compound. The conclusion is that using both analytical techniques combined with well-characterized CRMs represents a significant benefit for an accurate and reliable analysis of these harmful chemicals.

Introduction and Background

Pesticides are a group of chemical compounds that are primarily used to prevent and control harmful organisms and diseases during the plant growing process. Most of those chemicals are regulated by different agencies due to their harmful health effects. Cannabis is no different than other crops where pesticides are essential to improve quality and increase yield. While the USEPA and other federal agencies regulate pesticide residual limits on crops, no federal guidance has been established for pesticides and its residual content in cannabis due to its illegal federal status. Since residual pesticide analysis is a major part of ensuring cannabis is safe for human consumption, this has left consumers, especially individuals who use cannabis for therapeutic purposes, at risk of being exposed to a wide array of toxic chemicals. As a result, a reliable and accurate characterization of these contaminants is important for the safety of consumers and to reduce exposure.

In this study, AccuStandard was able to analyze and quantify 85 pesticides commonly found in cannabis and its related products. The analysis was conducted using 5 different Certified Reference Materials (CRMs) and using both LC-MS and GC-MS to examine method suitability. Compounds were accurately identified and confirmed using retention time and its respective mass spectrum.

This work also presents a comprehensive approach for the analysis of residual pesticides in cannabis to support labs in meeting the local and state regulatory guidelines. This has been accomplished by using suitable analysis techniques and reliable CRMs to help overcome the challenges of identifying these contaminants.

85 Targeted Compounds

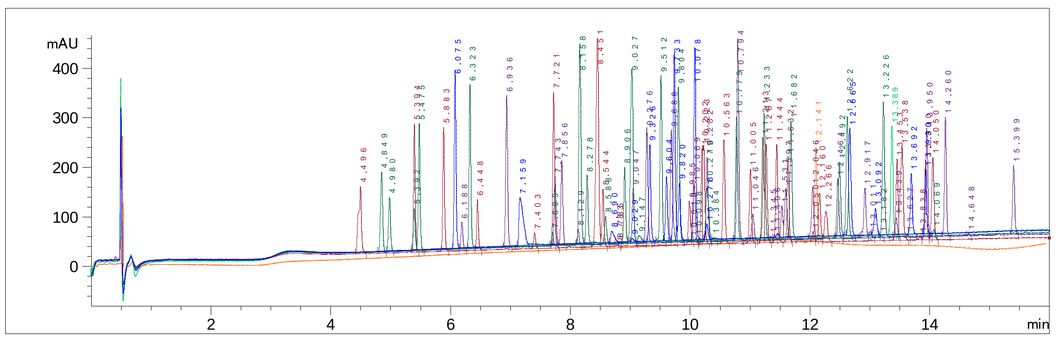
Abamectin	Chlorantraniliprole	Fenoxycarb	Methiocarb	Resmethrin
Acephate	Clofentezine	Fenpyroximate	Methomyl	Spinetoram
Acequinocyl	Clothianidin	Fensulfothion	Methoprene	Spinosad
Acetamiprid	Coumaphos	Fenthion	Mevinphos	Spirodiclofen
Alar	Cyantraniliprole	Fenvalerate	Myclobutanil	Spiromesifen
Aldicarb	Cyprodinil	Fipronil	Naled	Spirotetramat
Allethrin	Deltamethrin	Flonicamid	Novaluron	Spiroxamine
Azadirachtin	Diazinon	Fludioxonil	Oxamyl	Sumithrin
Azoxystrobin	Dichlorvos	Fluopyram	Paclobutrazol	Tebuconazol
Baygon	Dimethoate	Hexythiazox	Permethrin	Tebufenozide
Benzovindiflupyr	Dimethomorph	Imazalil	Piperonyl butoxide	Teflubenzuron
Bifenazate	Dinotefuran	Imidacloprid	Pirimicarb	Tetrachlorvinphos Z
Bifenthrin	Dodemorph acetate	Imidan	Prallethrin	Tetramethrin
Boscalid	Dursban	Iprodione	Propiconazole	Thiacloprid
Buprofezin	Ethoprop	Kresoxim-methyl	Pyraclostrobin	Thiamethoxam
Carbaryl	Etofenprox	Malathion	Pyrethrins	Thiophanate-methyl
Carbofuran	Etoxazole	Metalaxyl	Pyridaben	Trifloxystrobin

CRM Handling and Methods of Analysis

CRMs were designed and prepared to maximize stability, compatibility, and shelf life. Some compounds such as Spirodiclofen and Spiromesifen were prepared independently from the multiple component mixes due to their unstable nature. Mixes were sonicated for 45 minutes and acclimated to room temperature prior to analyzing to ensure solubility and improve each component's response. The concentration of all components was verified against another independently made standard.

LC Parameters

- General gradient method starting @ 100% water for 1 min @ 0.3 mL/min, the 100% Acetonitrile in 13 min, 100% Acetonitrile until T=16 min
- Column Zorbax Eclipse plus C-18, 2.1 mm X 50 mm, 1.8 u particlue size
- Agilent 1290 Infinity II LC/MS system
- Agilent 6125 quadruple MS detector



LC Retention Times:

D-8399-01 (Lot 223031166)

Peak #	Component
6.075	Imidacloprid (138261-41-3)
7.159	Imazalil (35554-44-0)
8.690	Spinosad (168316-95-8)
9.029	Spinosad (168316-95-8)
9.326	Spirotetramat (203313-25-1)
9.604	Myclobutanil (88671-89-0)
9.733	Azoxystrobin (131860-33-8)
9.820	Tebuconazol (107534-96-3)
10.078	Bifenazate (149877-41-8)
10.278	Malathion (121-75-5)
12.665	Etoxazole (153233-91-1)
13.092	Abamectin (71751-41-2)
13.692	Permethrin (52645-53-1)
13.930	Permethrin (52645-53-1)

D-8399-02 (Lot 223031554)

Peak #	Component
4.849	Oxamyl (23135-22-0)
4.980	Methomyl (16752-77-5)
5.392	Flonicamid (158062-67-0)
5.475	Thiamethoxam (153719-23-4)
6.323	Acetamiprid (135410-20-7)
8.158	Carbaryl (63-25-2)
8.278	Metalaxyl (57837-19-1)
8.588	Clofentezine (74115-24-5)
8.906	Dimethomorph (110488-70-5)
9.027	Chlorantraniliprole (500008-45-7)
9.027	Dimethomorph (110488-70-5)
9.147	Spinetoram (935545-74-7)
9.471	Spinetoram (935545-74-7)
9.512	Fludioxonil (131341-86-1)
9.804	Boscalid (188425-85-6)
10.279	Tilt (60207-90-1)
10.775	Kresoxim-methyl (143390-89-0)
11.233	Clofentezine (74115-24-5)
11.682	Trifloxystrobin (141517-21-7)
12.492	Hexythiazox (78587-05-0)
12.622	Fenpyroximate (111812-58-9)
13.226	Pyridaben (96489-71-3)

D-8399-03 (Lot 223031246)

Peak #	Component
0.593	Alar (1596-84-5)*
3.621	Acephate (30560-19-1)*
6.188	Dimethoate (60-51-5)
6.936	Aldicarb (116-06-3)
6.936	Thiacloprid (111988-49-9)
7.588	Meltatox (31717-87-0)*
7.743	Baygon (114-26-1)
7.856	Carbofuran (1563-66-2)
7.856	Spiroxamine (118134-30-8)
8.129	Azadirachtin (11141-17-6)
8.785	Naled (300-76-5)
9.047	Paclobutrazol (76738-62-0)
9.276	Methiocarb (2032-65-7)
9.686	Ethoprop (13194-48-4)
9.686	Imidan (732-11-6)
10.282	Fenoxycarb (72490-01-8)
10.794	Fipronil (120068-37-3)
10.794	Benzovindiflupyr (1072957-71-1)
11.046	Diazinon (333-41-5)
11.531	Pyrethrins (8003-34-7)
11.597	Prallethrin (23031-36-9)
12.046	Piperonyl butoxide (51-03-6)
12.464	Dursban (2921-88-2)
12.917	Pyrethrins (8003-34-7)
13.439	Pyrethrins (8003-34-7)
13.950	Etofenprox (80844-07-1)
14.260	Bifenthrin (82657-04-3)
15.399	Acequinocyl (57960-19-7)

D-8399-04 (Lot 223031374)

Peak #	Component
4.496	Dinotefuran (165252-70-0)
5.394	Pirimicarb (23103-98-2)
5.883	Clothianidin (210880-92-5)
6.448	Mevinphos (7786-34-7)
7.403	Dichlorvos (62-73-7)
7.721	Thiophanate-methyl (23564-05-8)
8.451	Cyantraniliprole (736994-63-1)
8.451	Cyprodinil (121552-61-2)
8.544	Fensulfothion (115-90-2)
9.985	Fluopyram (658066-35-4)
10.069	Buprofezin (69327-76-0)
10.202	Iprodione (36734-19-7)
10.223	Tetrachlorvinphos Z (22248-79-9)
10.563	Tebufenozide (112410-23-8)
11.005	Fenthion (55-38-9)
11.213	Pyraclostrobin (175013-18-0)
11.267	Coumaphos (56-72-4)
11.444	Teflubenzuron (83121-18-0)
11.632	Novaluron (116714-46-6)
12.050	Tetramethrin (7696-12-0)
12.160	Tetramethrin (7696-12-0)
12.266	Allethrin (584-79-2)
13.453	Resmethrin (10453-86-8)
13.538	Deltamethrin (52918-63-5)
13.538	Fenvalerate (51630-58-1)
13.930	Sumithrin (26002-80-2)
14.050	Methoprene (40596-69-8)

P-938S-CN (Lot 222111134)

Peak #	Component
13.389	Spirodiclofen (148477-71-8)

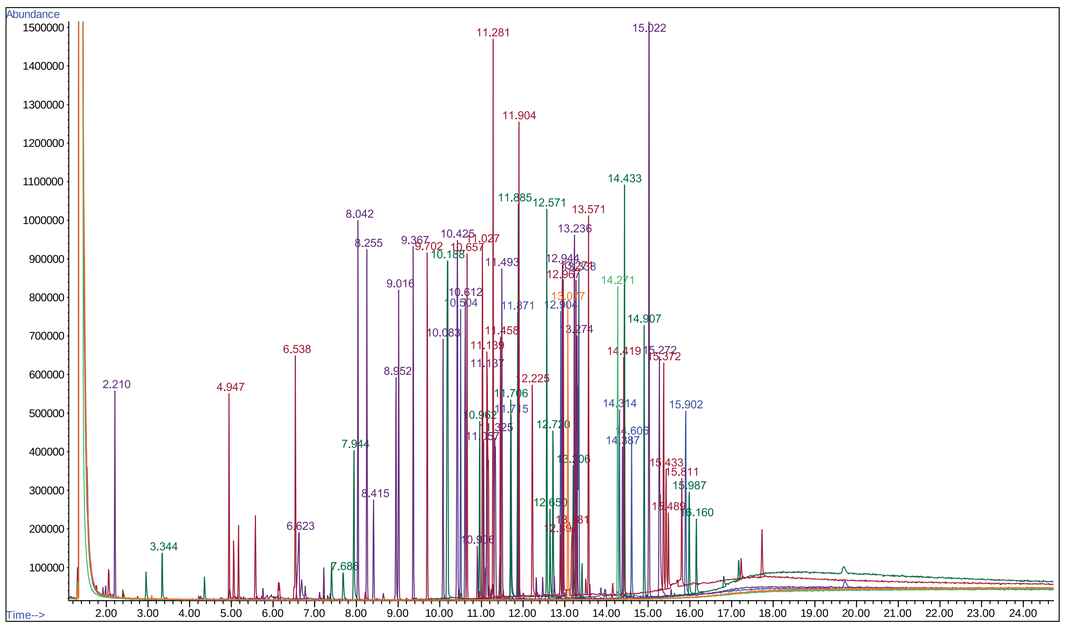
P-960S-CN (Lot 223031567)

Peak #	Component
12.141	Spiromesifen (283594-90-1)

* Compounds detected on MS

GC Parameters

- Cons. Split, 12psi constant flow. Split 20:1, 1 µL inj: GCMS, INJ 270c
- Column: DB-5MS 30m, 0.25ID, 0.25 µm
- Oven program: 80°C, 17°C /min to 340°C, 8min



GC Retention Times:

D-8399-01 (Lot 223031166)

Peak #	Component
10.504	Malathion (121-75-5)
11.715	Imazalil (35554-44-0)
11.871	Myclobutanil (88671-89-0)
12.904	Tebuconazol (107534-96-3)
13.338	Etoxazole (153233-91-1)
13.338	Bifenazate (149877-41-8)
14.314	Permethrin (52645-53-1)
14.387	Permethrin (52645-53-1)
14.606	Spirotetramat (203313-25-1)
15.902	Azoxystrobin (131860-33-8)
LCMS	Abamectin (71751-41-2)
LCMS	Imidacloprid (138261-41-3)
LCMS	Spinosad (168316-95-8)

D-8399-02 (Lot 223031554)

Peak #	Component
3.344	Methomyl (16752-77-5)
7.686	Oxamyl (23135-22-0)
10.188	Carbaryl (63-25-2)
10.188	Metalaxyl (57837-19-1)
11.706	Fludioxonil (131341-86-1)
11.885	Kresoxim-methyl (143390-89-0)
12.571	Trifloxystrobin (141517-21-7)
12.650	Tilt (60207-90-1)
12.720	Tilt (60207-90-1)
13.206	Acetamiprid (135410-20-7)
14.433	Pyridaben (96489-71-3)
14.907	Boscalid (188425-85-6)
15.987	Dimethomorph (110488-70-5)
16.160	Dimethomorph (110488-70-5)
LCMS	Chlorantraniliprole (500008-45-7)
LCMS	Clofentezine (74115-24-5)
LCMS	Fenpyroximate (111812-58-9)
LCMS	Flonicamid (158062-67-0)
LCMS	Hexythiazox (78587-05-0)
LCMS	Spinetoram (935545-74-7)
LCMS	Thiamethoxam (153719-23-4)

D-8399-03 (Lot 223031246)

Peak #	Component
2.210	Aldicarb (116-06-3)
6.623	Acephate (30560-19-1)
8.042	Baygon (114-26-1)
8.255	Ethoprop (13194-48-4)
8.415	Naled (300-76-5)
8.952	Dimethoate (60-51-5)
9.016	Carbofuran (1563-66-2)
9.367	Diazinon (333-41-5)
10.083	Spiroxamine (118134-30-8)
10.425	Methiocarb (2032-65-7)
10.612	Dursban (2921-88-2)
10.906	Meltatox (31717-87-0)
11.057	Fipronil (120068-37-3)
11.137	Meltatox (31717-87-0)
11.325	Prallethrin (23031-36-9)
11.493	Paclobutrazol (76738-62-0)
12.944	Piperonyl butoxide (51-03-6)
13.236	Bifenthrin (82657-04-3)
13.274	Fenoxycarb (72490-01-8)
13.274	Imidan (732-11-6)
15.022	Etofenprox (80844-07-1)
LCMS	Alar (1596-84-5)
LCMS	Thiacloprid (111988-49-9)
LCMS	Acequinocyl (57960-19-7)
LCMS	Azadirachtin (11141-17-6)
LCMS	Benzovindiflupyr (1072957-71-1)
LCMS	Pyrethrins (8003-34-7)

D-8399-04 (Lot 223031374)

Peak #	Component
4.947	Dichlorvos (62-73-7)
6.538	Mevinphos (7786-34-7)
9.702	Pirimicarb (23103-98-2)
10.657	Fenthion (55-38-9)
11.027	Cyprodinil (121552-61-2)
11.139	Allethrin (584-79-2)
11.281	Methoprene (40596-69-8)
11.458	Tetrachlorvinphos Z (22248-79-9)
11.904	Buprofezin (69327-76-0)
12.225	Fensulfothion (115-90-2)
12.897	Resmethrin (10453-86-8)
12.967	Resmethrin (10453-86-8)
13.181	Iprodione (36734-19-7)
13.271	Tetramethrin (7696-12-0)
13.571	Sumithrin (26002-80-2)
14.419	Coumaphos (56-72-4)
15.372	Fenvalerate (51630-58-1)
15.433	Pyraclostrobin (175013-18-0)
15.489	Fenvalerate (51630-58-1)
15.811	Deltamethrin (52918-63-5)
LCMS	Clothianidin (210880-92-5)
LCMS	Cyantraniliprole (736994-63-1)
LCMS	Dinotefuran (165252-70-0)
LCMS	Fluopyram (658066-35-4)
LCMS	Novaluron (116714-46-6)
LCMS	Tebufenozide (112410-23-8)
LCMS	Teflubenzuron (83121-18-0)
LCMS	Thiophanate-methyl (23564-05-8)

P-938S-CN (Lot 222111134)

Peak #	Component
14.271	Spirodiclofen (148477-71-8)

P-960S-CN (Lot 223031567)

Peak #	Component
13.077	Spiromesifen (283594-90-1)

Additional Notes

- Standards were designed based on the stability and compatibility of each individual compound
- Each mix was prepared in Acetonitrile at 100 µg/mL
- All analytes were confirmed using Mass Spectrometry

Conclusion

As more states legalize cannabis for both medicinal and recreational uses, cannabis testing labs face growing pressure to test samples for more pesticides efficiently and accurately to ensure the safety of consumers. During this work we were able to demonstrate the effectiveness of using appropriate and accessible analytical methodologies, in addition to well-characterized Certified Reference Materials (CRMs), in the identification and quantification of residual pesticides in cannabis. Using a combination of both LC-MS and GC-MS techniques offered a significant advantage for the selection of suitable methods to reliably and accurately analyze all targeted compounds in this study.