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Applikationsbericht

A Multi-Residue Method for the Analysis of Pesticides in Cannabis Using UPLC-MS/MS and APGC-MS/MS to Meet Canadian Regulatory Requirements

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Abstract

This application note presents the use of a simple sample extraction and d-SPE (dispersive solid phase extraction) cleanup where the resulting extract is analyzed by UPLC-MS/MS or APGC-MS/MS.

Benefits

- Sensitive and reproducible workflow for screening cannabis for the Canadian list of pesticides
- Minimal sample preparation followed by rapid UPLC and GC separations
- UPLC-MS/MS and APGC-MS/MS analysis of the same sample extracts on one tandem quadrupole mass spectrometer
- Analysis of large suites of pesticides in a single injection per chromatographic inlet
- Analysis of cannabis at legislatively relevant levels

Introduction

Health Canada requires mandatory testing for the presence of pesticide residues in cannabis before the product can be sold to consumers.[1,2] The regulations are present to ensure the highest safety and quality standards possible when it comes to the supply of cannabis for medical or recreational use. To adhere to testing requirements, licensed cannabis producers must demonstrate that no unauthorized pesticides have been used on their products and that there is no contamination of the products within the limits set out by Health Canada. Currently, the target list consists of 96 pesticides, with limits of quantitation as low as 20 ppb in dried cannabis. Tandem mass spectrometry is a sensitive and selective technique. When coupled with both gas (GC) and liquid chromatography (LC), it provides a comprehensive analysis for a wide range of pesticide residues with sufficient sensitivity to meet the Health Canada regulations. The advantage of ultraperformance liquid chromatography (UPLC) coupled with tandem quadrupole mass spectrometry (MS/MS) for multi-residue pesticide analysis is widely reported.[3] More recently, the use of GC-MS/MS operated at atmospheric pressure (APGC) has been shown to offer significant improvements in performance over EI for challenging pesticides, in terms of selectivity, specificity and speed of analysis.[4,5] Regulations for cannabis testing will most likely evolve and possibly become even more rigorous. The use of both LC-MS/MS and GC-MS/MS ensures system flexibility that can be adapted in the event that more pesticides are regulated.

In this Application Note, we present the use of a simple sample extraction and d-SPE (dispersive solid phase extraction) cleanup where the resulting extract is analyzed by UPLC-MS/MS or APGC-MS/MS. A single workflow for the multi-residue analysis of pesticides in cannabis is demonstrated. Utilizing the universal source of the Waters Xevo TQ-S micro allows for LC and GC analyses to be completed on the same tandem quadrupole MS instrument. The performance of the method will be highlighted in terms of sensitivity, recovery, and linearity for both LC and GC analysis.

Experimental

Materials and reagents

1. Pesticide standards

Pesticide analytical standards were purchased from LGC Standards. Mix 1 consisted of 35 pesticides at 50 ppm in acetonitrile, Mix 2 consisted of 45 pesticides at 100 ppm in acetonitrile, and Mix 3 consisted of 14 pesticides at 100 ppm in toluene. Dimethomorph was also purchased from LGC Standards at 10 ppm in acetonitrile. Benzovindiflupyr was purchased separately from Chem Service at 100 ppm in methylene chloride solution. All 96 pesticides were combined in a 1 ppm stock solution of each.

2. Reagents

LC-MS-grade methanol, LC-MS-grade acetonitrile, and RO (reverse osmosis) water were all purchased from Fisher Scientific and were used as received. Formic acid was purchased from Waters (p/n: 186006691) and was used as received.

3. Miscellaneous

Helium and argon gases were obtained from Air Liquide. A Thermo Fisher Scientific vortex (0-3200 rpm), a Fisher Scientific accuSpin 400 centrifuge, a Fisher Scientific 60L gravity oven, and a Mettler Toledo AE50 analytical balance (0.1 mg) were all used in the sample preparation procedure.

Sample preparation

Preparation

The representative samples were dipped in liquid nitrogen and frozen before grinding. After freezing, but before grinding, all stems and seeds were removed from the sample. The ground sample was equilibrated to room temperature. Several 0.5-g portions of ground cannabis were weighed. The initial mass was recorded. To ensure that all the liquid nitrogen had evaporated, and an accurate sample mass was obtained, the sample sat on the scale until there was <1 mg change in mass over a 10-minute period.

Pesticide extraction

The 0.5-g samples of ground cannabis were placed in a 10-mL centrifuge tube and 5 mL of LC-MS/MS-grade acetonitrile was added. The sample was then vortexed for five minutes followed by centrifugation at 5000 rpm for five minutes. One milliliter of the supernatant was removed and used in the clean-up step.

Clean-up

One milliliter of the supernatant from the pesticide extraction was placed in a d-SPE cartridge (150 mg $MgSO_4$, 50 mg PSA, 50 mg C_{18}, and 7.5 mg graphitized carbon black). The cartridge was shaken for one minute and centrifuged for five minutes at 5000 rpm. The resulting cannabis extracts were directly pipetted into clean 2-mL vials in preparation for analysis by LC-MS/MS and APGC-MS/MS.

Calibration preparation

Calibration standards were made using a stock solution of 96 pesticides (1 ppm stock). Matrix-matched calibrations were used to ensure that the signals obtained in the analysis were representative of what the signal would be in cannabis samples. Standards ranging from 1–6400 ppb were made to accommodate the different ionization efficiencies of all analytes. Pesticides with low detection limits used the lower concentration standards and the pesticides with higher detection limits used higher concentration standards for their calibration curves.

Instrumentation and software

A Waters ACQUITY UPLC H-Class PLUS System coupled with a Waters Xevo TQ-S micro Tandem Quadrupole Mass Spectrometer (MS/MS) with electrospray as the ionization mode was used to carry out the analysis of 84 of the pesticides by LC-MS/MS (see Appendix A). An Agilent 7890B gas chromatograph (GC) coupled with a Waters Xevo TQ-S micro Tandem Quadrupole Mass Spectrometer was used to carry out the analysis of the remaining 12 pesticides with APGC as the ionization mode. A nitrogen generator (Peak Scientific) was used as the source of the N_2 gas. MassLynx MS Software v4.2 was used for data acquisition and processing for both LC-MS/MS and GC-MS/MS methods.

UPLC conditions

Separation mode:	Gradient
Column:	ACQUITY UPLC BEH C_{18}, 1.7 µm, 2.1 × 100 mm
Solvent A:	Methanol
Solvent B:	Water
Solvent C:	2% formic acid in RO water
Flow rate:	0.500 mL/min
Column temp.:	60 °C
Sample temp.:	10 °C
Injection volume:	2 µL

Gradient table:

Time (min)	%A	%B	%C
0	2%	93%	5
8	95%	0%	5
9	95%	0%	5
9.1	2%	93%	5
12	2%	93%	5

Xevo TQ-S micro conditions

Ionization mode:	ESI+
Capillary voltage:	1.2 kV
Cone voltage:	30 V
Collision energy:	Various eV (see Appendix)
Desolvation temp.:	600 °C
Source temp.:	150 °C
Desolvation gas flow:	1000 L/hr
Cone gas:	50 L/hr

All MS/MS parameters including precursor ion (*m/z*), product ion (*m/z*), cone voltage (V), and collision energy (CE) for the 84 pesticides analyzed by LC-MS/MS can be found in Appendix A.

GC conditions

GC system:	Agilent 7890B
Column:	Agilent DB-5 MS (30 m × 0.250 mm × 0.25 µm)
Carrier gas:	Helium
Flow rate:	2 mL/min
Injection type:	Pulsed splitless
Injector temp.:	280 °C
Equilibration time:	1.5 min
Injection volume:	2 µL
Makeup gas:	Nitrogen at 350 mL/min

GC oven program

Rate (°C/min)	Temp. (°C)	Hold (min)
–	60	0.45
18.7	320	3.65

Total run time = 18.0 min

GC-MS/MS parameters

MS system:	Xevo TQ-S micro
Ionization mode:	APGC+

Corona:	2.0 µA
Transfer line temp.:	320 °C
Source temp.:	150 °C
Solvent delay:	3.5 min
Acquisition mode:	MRM

All MS/MS parameters including precursor ion (*m/z*), product ion (*m/z*), cone voltage (V), and collision energy (CE) for the 12 pesticides analyzed by GC-MS/MS can be found in Appendix B.

Method development and optimization

LC-MS/MS and GC-MS/MS data analysis

The UPLC and GC parameters were optimized to ensure adequate separation of pesticide peaks with reduced background noise and optimum peak shapes. Upon completion of the sample run, a "multiplier" must be input into the UPLC and GC to account for the dilutions and sample mass weighed. The following formula is used to calculate the multiplier:

$$Multiplier\% = \frac{Vextraction}{Mass} \times 100$$

where Vextraction is the total volume of the extract used (5 mL) and Mass is the mass of the dried cannabis weighed for the extraction (0.5 g). This will convert all results in ppb in cannabis (µg of pesticide/g of cannabis).

Validation of method (sample spiking and recovery)

To validate the method, sample spikes were performed on ground cannabis prior to the extraction and clean-up. The pesticide mixes were spiked into 0.5 g of fresh ground "pesticide-free" cannabis samples. Extraction and clean-up were performed resulting in 2000, 1000, 500, 250, 100, 50, 25, 10, 5, and 2 ppb spiked samples. After applying the multiplier (described above), the concentration of the pesticides mentioned above are 10x higher in the cannabis sample.

The spiking procedure was performed at nine different spike concentrations for each pesticide to obtain the limit of quantification (LOQ) for each individual pesticide. Once the LOQ was established, three spikes of each analyte at their respective LOQ were performed to obtain average spike recoveries and relative standard deviations (RSD) for each pesticide individually.

As shown in Table 1, spike recoveries for all pesticides at their LOQs averaged between 81.7% and 117.6%. The acceptable % recovery limits for method validation are between 70% and 120%. Low relative standard deviations (RSD) were also reported for all 96 spike recoveries (all <20%). The acceptable RSD for method validation is <20%.

It should be noted that the recovery for daminozide is determined separately since it is strongly retained by the PSA sorbent. For spike recoveries and to test for the presence of daminozide in cannabis samples, a separate LC-MS/MS run is performed following sample extraction but before clean-up.

#	Pesticide (conc. in ppb)	Average spike recovery (%)	RSD (%)	Method
1	Abamectin (20)	97.4	10.7	LC
2	Acephate (20)	91.5	2.5	LC
3	Acequinocyl (100)	98.5	3	LC
4	Acetamiprid (50)	81.7	0.5	LC
5	Aldicarb (50)	105.7	2.9	LC
6	Allethrin (100)	84.6	2.5	LC
7	Azadirechtin (50)	99.5	5.3	LC
8	Azoxystrobin (20)	91.3	14.9	LC
9	Benzovindiflupyr (20)	110.8	8.8	LC
10	Bifenzate (20)	87.3	3	LC
11	Bifenthrin (250)	93.5	14.5	GC
12	Boscalid (20)	93.8	16.1	LC
13	Buprofenzin (20)	82.8	3.3	LC
14	Carbaryl (20)	93.6	1.9	LC
15	Carbofuran (20)	86.5	5.1	LC
16	Chlorantraniliprole (20)	90.7	16.7	LC
17	Chlorphenapyr (20)	97.3	14.3	LC
18	Chlorpyrifos (20)	117.6	3.2	LC
19	Clofentezine (20)	111.8	1.3	LC
20	Clothiandin (20)	87.7	5.6	LC
21	Coumaphos (20)	90.8	4.2	LC
22	Cyantranilipole (20)	84.4	2.9	LC
23	Cyfluthrin (250)	109.9	13.4	GC
24	Cypermethrin (100)	98.4	16.1	LC
25	Cyprodinil (20)	82	2.8	LC
26	Daminozide (100)	82	3.2	LC
27	Deltamethrin (100)	111.9	7.2	GC
28	Diazinon (20)	88.4	2.6	LC
29	Dichlorvos (20)	87.3	4.5	LC
30	Dimethoate (20)	82.2	0.4	LC
31	Dimethomorph (20)	98.3	4.9	LC
32	Dinotefuran (20)	85.8	5	LC
33	Dodemorph (20)	87.4	8.4	LC
34	Endosulfan-alpha (500)	107.6	12.4	GC
35	Endosulfan-beta (500)	99.1	11.8	GC
36	Endosulfan-sulfate (500)	89.3	0.9	LC
37	Ethoprophos (20)	83.6	2.2	LC
38	Etofenprox (20)	90	6.7	LC
39	Etoxazole (20)	81.7	0.4	LC
40	Etridiazole (500)	85.2	1.5	LC
41	Fenoxycarb (20)	91.9	12	LC
42	Fenpyroximate (20)	86.6	4.4	LC
43	Fensulfothion (20)	89.1	1.8	LC
44	Fenthion (50)	102.2	5.5	LC
45	Fenvalerate (1000)	87.5	9.7	GC
46	Fipronil (50)	98.9	19.9	LC
47	Flonicamid (20)	88.9	1.9	LC
48	Fludioxinil (20)	96.5	16.8	GC
49	Fluopyram (20)	85.9	2.5	LC
50	Hexythiazox (250)	103.6	10	LC
51	Imazalil (50)	83.3	1.4	LC
52	Imidacloprid (20)	86.4	0.5	LC
53	Iprodione (20)	115.1	6.5	LC
54	Kinoprene (5000)	96	4.8	GC
55	Kresoxim-methyl (20)	117.1	1.9	LC
56	Malathion (20)	83.8	1.7	LC
57	Metalaxyl (20)	91.1	2.8	LC
58	Methiocarb (20)	106.9	8.2	LC
59	Methomyl (20)	82.2	2.5	LC
60	Methoprene (100)	100.5	3.3	LC
61	Methyl parathion (100)	101.2	11.3	LC
62	Mevinphos I (20)	82	0.5	LC
63	MGK-264 (500)	100.2	7.6	GC
64	Myclobutanil (20)	98.5	3.1	LC
65	Naled (20)	91.1	9.3	LC
66	Novaluron (50)	107.4	0.8	LC
67	Oxamyl (50)	84.7	3.9	LC
68	Paclobutrazol (20)	85.4	6.3	LC
69	Permethrin (100)	89.1	6.4	GC
70	Phenothrin (20)	92.4	17.1	LC
71	Phosmet (50)	106.3	12.1	LC
72	Piperonyl butoxide (50)	92.7	2.6	LC
73	Pirimicarb (20)	84.5	2.1	LC
74	Prallethrin (50)	109.5	5.4	LC
75	Propiconazole (100)	102.9	5.1	LC
76	Propoxur (20)	109.3	1.4	LC
77	Pyraclostrobin (20)	83.9	3.1	LC
78	Pyrethrin II (20)	109.1	4.6	LC
79	Pyridaben (20)	114.2	1.1	LC
80	Quintozene (250)	98.5	11.7	GC
81	Resmethrin (100)	100.8	6	GC
82	Spinetoram (50)	102.5	7.2	LC
83	Spinosad A (100)	95.4	7.7	LC
84	Spirodiclofen (20)	102	15.6	LC
85	Spiromesifen (100)	82.5	2.9	LC
86	Spirotetramat (20)	88.6	3.7	LC
87	Spiroxamine II (20)	90.1	6.7	LC
88	Tebuconazole (20)	87.6	1.1	LC
89	Tebufenozide (20)	104.5	9	LC
90	Teflubenzuron (50)	94.4	5.2	LC
91	Tetrachlorvinphos (20)	92.9	9.8	LC
92	Tetramethrin (20)	82	5	LC
93	Thiacloprid (20)	88.1	0.4	LC
94	Thiamethoxam (20)	84.6	0.7	LC
95	Thiophanate-methyl (50)	104.3	11.4	LC
96	Trifloxystrobin (20)	107.2	3.1	LC

Table 1. Spike recoveries for the 96 pesticides in dried cannabis sample.

Limits of quantification (LOQs)

The LOQs were calculated for all 96 pesticides. To determine the LOQs, pesticide-free cannabis samples were spiked with various concentrations of standards ranging from 1–2000 ppb. Sample spike recoveries between 80% and 120% were deemed acceptable. Once the lowest acceptable spike recoveries (lowest concentrated spike) were determined for each pesticide, three separate runs were performed and only after all three runs fell within the acceptable limits was the LOQ established. As shown in Table 2, all LOQ values are within Health Canada's limits.

#	Analyte	LOQ in cannabis (ppb)	LOQ Health Canada (ppb)	Method
1	Abamectin	20	N/A	LC-MS/MS
2	Acephate	20	20	LC-MS/MS
3	Acetamiprid	50	100	LC-MS/MS
4	Acequinocyl	100	N/A	LC-MS/MS
5	Aldicarb	50	1000	LC-MS/MS
6	Allethrin	100	200	LC-MS/MS
7	Azadirachtin	50	1000	LC-MS/MS
8	Azoxystrobin	20	20	LC-MS/MS
9	Benzovindiflupyr	20	20	LC-MS/MS
10	Bifenazate	20	20	LC-MS/MS
11	Bifenthrin	250	N/A	GC-MS/MS
12	Boscalid	20	20	LC-MS/MS
13	Buprofezin	20	20	LC-MS/MS
14	Carbaryl	20	50	LC-MS/MS
15	Carbofuran	20	20	LC-MS/MS
16	Chlorantraniliprole	20	N/A	LC-MS/MS
17	Chlorphenapyr	20	N/A	LC-MS/MS
18	Chlorpyrifos	20	N/A	LC-MS/MS
19	Clofentezine	20	20	LC-MS/MS
20	Clothianidin	20	50	LC-MS/MS
21	Coumaphos	20	20	LC-MS/MS
22	Cyantranilipole	20	N/A	LC-MS/MS
23	Cyfluthrin	250	N/A	GC-MS/MS
24	Cypermethrin	100	N/A	LC-MS/MS
25	Cyprodinil	20	N/A	LC-MS/MS
26	Daminozide	100	N/A	LC-MS/MS
27	Deltamethrin	100	N/A	GC-MS/MS
28	Diazinon	100	N/A	LC-MS/MS
29	Dichlorvos	20	100	LC-MS/MS
30	Dimethoate	20	20	LC-MS/MS
31	Dimethomorph	20	N/A	LC-MS/MS
32	Dinotefuran	20	100	LC-MS/MS
33	Dodemorph	20	N/A	LC-MS/MS
34	Endosulfan-alpha	500	N/A	GC-MS/MS
35	Endosulfan-beta	500	N/A	GC-MS/MS
36	Endosulfan sulfate	500	N/A	LC-MS/MS
37	Ethoprophos	20	20	LC-MS/MS
38	Etofenprox	20	N/A	LC-MS/MS
39	Etoxazole	20	20	LC-MS/MS
40	Etridiazol	20	N/A	LC-MS/MS
41	Fenoxycarb	20	20	LC-MS/MS
42	Fenpyroximate	20	20	LC-MS/MS
43	Fensulfothion	20	20	LC-MS/MS
44	Fenthion	50	N/A	LC-MS/MS
45	Fenvalerate	1000	N/A	GC-MS/MS
46	Fipronil	50	60	LC-MS/MS
47	Flonicamid	20	50	LC-MS/MS
48	Fludioxonil	20	20	GC-MS/MS
49	Fluopyram	20	20	LC-MS/MS
50	Hexythiazox	250	N/A	LC-MS/MS
51	Imazalil	50	N/A	LC-MS/MS
52	Imidacloprid	20	20	LC-MS/MS
53	Iprodione	20	1000	LC-MS/MS
54	Kinoprene	5000	N/A	GC-MS/MS
55	Kresoxim-methyl	20	N/A	LC-MS/MS
56	Malathion	20	20	LC-MS/MS
57	Metalaxyl	20	20	LC-MS/MS
58	Methiocarb	20	20	LC-MS/MS
59	Methomyl	20	50	LC-MS/MS
60	Methoprene I	100	N/A	LC-MS/MS
61	Methyl parathion	100	N/A	LC-MS/MS
62	Mevinphos I	20	50	LC-MS/MS
63	MGK-264	5000	N/A	GC-MS/MS
64	Myclobutanil	20	20	LC-MS/MS
65	Naled	20	N/A	LC-MS/MS
66	Novaluron	50	50	LC-MS/MS
67	Oxamyl	50	3000	LC-MS/MS
68	Paclobutrazol	20	20	LC-MS/MS
69	Permethrin	1000	N/A	GC-MS/MS
70	Phenothrin	20	50	LC-MS/MS
71	Phosmet	50	N/A	LC-MS/MS
72	Piperonyl butoxide	50	N/A	LC-MS/MS
73	Pirimicarb	20	20	LC-MS/MS
74	Prallethrin	50	N/A	LC-MS/MS
75	Propiconazole	100	N/A	LC-MS/MS
76	Propoxur	20	20	LC-MS/MS
77	Pyraclostrobin	20	20	LC-MS/MS
78	Pyrethrins II	20	50	LC-MS/MS
79	Pyridaben	20	50	LC-MS/MS
80	Quintozene	250	N/A	GC-MS/MS
81	Resmethrin	100	100	GC-MS/MS
82	Spinetoram	50	N/A	LC-MS/MS
83	Spinosad A	100	N/A	LC-MS/MS
84	Spirodiclofen	20	N/A	LC-MS/MS
85	Spiromesifen	100	3000	LC-MS/MS
86	Spirotetramat	20	20	LC-MS/MS
87	Spiroxamine (II)	20	N/A	LC-MS/MS
88	Tebuconazole	20	N/A	LC-MS/MS
89	Tebufenozide	20	20	LC-MS/MS
90	Teflubenzuron	50	50	LC-MS/MS
91	Tetrachlorvinphos	20	20	LC-MS/MS
92	Tetramethrin	20	100	LC-MS/MS
93	Thiacloprid	20	20	LC-MS/MS
94	Thiamethoxam	20	20	LC-MS/MS
95	Thiophanate-methyl	50	50	LC-MS/MS
96	Trifloxystrobin	20	20	LC-MS/MS

Table 2. Experimental limits of detection for all 96 pesticides using the LC-MS/MS and GC-MS/MS methods.

Results and Discussion

Pesticides analysis by UPLC-MS/MS

Using the LC-MS/MS method, 84 pesticides were analyzed. The compounds analyzed by LC-MS/MS and the parameters used are listed in Table 2 and Appendix A. Representative MRM chromatograms for the pesticides acetamiprid (50 ppb), cyprodinil (25 ppb), fenoxycarb (25 ppb), and tetrachlorvinphos (25 ppb) in a pesticide-free extracted cannabis matrix are shown in Figure 1.

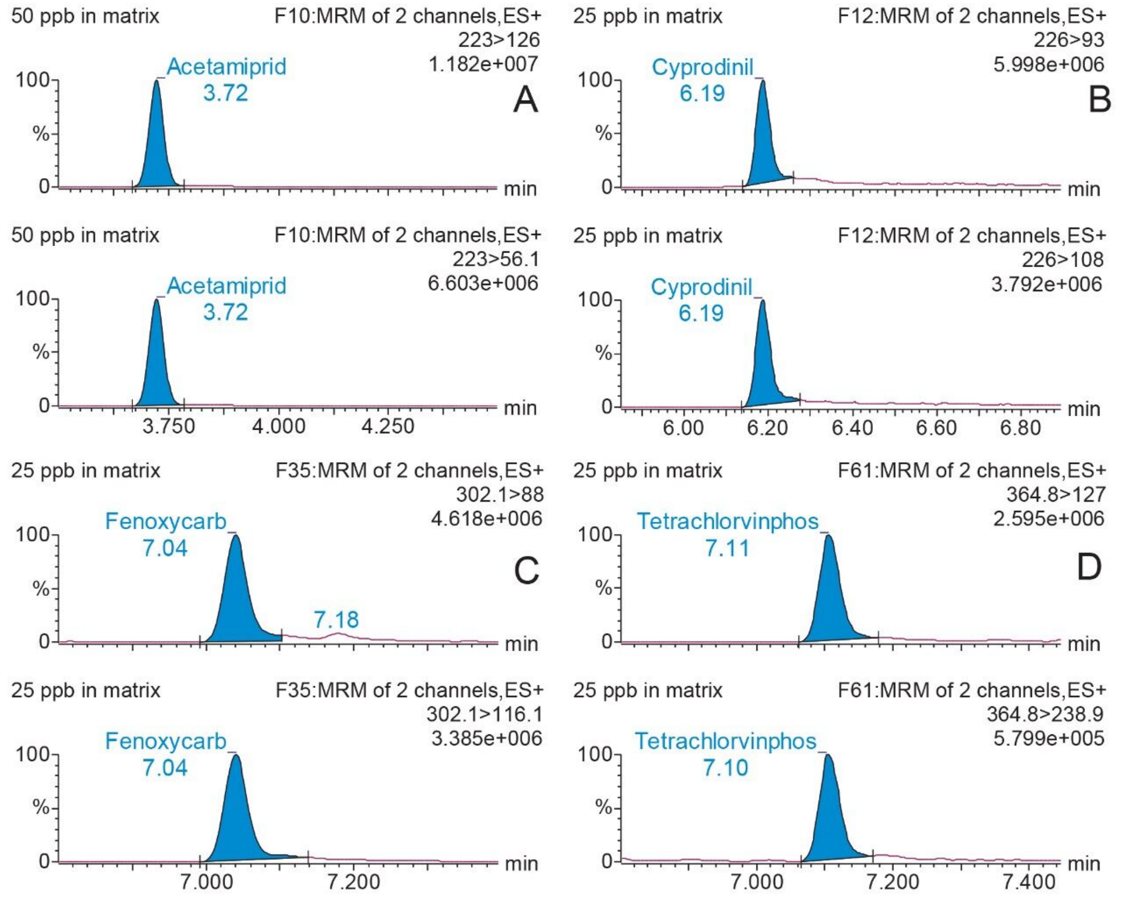

Figure 1. Representative MRM chromatograms showing the primary quantification and the secondary qualifier transition for acetamiprid (A, 50 ppb), cyprodinil (B, 25 ppb), fenoxycarb (C, 25 ppb), and tetrachlorvinphos (D, 25 ppb) in pesticide-free cannabis extracted using the sample preparation protocol reported.

Matrix-matched calibration curves were generated using pesticide-free extracted cannabis. An example of the calibration curves for the pesticides acetamiprid, cyprodinil, fenoxycarb, and tetrachlorvinphos are shown in Figure 2. Linear calibration curves (R^2>0.990) for all pesticides were obtained over the range tested as shown in the figure.

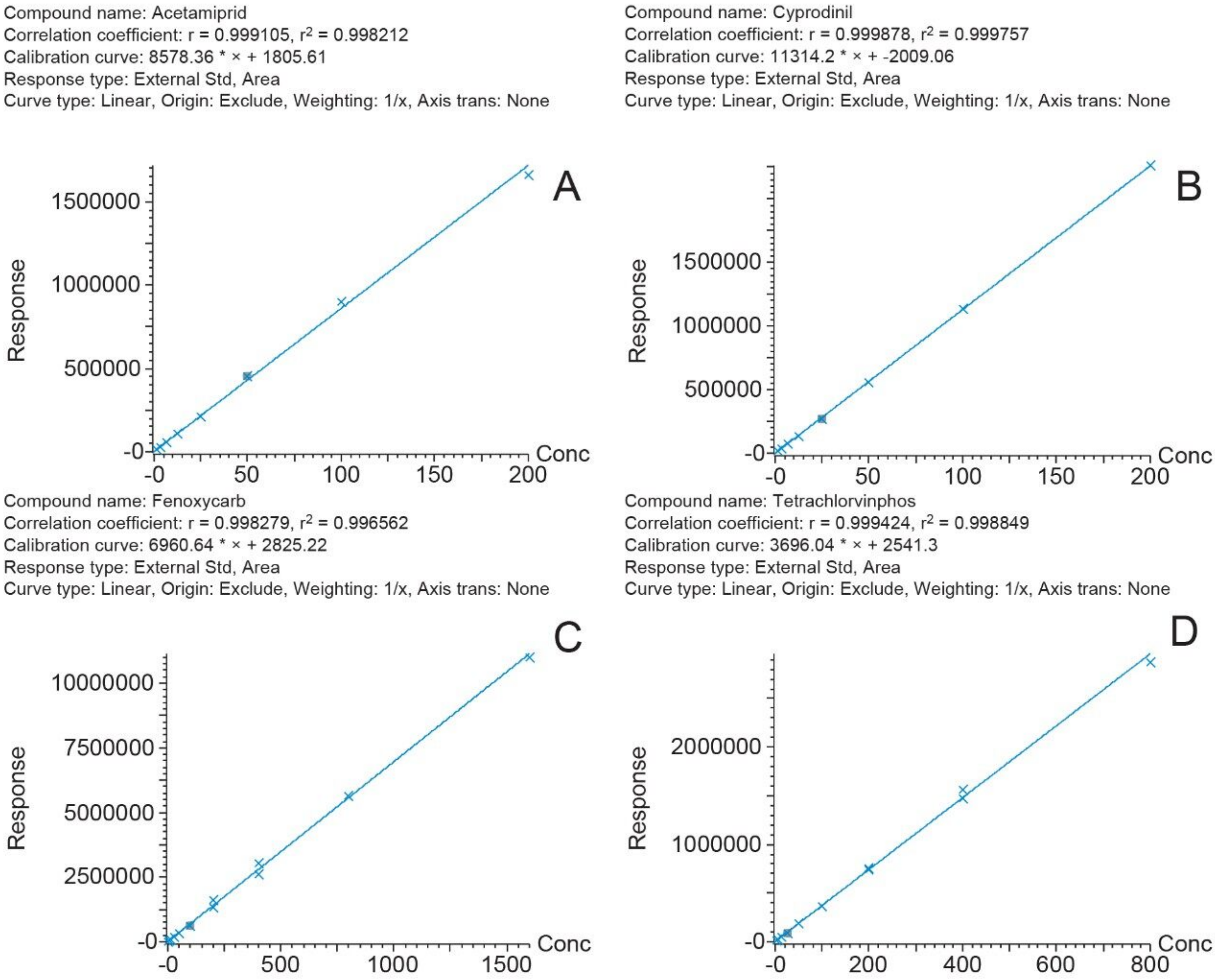

Figure 2. Representative examples of calibration curves for acetamiprid (A, 0.78–200 ppb), cyprodinil (B, 0.78–200 ppb), fenoxycarb (C, 0.78–1500 ppb), and tetrachlorvinphos (D, 0.78–800 ppb), demonstrating linearity over the ranges tested for these compounds.

Pesticides analysis by GC-MS/MS

Analysis of pesticide residues in cannabis also required the use of GC-MS/MS to meet the Canadian pesticide regulations. A complete list of compounds analyzed by GC-MS/MS and the parameters used is provided in Table 2 and Appendix B. Example chromatograms for endosulfan alpha and fenvalerate are shown in Figure 3.

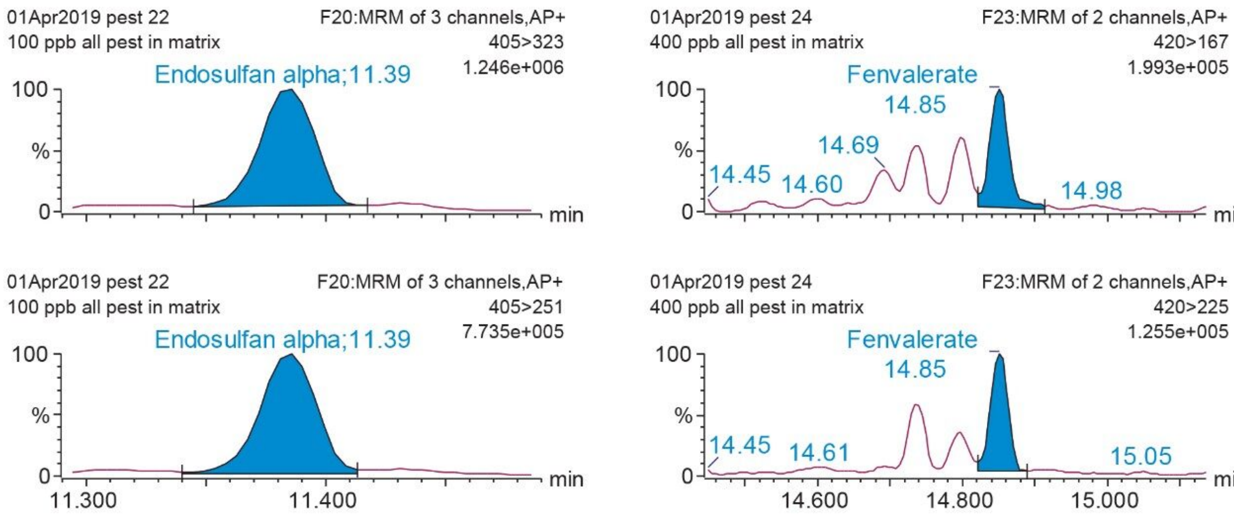

Figure 3. Representative MRM chromatograms showing the primary quantification and the secondary qualifier transition for endosulfan alpha (100 ppb) and fenvalerate at a level and 400 ppb (ng/g) in pesticide-free cannabis extracted using the sample preparation protocol reported.

An example of the calibration curves for the pesticides endosulfan alpha and fenvalerate are shown in Figure 4. Linear calibration curves (R^2>0.990) for both pesticides were obtained over the range tested, as shown in the figure.

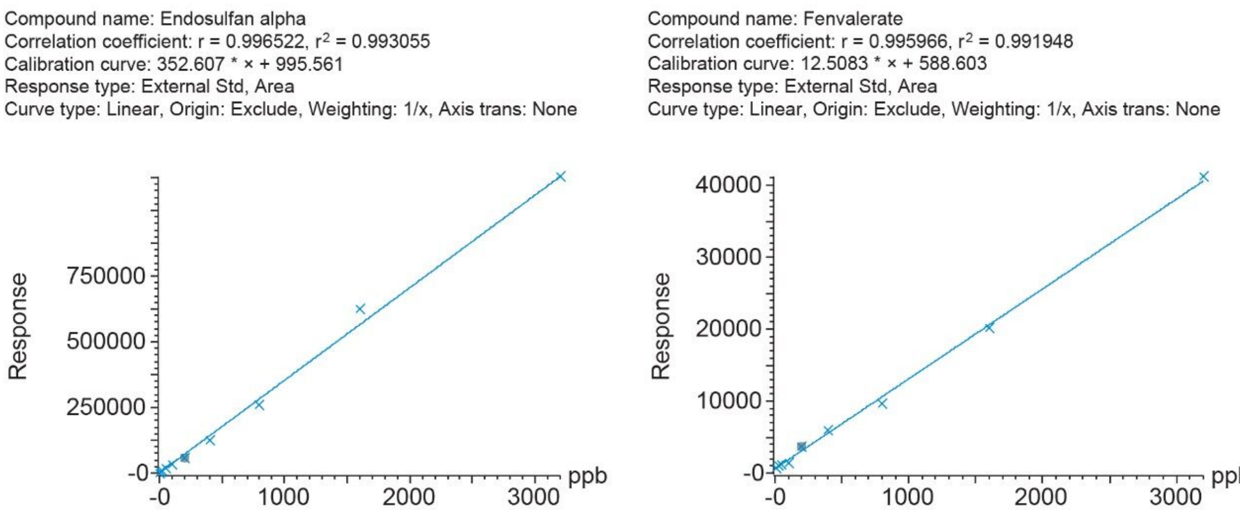

Figure 4. Representative examples of calibration curves for endosulfan alpha and fenvalerate demonstrating linearity over the ranges tested for these compounds.

Conclusion

The simple sample extraction and d-SPE clean-up method followed by UPLC-MS/MS and GC-MS/MS analysis provides a rapid, sensitive, and robust workflow for the determination of the Canadian pesticide list in challenging cannabis matrices. Complex multi-residue pesticide analysis in a cannabis matrix was demonstrated using both UPLC and APGC analysis on the same tandem quadrupole instrument (Xevo TQ-S micro) with detection at the maximum action levels for each of the 96 pesticides in the Canadian pesticide list. Having the flexibility of universal source architecture to provide access to both UPLC-MS/MS and GC-MS/MS on the same instrument, allows for an increase of laboratory efficiency, while maintaining required sensitivity and repeatability. This method meets the action levels for the Canadian pesticide list and mycotoxins in cannabis matrices.

References

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Appendix A.

MS/MS parameters for pesticides using UPLC.

	Analyte	Retention time (min)	MW (g/mol)	Precursor (*m/z*)	Product (*m/z*)	CV	CE	Health Canada detection limit (ppb)
1	Abamectin	8.65	873.09	895.46	182.9	76	48	N/A
				895.46	327.02	76	52	
				895.46	751.22	76	44	
2	Acephate	1.88	183.2	183.9	94.6	20	25	20
				183.9	142.8	20	10	
3	Acetamiprid	3.7	222.67	223	56.1	30	15	100
				223	126	30	20	
4	Acequinocyl	9.4	384.51	343.2	115	35	40	N/A
				343.2	189.1	35	20	
5	Aldicarb	4.37	190.261	213.1	89.1	35	20	1000
				213.1	116.1	35	11	
6	Allethrin	7.92	302.4079	303.03	90.95	20	44	200
				303.03	134.94	20	10	
7	Azadiractin	5.6	720.721	703.2	567	10	10	1000
				703.2	585	10	10	
				703.2	685	10	10	
8	Azoxystrobin	6.29	403.394	404.1	328.9	15	30	20
				404.1	372	15	16	
9	Benzovindiflupyr	7.25	398.235	398	322	20	18	20
				398	342	20	10	
10	Bifenazate	6.72	300.3523	301.1	170	25	20	20
				301.1	198	25	10	
11	Boscalid	6.46	343.2067	342.9	139.9	25	20	20
				342.9	307	25	45	
12	Buprofezin	7.77	305.44	306.1	115.9	20	16	20
				306.1	201	20	12	
13	Carbaryl	5.23	201.22	202.1	127	30	22	50
				202.1	145	30	28	
14	Carbofuran	5.08	221.256	222.11	123	5	20	20
				222.11	165.1	5	10	
15	Chlorantraniliprole	6.08	483.15	481.6	283.9	15	23	N/A
				481.6	450.9	15	25	
16	Chlorfenapyr	7.5	407.6	409	59	58	16	N/A
				409	379	58	10	
17	Chlorpyrifos	8.04	350.59	350.1	97	25	33	N/A
				350.1	197.9	25	19	
18	Clofentezine	7.37	303.146	303	102	20	35	20
				303	138	20	15	
19	Clothianidin	3.3	249.678	250	132	25	15	50
				250	169	25	10	
20	Coumaphos	7.2	362.77	363	289	32	24	20
				363	307	32	16	
21	Cyantranilipole	5.49	473.715	475	286	20	13	N/A
				475	444	20	17	
22	Cypermethrin	7	416.3	415.8	375.12	6	4	N/A
				415.8	225.12	6	20	
23	Cyprodinil	6.22	225.29	226	93	5	35	N/A
				226	108	5	25	
24	Daminozide	0.9	160.171	161	61	24	12	N/A
				161	143	24	12	
25	Diazinon	7.27	304.25	305.1	96.9	20	35	N/A
				305.1	169	20	22	
26	Dichlorvos	4.92	220.98	221	79	23	34	100
				221	109	23	22	
27	Dimethoate	3.58	229.26	230	124.8	20	22	20
				230	198.8	20	10	
28	Dimethomorph	6.41	387.9	388.1	165	15	30	N/A
				388.1	300.9	15	20	
29	Dinotefuran	2.22	202.214	203	113	15	10	100
				203	129	15	10	
30	Dodemorph	5.6	281.48	282.1	98	40	28	N/A
				282.1	116	40	21	
31	Endofulfan Sulfate	6.59	422.903	423.04	124.97	14	34	N/A
				423.04	204.12	14	24	
32	Ethoprophos	6.87	242.332	242.97	97	18	31	20
				242.97	130.95	18	20	
33	Etofenprox	8.83	376.496	394.3	106.9	20	43	N/A
				394.3	177	20	15	

	Analyte	Retention time (min)	MW (g/mol)	Precursor (*m/z*)	Product (*m/z*)	CV	CE	Health Canada detection limit (ppb)
34	Etoxazole	8.2	359.417	360.2	57.2	60	25	20
				360.2	141.1	60	25	
35	Etridiazol	4.21	247.518	247.02	148.99	10	12	N/A
				247.02	205.97	10	12	
36	Fenoxycarb	7.03	301.34	302.1	88	10	20	20
				302.1	116.1	10	11	
37	Fenpyroximate	8.31	421.497	422.2	138.1	5	30	20
				422.2	366.1	5	20	
38	Fensulfothion	5.83	308.347	309	157.1	36	25	20
				309	173.1	36	22	
39	Fenthion	7.12	278.33	279	104.9	25	25	N/A
				279	168.9	25	18	
40	Fipronil	7.03	437.15	453.9	250	42	25	60
				453.9	330	42	13	
				453.9	368.1	5	25	
41	Flonicamid	2.74	229.1586	230.1	148.08	35	25	50
				230.1	203.7	35	15	
42	Fluopyram	6.78	396.717	397	173.2	30	41	20
				397	208.1	30	35	
43	Hexythiazox	8.11	352.877	353	168.1	10	25	N/A
				353	228.1	10	15	
44	Imazalil	5.25	297.18	297	69	25	20	N/A
				297	159	25	20	
45	Imidacloprid	3.36	255.661	256.1	174.9	25	20	20
				256.1	209	25	12	
46	Iprodione	6.99	330.165	330	245	35	15	1000
				330	288.1	35	15	
47	Kresoxim-methyl	7.13	313.353	314.2	115.9	30	12	N/A
				314.2	131	30	25	
48	Malathion	6.48	330.358	331	98.9	30	25	20
				331	126.9	30	12	
49	Metalaxyl	5.88	279.33	280.1	192.1	10	20	20
				280.1	220.1	10	15	
50	Methiocarb	6.29	225.306	226	121	25	20	20
				226	169	25	10	
51	Methomyl	2.74	162.2101	162.9	88	15	10	50
				162.9	105.9	15	10	
52	Methoprene	6.05	310.48	312.41	72.08	82	38	N/A
				312.41	81.06	82	38	
53	Methyl parathion	6.11	263.204	264	125.1	38	18	N/A
				264	232.1	38	14	
54	Mevinphos	3.75	224.1483	225.1	127.1	15	15	50
				225.1	193.1	15	10	
55	Myclobutanil	6.62	288.779	289.1	70.2	25	15	20
				289.1	125.1	25	30	
56	Naled	5.94	380.778	382.8	109	30	27	N/A
				382.8	127	30	17	
57	Novaluron	7.77	492.706	493.02	141	5	30	50
				493.02	158.03	5	15	
58	Oxamyl	2.66	219.259	237	72	15	10	3000
				237	90	15	10	
59	Paclobutrazol	6.49	293.79	294.1	70.2	10	20	20
				294.1	125.1	10	35	
60	Phenothrin	6.48	350.451	352.89	195.02	32	14	50
				352.89	227.14	32	16	
61	Phosmet	6	317.314	318	77	28	46	N/A
				318	160	28	22	
62	Piperonyl butoxide	7.98	338.438	356.3	119	20	35	N/A
				356.3	176.9	20	10	
63	Pirimicarb	4	238.29	239.1	72	25	20	20
				239.1	182.1	25	15	
64	Prallethrin	7.62	300.4	301.2	133	5	12	N/A
				301.2	169	5	9	
65	Propiconazole	7.37	342.22	342.1	69.1	35	30	N/A
				342.1	158.9	35	20	
66	Propoxur	5.02	209.2417	210.1	92.9	15	25	20
				210.1	110.9	15	12	
67	Pyraclostrobin	7.34	387.82	388.1	163	25	25	20
				388.1	193.9	25	12	
68	Pyrethrin	7.64	371.461	373.2	133	37	19	50
				373.2	161	37	8	

	Analyte	Retention time (min)	MW (g/mol)	Precursor (*m/z*)	Product (*m/z*)	CV	CE	Health Canada detection limit (ppb)
69	Pyridaben	8.55	364.93	365.1	147.1	5	24	50
				365.1	309.1	5	12	
70	Spinetoram	7.49	748.011	748.53	98.07	60	35	N/A
				748.53	142.16	60	30	
71	Spinosad	7.05	731.968	732.6	98.1	35	35	N/A
				732.6	142	35	30	
72	Spirodiclofen	8.37	411.319	411.14	71.16	35	15	N/A
				411.14	313.1	35	10	
73	Spiromesifen	8.24	370.4819	371.1	273.1	35	5	3000
				388.2	273.1	35	25	
74	Spirotetramat	6.81	373.449	374	302	20	30	20
				374	330	20	15	
75	Spiroxamine	6.06	297.476	298	100	40	32	N/A
				298	144	40	20	
76	Tebuconazole	7.18	307.82	308.2	70.1	30	24	N/A
				308.2	124.9	30	40	
77	Tebufenozide	7.05	352.478	353.22	105.13	10	20	20
				353.22	133.14	10	10	
78	Teflubenzuron	7.92	381.108	381	141	25	30	50
				381	158	25	15	
79	Tetrachlorvinphos	7.1	365.952	364.8	127	32	16	20
				364.8	238.9	32	20	
80	Tetramethrin	6.49	331.406	330.91	98.95	34	18	100
				330.91	126.99	34	10	
81	Thiacloprid	4.02	252.72	253	90	35	40	20
				253	125.8	35	20	
82	Thiamethoxam	2.86	291.71	292	132	25	20	20
				292	211.2	25	10	
83	Thiophanate methyl	4.92	342.39	343	93	25	35	50
				343	151	25	20	
84	Trifloxystrobin	7.59	408.37	409.2	145	25	40	20
				409.2	185.9	25	14	

Appendix B

MS/MS parameters for pesticides using GC.

	Analyte	Retention time (min)	MW (g/mol)	Precursor (*m/z*)	Product (*m/z*)	CE	Health Canada detection limit (ppb)
1	Bifenthrin	12.78	422.87	181	115	30	20
				181	165	20	
				181	166	30	
2	Cyfluthrin	14.07	434.3	434	91	30	N/A
				434	127	30	
				434	191	10	
3	Deltamethrin	15.75	505.21	506	93	50	N/A
				506	281	15	
4	Endosulfan Alpha	11.38	406.90	405	251	20	N/A
				405	323	10	
5	Endosulfan Beta	11.98	406.90	405	217	30	N/A
				405	323	10	
6	Fenvelarate	16.32	419.9	419.8	124.8	40	N/A
				419.8	286.9	10	
7	Fludioxonil	11.58	248.18	248	154	20	20
				248	182	20	
8	Kinoprene	10.73	276.42	277	78.99	30	N/A
				277	109	30	
				277	132	30	
9	MGK-264	10.8	275.38	276.2	98	20	N/A
				276.2	210.1	10	
10	Permethrin	13.75	391.28	355	319	10	N/A
				391	183	30	
				391	355	10	
11	Quintozine	9.31	250.32	248	213	30	N/A
				295.8	249.82	30	
				295.8	278.89	30	
12	Resmethrin	11.89	338.44	338.9	170.9	15	100
				338.9	292.9	10	

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Xevo TQ-S micro Triple Quadrupole Mass Spectrometry <https://www.waters.com/134798856>

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