Impact of Using 1.5 mm Column ID and Various Stationary Phases on LC/MS Pesticide Screening Analysis

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Background

- Pesticide screening analysis is used for testing various matrices, including food, soil, water, and cannabis
- Comparison of retention times and peak shapes from 3 different superficially porous particle alkyl stationary phases:
  - HALO® C18, HALO® LPH-C18, and HALO® AQ-C18
- Investigation on how changing from a 2.1 mm ID column to a 1.5 mm ID column impacts the results

Methods

Sample: Oregon Pesticide Mixture 10x Action Limit 2-20 µg/mL in ACN from LGC (DRE-GA09000244AL)

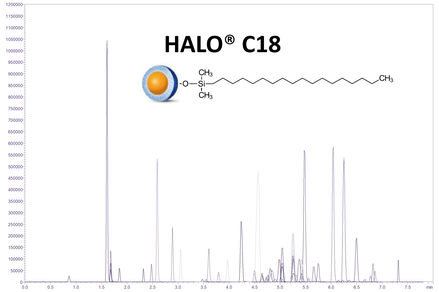
Columns: HALO 90 Å C18, 2.7 µm, 2.1 x 50 mm (92812-402)
HALO 90 Å LPH-C18, 2.7 µm, 2.1 x 50 mm (92822-416)
HALO 90 Å AQ-C18, 2.7 µm, 2.1 x 50 mm (92812-422)
HALO 90 Å AQ-C18, 2.7 µm, 1.5 x 50 mm (9281X-422)
Competitor SPP 100 Å 100% Aqueous Compatible Phase, 2.6 µm, 2.1 x 50 mm

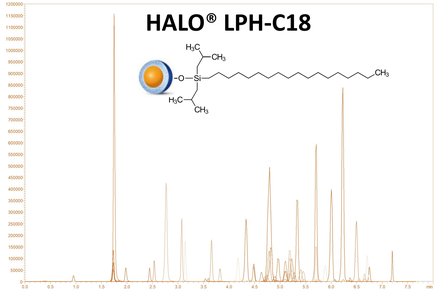
Mobile Phase A: Water with 5 mM ammonium formate & 0.1% Formic Acid
Mobile Phase B: Methanol with 5 mM ammonium formate & 0.1% Formic Acid

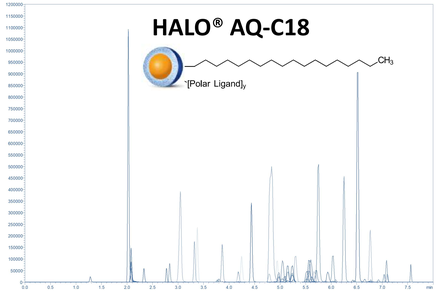
Gradient 1: 0-100% B in 7 min, hold at 100% for 1 min, then ramp to 0% B in 0.5 min, hold at 0% B for 3.5 min (AQ-C18, SPP 100% Aqueous Compatible Phase)
Gradient 2: 5-100% B in 6.65 min, hold at 100% for 1.35 min, then ramp to 0% B in 0.5 min, hold at 0% B for 3.5 min (C18, LPH-C18)

Flow Rate: 0.5 mL/min (2.1 mm) or 0.25 mL/min (1.5 mm)
Temperature: 35 °C
Detection: + ESI MS/MS for all except fludioxinil and fipronil
Injection Volume: 1 µL of 0.4 – 4 µg/mL
Sample Solvent: 80/20 Mobile Phase A/ACN
MS System: Shimadzu 8040 triple quadrupole
LC System: Shimadzu Nexera X2
Nebulizer Gas Flow: 2 L/min
DL Temperature: 250 °C
Heat Block Temperature: 400 °C
Drying Gas Flow: 15 L/min
Column outlet to Ground: AMT MarvelXACT™ PEEKsil™ 75 µm ID x 600 mm
Ground to Source: AMT MarvelXACT™ PEEKsil™ 75 µm ID x 150 mm

Stationary Phase Screening: Which C18 Should I Use?







Name	m/z	AQ-C18 Retention Time	LPH-C18 Retention Time	C18 Retention Time
Daminozide	161.1000>143.1000	0.48	0.38	0.34
Acephate	184.1000>143.1000	1.28	0.95	0.86
Oxamyl	237.1000>72.1000	2.03	1.75	1.61
Flonicamid	230.1000>203.1000	2.08	1.73	1.68
Methomyl	163.1000>88.1000	2.12	1.83	1.70
Thiamethoxam	292.1000>132.1000	2.33	1.98	1.85
Imidacloprid	256.1000>175.1000	2.77	2.44	2.32
Dimethoate	230.1000>125.1000	2.84	2.53	2.48
Acetamiprid	223.1000>126.1000	3.05	2.77	2.59
Aldicarb	208.1000>89.1000	3.32	3.14	3.05
Thiacloprid	253.1000>126.1000	3.38	3.07	2.89
Dichlorvos	221.1000>109.1000	3.77	3.54	3.48
Propoxur	210.1000>111.1000	3.80	3.59	3.55
Carbofuran	222.1000>165.1000	3.87	3.66	3.60
Carbaryl	202.1000>145.1000	4.18	3.82	3.79
Imazalil	297.1000>159.1000	4.24	4.17	3.97
Metalaxyl	280.2000>220.1000	4.44	4.33	4.24
Naled	381.1000>127.1000	4.61	4.35	4.33
Parathion-methyl	264.2000>232.1000	4.67	4.55	4.51
Chlorantraniliprole	481.9000>283.9000	4.79	4.48	4.49
Spiroxamine	298.1000>144.1000	4.83	4.79	4.57
Phosmet	318.1000>160.1000	4.94	4.48	4.50
Methiocarb	226.1000>121.1000	4.97	4.63	4.64
Azoxystrobin	404.1000>344.1000	4.97	4.70	4.64
Paclobutrazol	294.1000>70.2000	5.05	4.79	4.80
Boscalid	343.1000>307.1000	5.09	4.74	4.76
Fludioxinil	246.6000>125.9000	5.14	4.70	4.73
Malathion	331.1000>99.1000	5.15	4.82	4.84
Myclobutanil	289.1000>69.9000	5.15	4.90	4.90
Pyrethrin I	329.1000>161.1000	5.18	6.30	6.32
Spirotetramat	374.1000>330.1000	5.24	5.10	5.04
Ethoprophos	243.1000>130.9000	5.26	5.10	5.04
Bifenazate	301.1000>170.2000	5.30	4.96	4.98
Fipronil	434.9000>330.8000	5.52	5.19	5.26
Fenoxycarb	302.1000>116.1000	5.57	5.23	5.25
Tebuconazole	308.2000>70.1000	5.60	5.34	5.37
Kresoxim-methyl	314.1000>116.1000	5.62	5.28	5.31
Propiconazole	342.1000>69.1000	5.67	5.46	5.42
Diazinon	305.1000>169.1000	5.71	5.41	5.43
Spinosad A	732.6000>142.1000	5.75	5.70	5.48
MGK 264	276.1000>210.1000	5.89	5.64	5.66
Prallethrin	301.2000>133.1000	5.91	5.70	5.69
Spinosad D	746.5000>142.1000	5.93	5.88	5.66
Pyrethrin II	373.2000>161.1000	6.01	5.79	5.75
Chlorfenapyr	409.2000>59.0000	6.03	5.70	5.75
Trifloxystrobin	409.1000>186.1000	6.03	5.71	5.75
Clofentezine	303.1000>138.1000	6.09	5.47	5.56
Piperonyl butoxide	356.2000>177.1000	6.25	6.01	6.04
Hexythiazox	353.1000>228.1000	6.43	6.07	6.14
Chlorpyrifos	351.9000>124.9000	6.45	6.04	6.15
Spiromesifen	388.2000>273.1000	6.46	6.24	6.22
Etoxazole	360.2000>141.1000	6.52	6.23	6.25
Fenpyroximate	422.2000>366.1000	6.66	6.37	6.35
Cyfluthrin	451.1000>191.1000	6.70	6.29	6.38
Cypermethrin	433.1000>191.0000	6.75	6.36	6.44
Pyridaben	365.2000>147.0000	6.77	6.50	6.49
Abamectin	890.7000>305.3000	6.78	6.66	6.68
Permethrin	408.1000>183.1000	7.04	6.66	6.77
Etofenprox	394.3000>177.1000	7.09	6.70	6.82
Bifenthrin	440.1000>166.2000	7.10	6.75	6.86
Acequinocyl	343.2000>189.1000	7.56	7.20	7.31

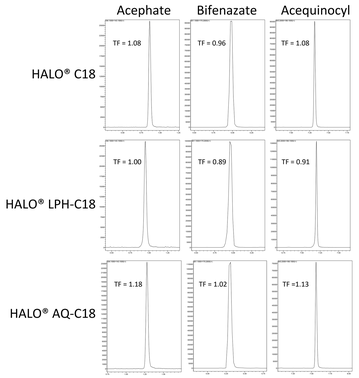
C18: Best for wide range of polarities
Endcapped

LPH-C18: Designed for low pH mobile phases
Not endcapped

AQ-C18: 100% aqueous compatible phase
Endcapped
More retention for polar compounds

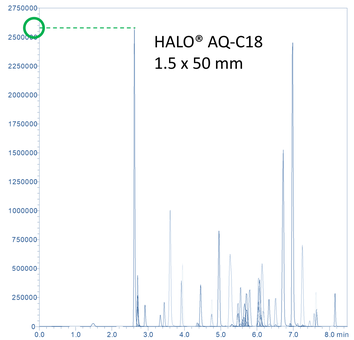
Peak Statistics

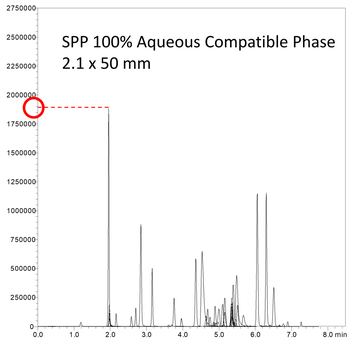
- Retention Order: AQ-C18 > LPH-C18> C18
- Peak Widths: average of 0.04 ± 0.01 for all
- Peak Tailing: AQ-C18 > C18 > LPH-C18



Based on these results, the AQ-C18 column was selected for investigation in the 1.5 mm ID

HALO® AQ-C18 1.5 mm ID Compared to SPP 2.1 mm ID





- 1 µL of sample was injected on both the HALO® AQ-C18 1.5 mm ID column and the SPP 100% Aqueous Compatible Phase in 2.1 mm ID
- Area for the 61 MRMs that were monitored was an average of 2 times larger on the HALO® 1.5 mm ID column compared to the competitor 2.1 mm ID column
- Source conditions were kept the same for both columns for equivalency comparisons so some compounds, namely MGK 264, cyfluthrin, bifenthrin, and acequinocyl experienced greater signal enhancement than others

Conclusions

- HALO® AQ-C18 gave the best compromise of retention time (highest) and peak shape (1.08 on average) across all of the compounds in the Oregon pesticide mix
- Injecting the same amount of sample on a 1.5 mm ID column as a 2.1 mm ID column leads to an increased response for enhanced peak interrogation and area as well as a 50% reduction of the mobile phase consumed
- Using 1.5 mm ID columns for MS analysis is a good alternative for those that do not want to move to micro flow or capillary systems, but still want signal enhancement and mobile phase savings