SHIMADZU
Excellence in Science

Cannabis Testing Solutions

LCMS for pesticide screening

CIPS
Shimadzu Europa GmbH

Analysis of pesticides

Image: unitedpatientsgroup.net

Image: nhpr.org

High value crop, high risk of insect/mold attack

Spider mites

Caterpillar

Bud rot

Aphids

Powdery mildew

Images: http://www.growweedeasy.com/bugs-pests-symptoms-marijuana-grow

Analysis of pesticides

- Furalaxyl

→ Furalaxyl is one of the ingredients of the pesticide Fongarid

→ a fungicide for combating root and stem rot which penetrates the plant's system via the leaves and roots. Therefore, such fungicides are also referred to as "systemic fungicides”

→ It takes almost 50 days to halve the concentration of this pesticide in the flower tips

→ this active ingredient may only be used in ornamental plants and arboriculture

Analysis of pesticides

- Propamocarb

  → Propamocarb is contained in Previcur N (Bayer)

  → as Furalaxyl it is a fungicide used against foot and root rot.

  → takes about 25 days to halve the concentration of this pesticide in the flower tips

  → this active ingredient may only be used in ornamental plants and arboriculture

Analysis of pesticides

- Abamectin

  → Abamectin is contained in Vertimec

  → Although this known contact and stomach insecticide is of natural origin, it is no less toxic

  → It is mostly used against spider mites, but also works against miner flies and thrips

  → All three pesticides can cause severe health problems in humans

Analysis of pesticides

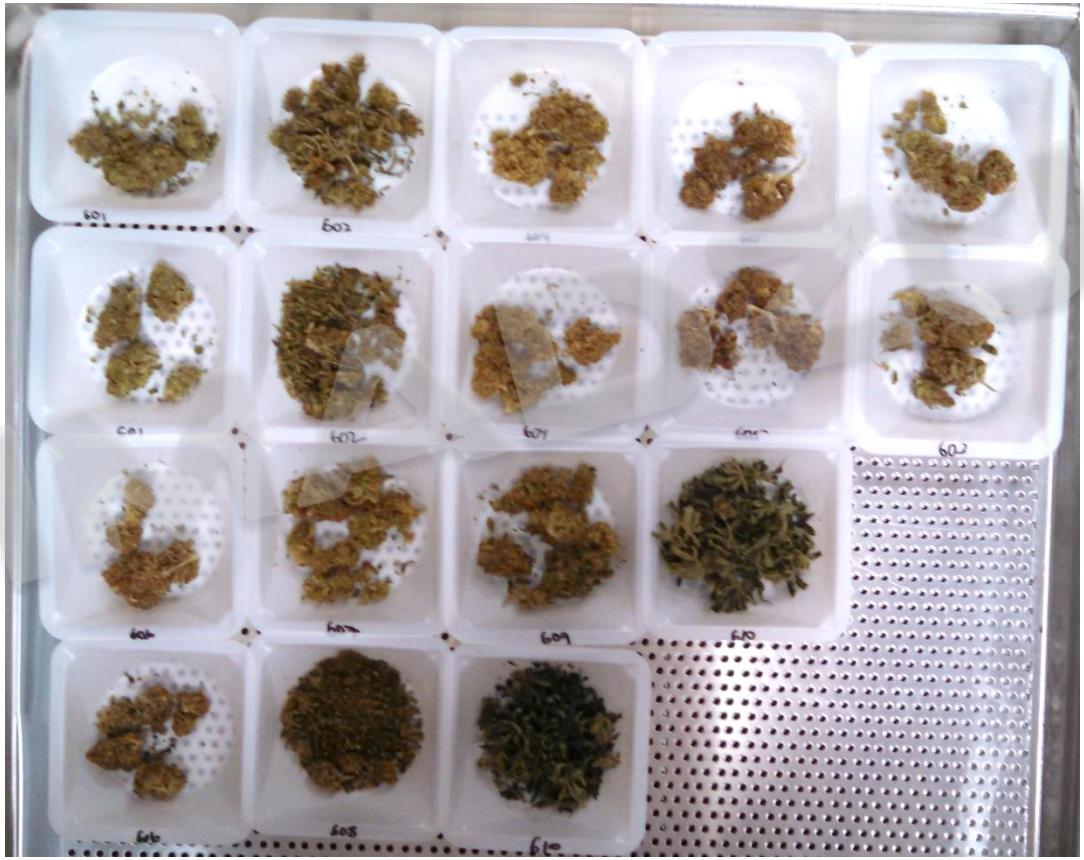
- Conventional testing for pesticides in fruits and vegetables

- Regulations mainly made by EU government
- Local and EU-level pesticide testing by EFSA

→ without official regulations each country can set their own limits for pesticide residues

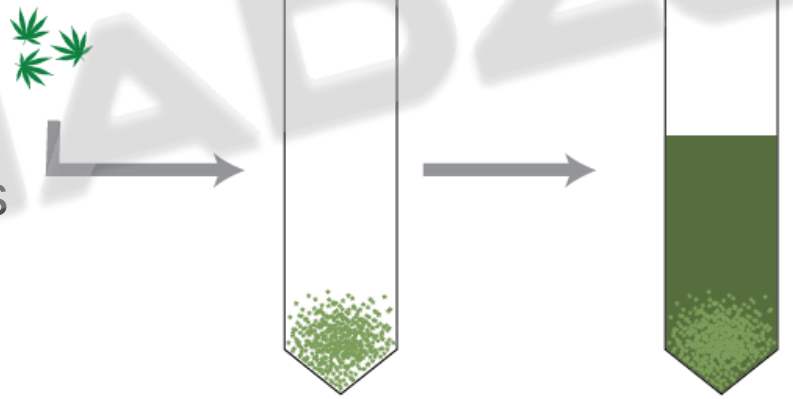
Analysis of pesticides

- Sample preparation
  - Test portion size 1.5 g dried flower
  - Homogenize the sample
  - Extract the sample using QuEChERS
  - Clean up the extract
  - Analyze the extract



Analysis of pesticides

- Sample preparation simplified
  - Grind test portion
  - Add 10 mL 1% acetic acid in acetonitrile vortex and shake
  - Spin at least 2 min at 3000 RCF
  - Transfer supernatant into a glass vial and inject an aliquot



Analysis of pesticides

- Sample preparation simplified

Dried flower

Ground

Solvent extracted

Analysis of pesticides

A system combining

high sensitivity and high speed

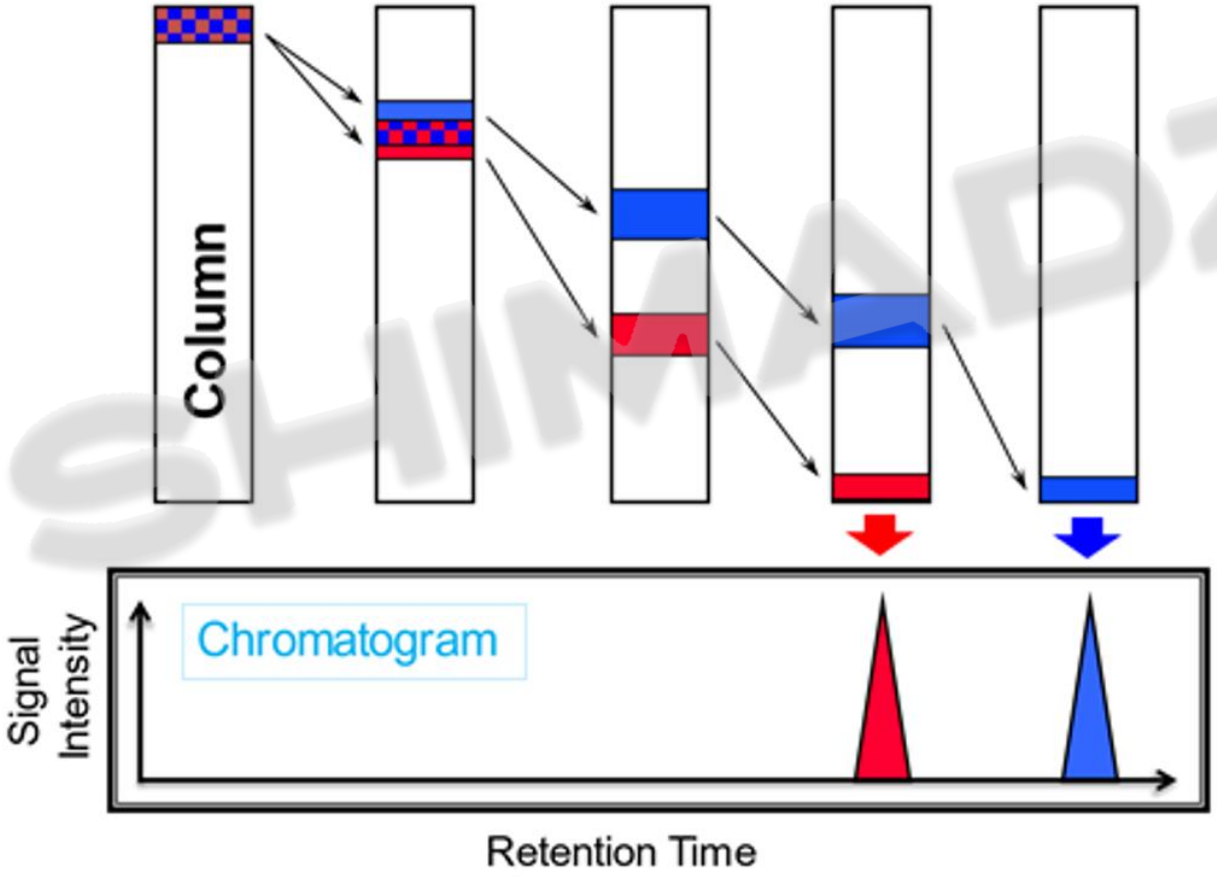
for better data quality :

LCMS-8050

Analysis of pesticides

LC separation

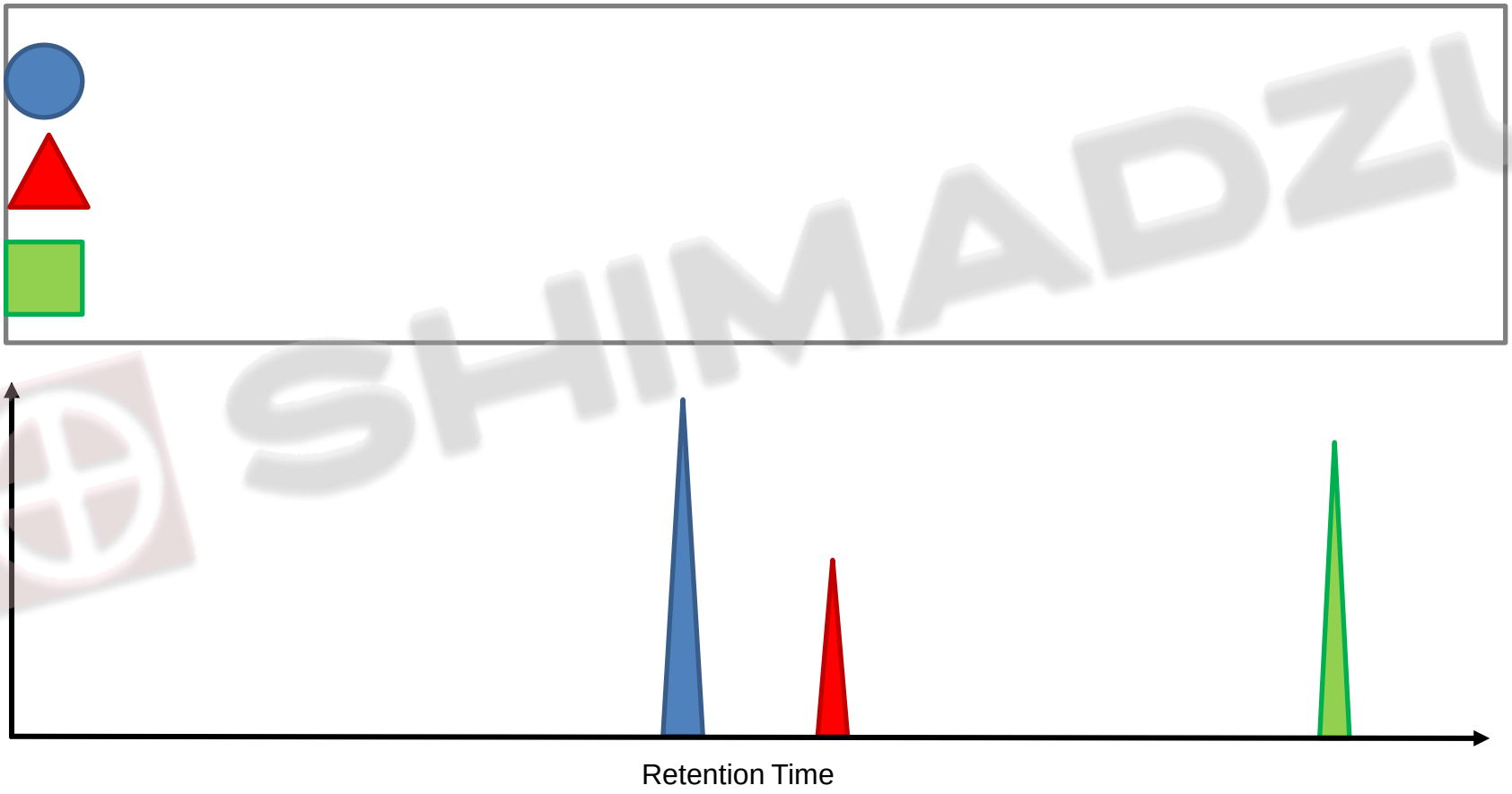
→ Separation due to differences in attraction



Analysis of pesticides

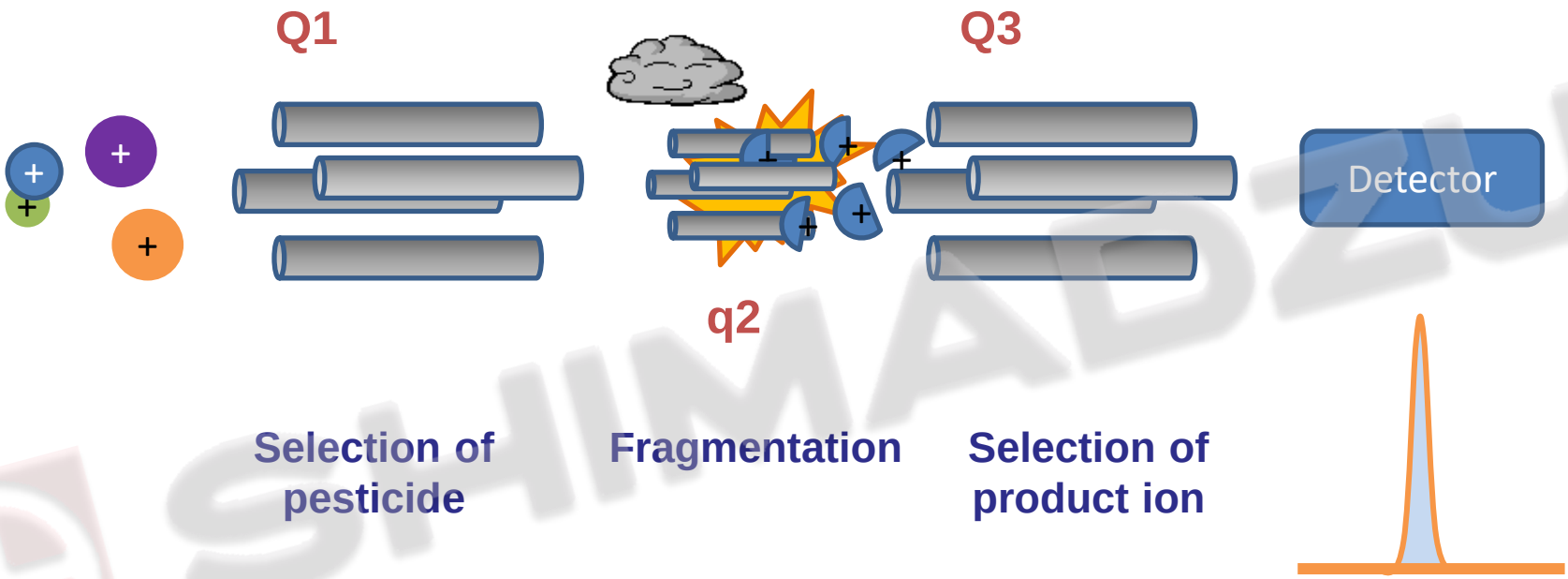
LC separation

→ Separation due to differences in attraction



Analysis of pesticides

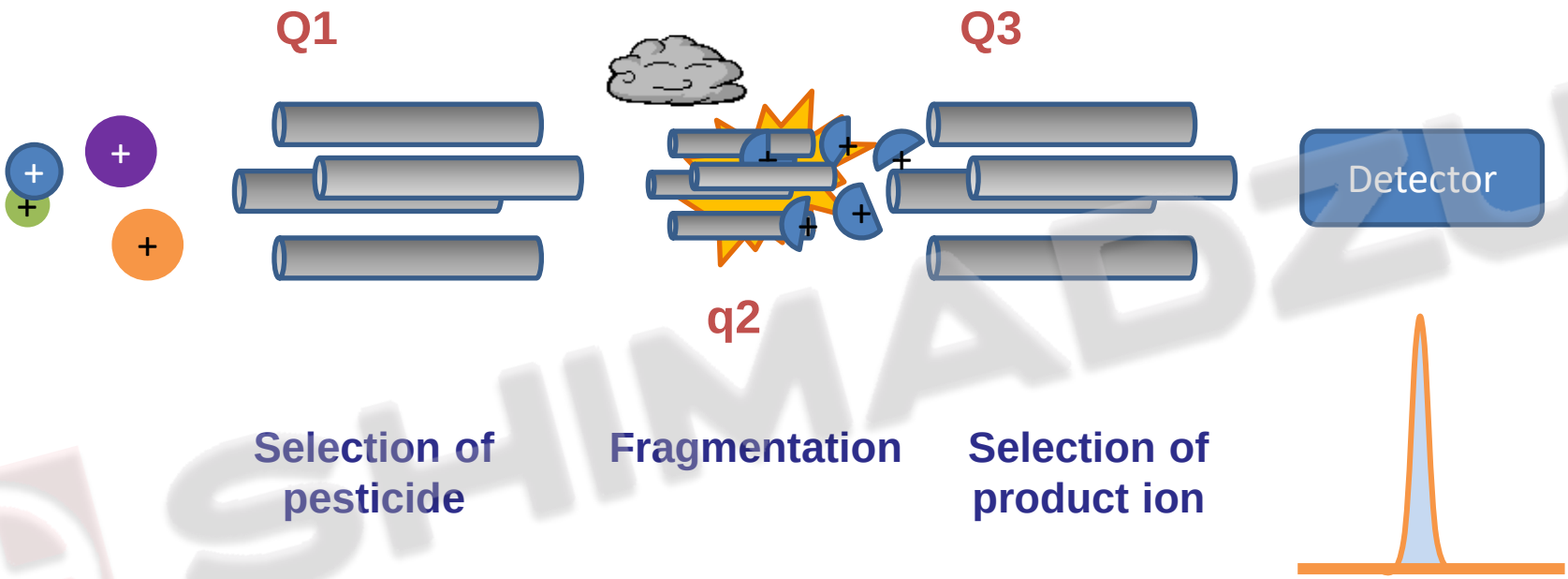
MS Detection



High sensitivity → Most isobaric impurities (same m/z as target) are excluded before reaching the detector, because fragments are different

Analysis of pesticides

MS Detection

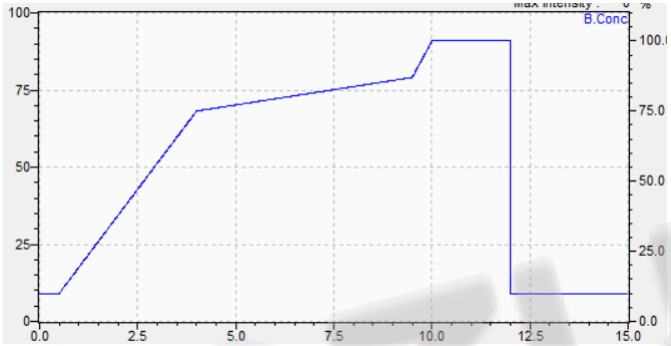


High selectivity → Only compounds with:

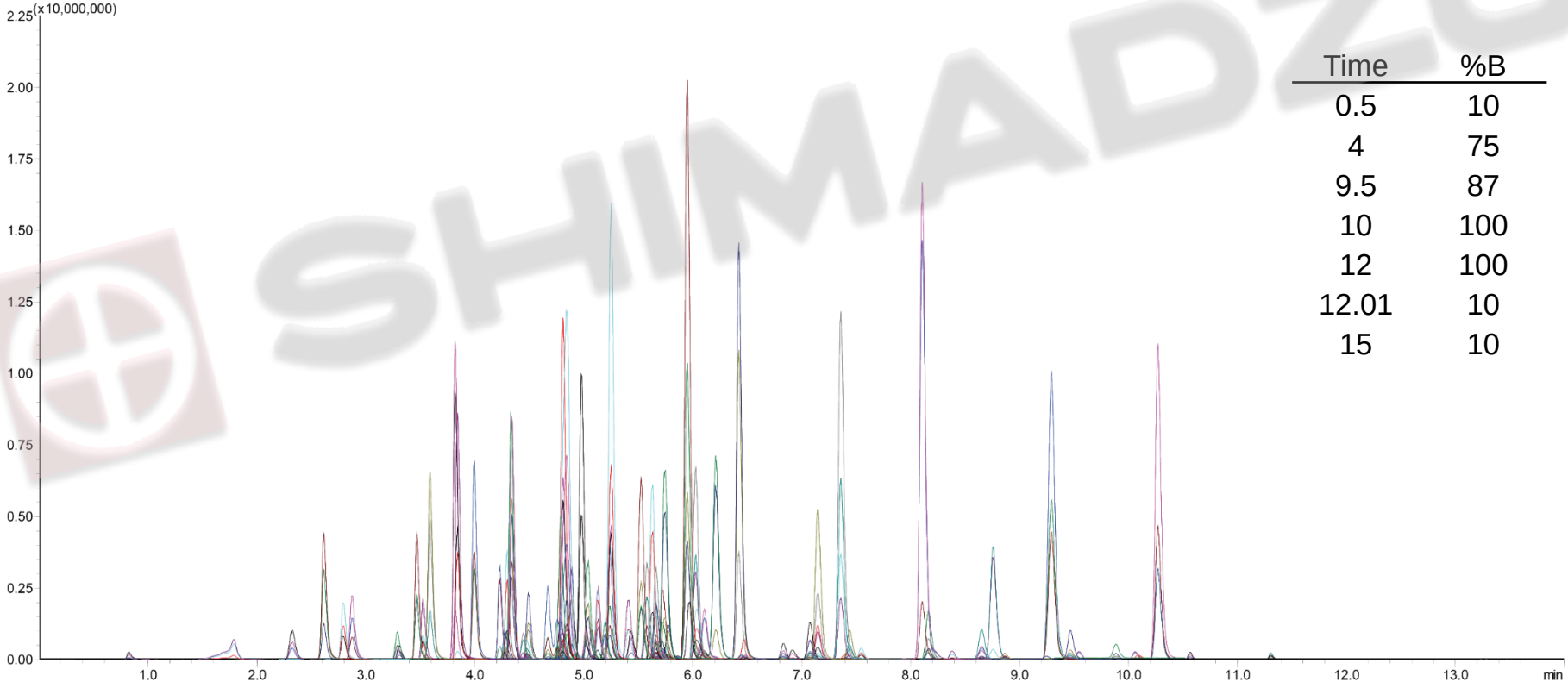
1. Selected m/z-ratio (precursor) **AND**
2. Selected fragments can reach the detector

Analysis of pesticides

LC Column: Restek Raptor ARC-18 2x150 mm
Pump A: 5 mM Amm Ac/0.1% Formic Acid
Pump B: Methanol
Injection solvent: ACN
Injection volume: 1 µL



Time	%B
0.5	10
4	75
9.5	87
10	100
12	100
12.01	10
15	10



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Analysis of pesticides

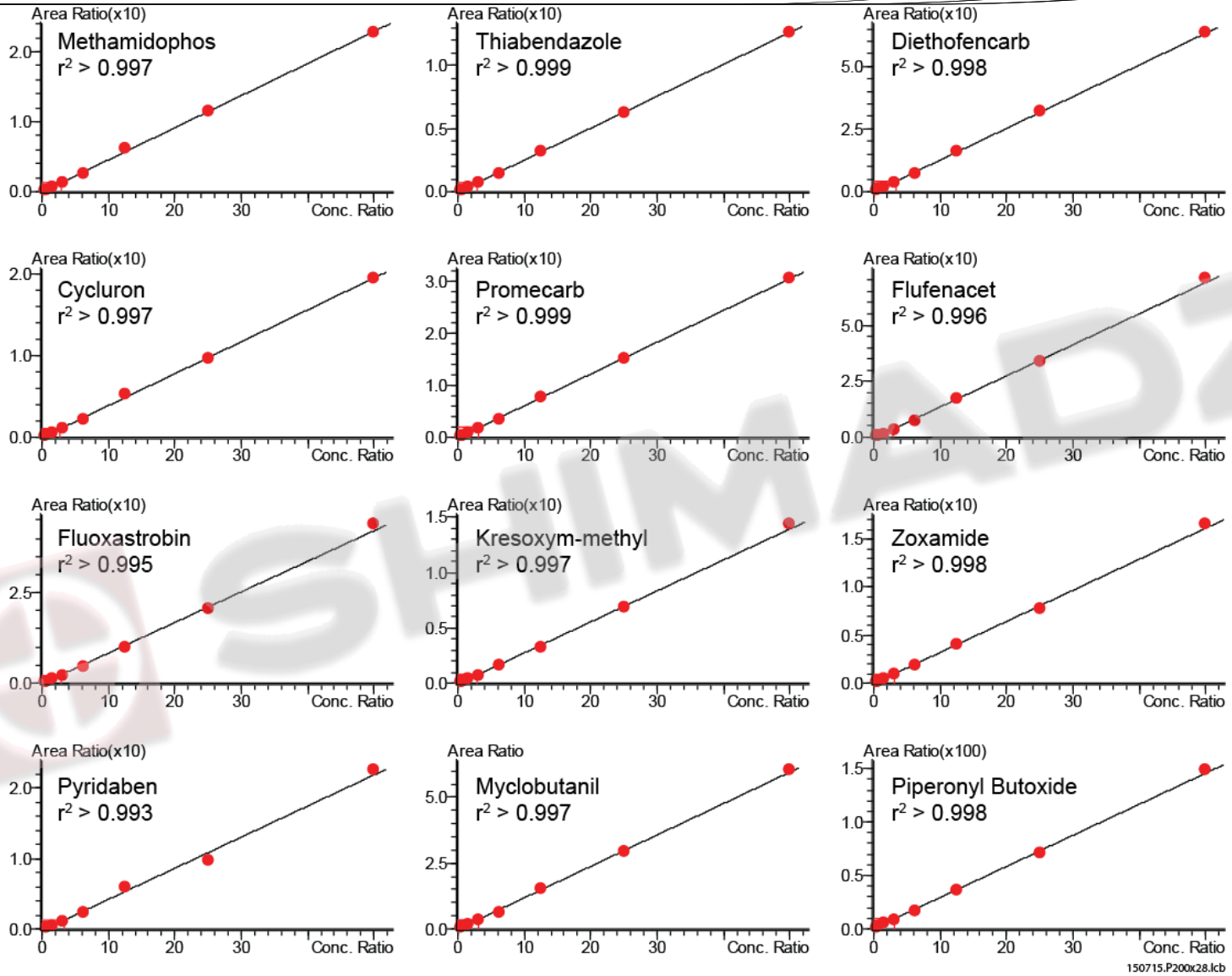
- Multi-Component Analysis

Type	Event#	+/-	Compound Name m/z	Time (0.088 min - 8.838 min)
MRM	1	+	Propargite 373.00>254.90	
MRM	2	+	CYROMAZINE 167.00>85.10	
MRM	3	+	CHLORPROPHAM 214.00>20	
MRM	4	+	PROPAMOCARB 189.00>102.	
MRM	5	+	Propamocarb 189.00>102.10	
MRM	6	+	Barbamate 258.90>218.05	
MRM	7	+	Propetamphos 282.00>15.35	
MRM	8	+	Pymetrozine 218.00>105.05	
MRM	9	+	Pyrethrin II 373.10>123.10	
MRM	10	+	Aminocarb 209.00>152.10	
MRM	11	+	ACEPHATE 184.00>142.95	
MRM	12	+	Propyzamide 256.00>224.25	
MRM	13	+	Carbendazim 192.00>160.10	
MRM	14	+	Omethoate 214.00>125.10	
MRM	15	+	Butocarboxim-sulfoxide 207.	
MRM	16	+	Pyrethrin I 329.20>52.25	
MRM	17	+	Thiabendazole 202.10>175.05	
MRM	18	+	NITENPYRAM 271.00>56.15	
MRM	19	+	Butoxycarboxim 223.00>53.4	
MRM	20	+	Fluodioxinil 229.00>180.70	
MRM	21	+	Aldoxycarb(AldicarbSulfone)	
MRM	22	+	Oxamyl 237.00>72.10	
MRM	23	+	Fonofos 247.00>169.00	
MRM	24	+	Methomyl 163.00>88.05	
MRM	25	+	Dimethirimol 210.20>71.15	
MRM	26	+	Methiocarb sulfone 258.00>1	
MRM	27	+	TERBACIL 217.00>97.20	
MRM	28	+	Propham 180.00>33.30	
MRM	29	+	Thiamethoxam 292.00>211.10	
MRM	30	+	Fenamiphos 304.00>225.70	
MRM	31	+	Ethoprophos 243.00>108.15	
MRM	32	+	Ethiofencarb sulfoxide 242.0	
MRM	33	+	DIFENZOQUAT 249.00>77.10	
MRM	34	+	Pirimicarb 239.00>72.10	
MRM	35	+	TriflumizoleMetabolite 296.00	
MRM	36	+	MALATHION 331.00>46.35	
MRM	37	+	Hexythiazox 353.00>171.00	
MRM	38	+	Metamitron 203.00>166.40	
MRM	39	+	VAMIDOTHION 288.00>146.0	
MRM	40	+	Clothianidin 250.00>169.00	

Dwell time 1msec
Pause time 1msec

MRM	287	-	Gibberellin 345.00>142.95	
MRM	288	-	Fluroxypyr 252.90>195.05	
MRM	289	-	Fluazinam 462.50>416.00	
MRM	290	-	1-Naphthaleneacetic Acid 18	
MRM	291	-	4-Chlorophenoxyacetic 184.9	
MRM	292	-	Cloprop 198.90>127.15	
MRM	293	-	Bromoxynil 275.70>81.00	
MRM	294	-	BENTAZONE 239.00>132.10	
MRM	295	-	MCPA(MCP) 198.90>141.05	
MRM	296	-	2,4-D(2,4-PA) 219.80>162.15	
MRM	297	-	Triclopyr 255.80>197.95	
MRM	298	-	Ioxynil 369.70>126.85	
MRM	299	-	Mecoprop (MCPP) 213.00>14	
MRM	300	-	Dichlorprop 232.90>161.00	
MRM	301	-	MCPB 227.00>141.00	
MRM	302	-	FLUDIOXONIL 247.00>126.00	
MRM	303	-	BENFURESATE 255.00>196.	
MRM	304	-	2,4,5-T 253.00>195.00	
MRM	305	-	Clodinafopacid 310.20>237.85	
MRM	306	-	Halosulfuron-methyl 433.70>	
MRM	307	-	Tebufenozide 351.10>149.00	
MRM	308	-	FLUOROIMIDE 240.00>168.05	
MRM	309	-	THIFLUZAMIDE 525.00>125.0	
MRM	310	-	FIPRONIL 435.00>330.00	
MRM	311	-	TRICHLAMIDE 338.00>116.90	
MRM	312	-	Fomesafen 437.00>194.95	
MRM	313	-	Teflubenzuron 380.60>340.90	
MRM	314	-	Acifluorfen 359.90>315.95	
MRM	315	-	Novalron 491.10>470.90	
MRM	316	-	FLUSULFAMIDE 413.00>170.	

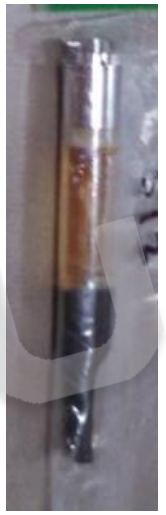
Analysis of pesticides



Analysis of pesticides

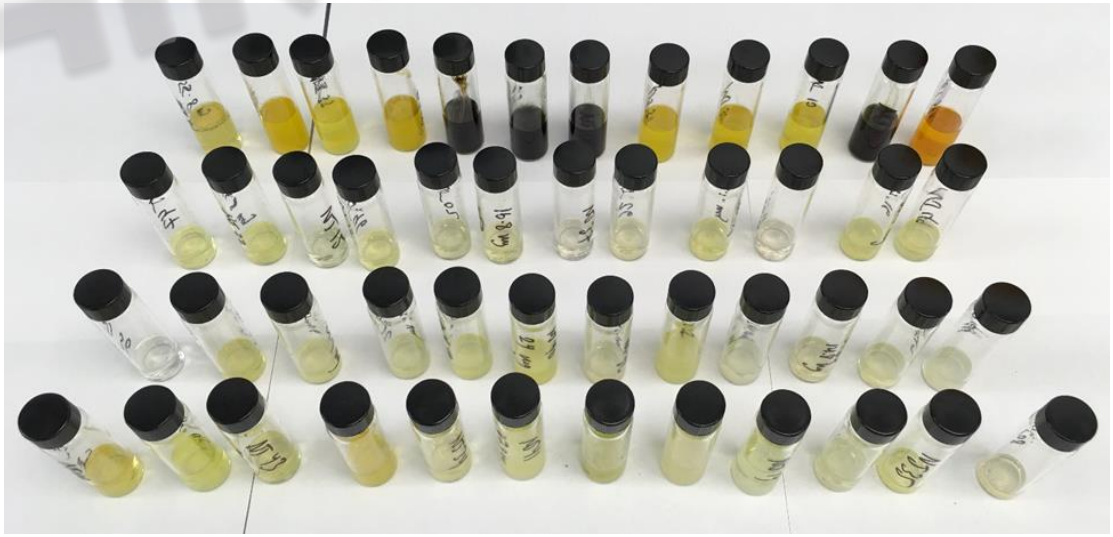
- Cannabis concentrates

Shatter
Oil
Hash
Resin
Crumble
Butter
Wax
Caramel
Tincture



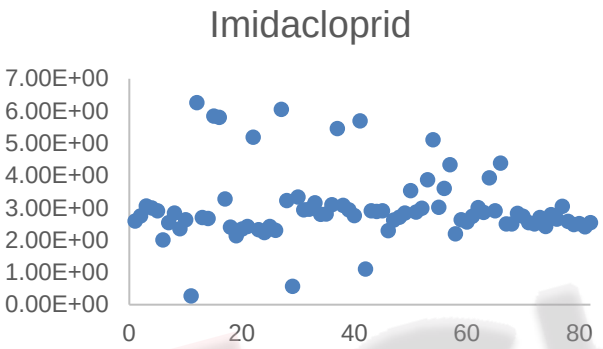
Analysis of pesticides

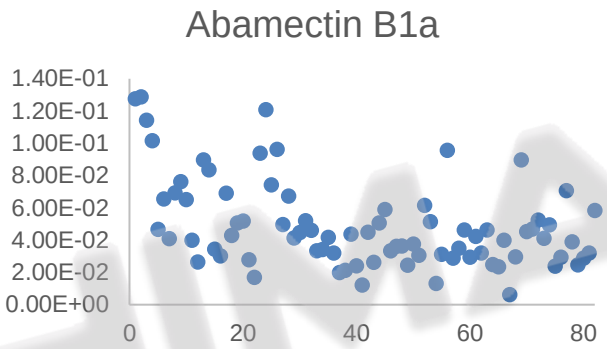
- Dilute and shoot of concentrate samples
  - Weigh sample into vial (20 mg) and diluted to10 mg/mL with MeOH
  - Shake vigorously and allow to dissolve
  - Filter by syringe filter or filter vials (preferred)
  - Spike a second aliquot of each at 100 ng/mL authentic standard
  - Run all samples spiked with IS

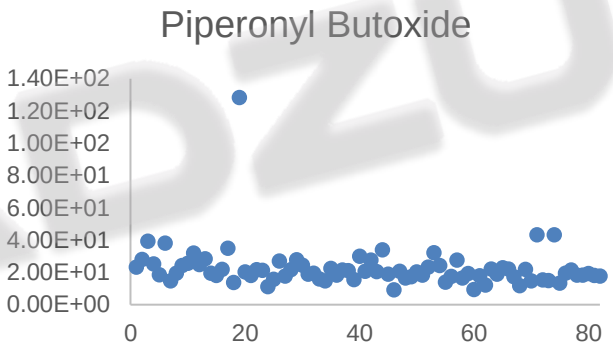


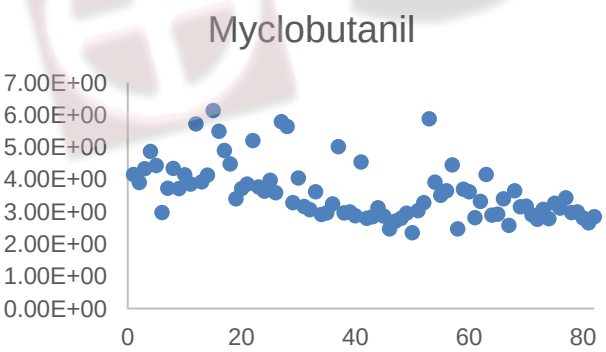
Analysis of pesticides

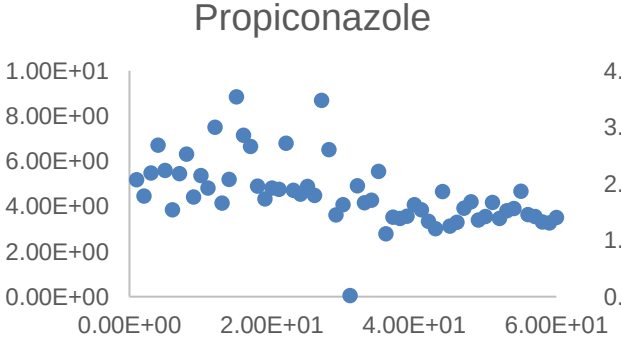
- Spike recovery from single point standard addition in concentrates

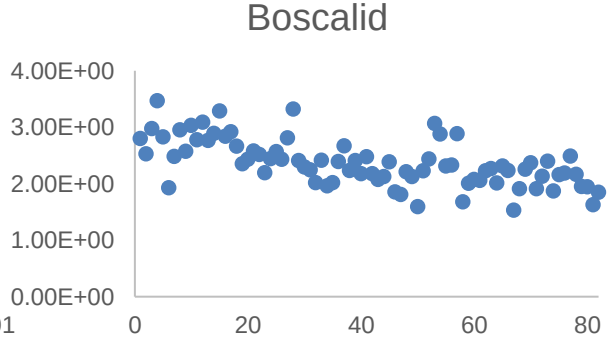






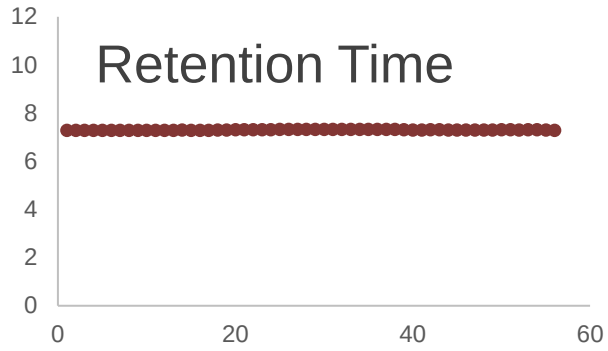


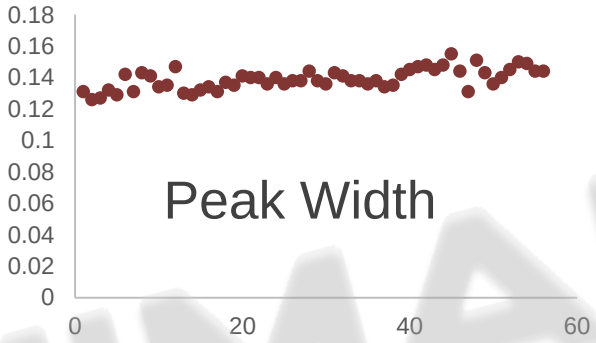


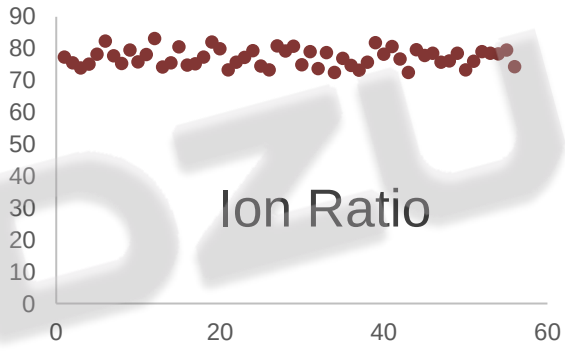


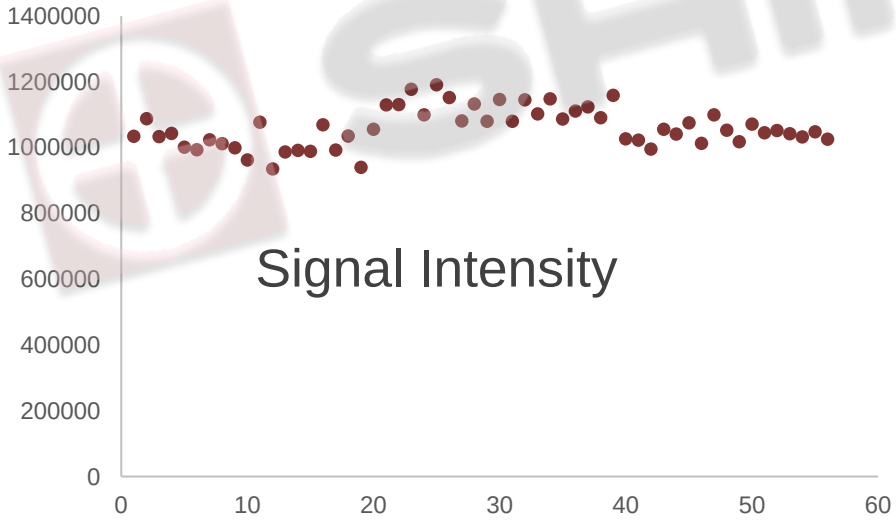
Analysis of pesticides

- Robustness tested over 2 weeks at Trace Analytics









- 34 batches were run
- over 800 injections of dried flower samples and dilute-and-shoot concentrates

Analysis of pesticides

- Summary
  - Chemicals are widely used in cannabis cultivation, sometimes unknowingly
  - Growers may switch to new pesticides that are not currently on any monitoring lists
  - LCMS methods can be easily adapted
  - LCMS performance was very robust and sensitive

Disclaimer

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