Ultra-trace level GC/MS/MS analysis of Organochlorine Pesticides using a large volume injection with a temperature programmed inlet

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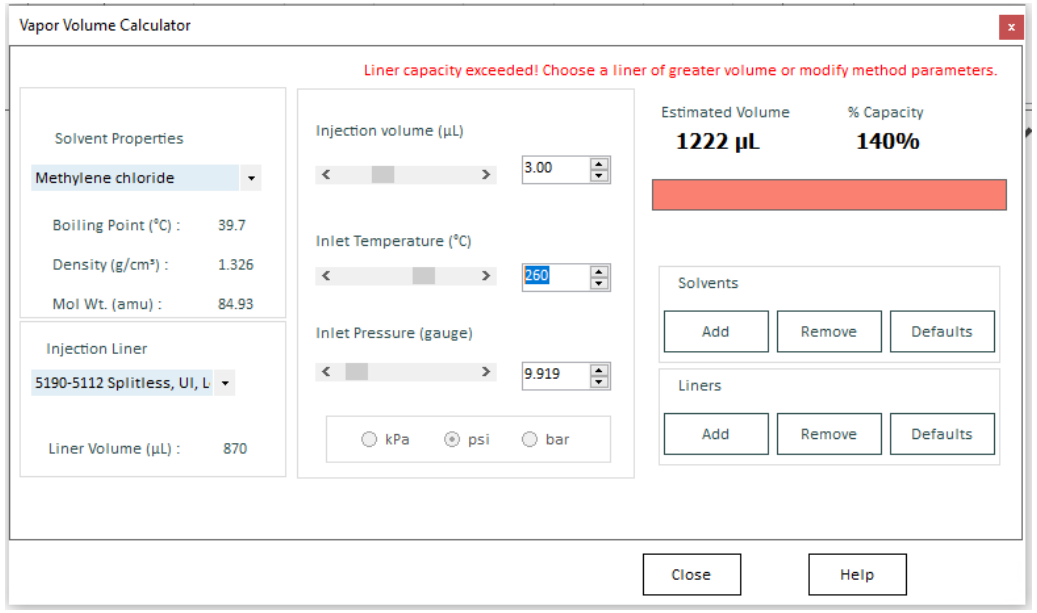
Analysis of Organochlorine Pesticides (EPA method 8081)

- Organochlorine pesticides (OCP's) are synthetic pesticides that have vast applications, being used heavily in the chemical and agriculture industries.
- Most OCP's are known for high toxicity and can bioaccumulate in the environment.
- Contamination of OCP's can occur in air, water and soil matrices.
- Historically this method has been done by GC/ECD either single or dual detectors.
- Problems of coelution, interferences, and compound breakdown present many issues when determining the OCP's on GC/ECD detectors.
- Utilizing a programmable temperature inlet helps minimize sample breakdown to sensitive compounds like Dieldrin and Endrin.
- GC QQQ detection allows for lower detection limits, elimination of coelution and interferences.
- Customer requests have been surfacing of a need to hit 0.05ppb for the OCP cmpds.

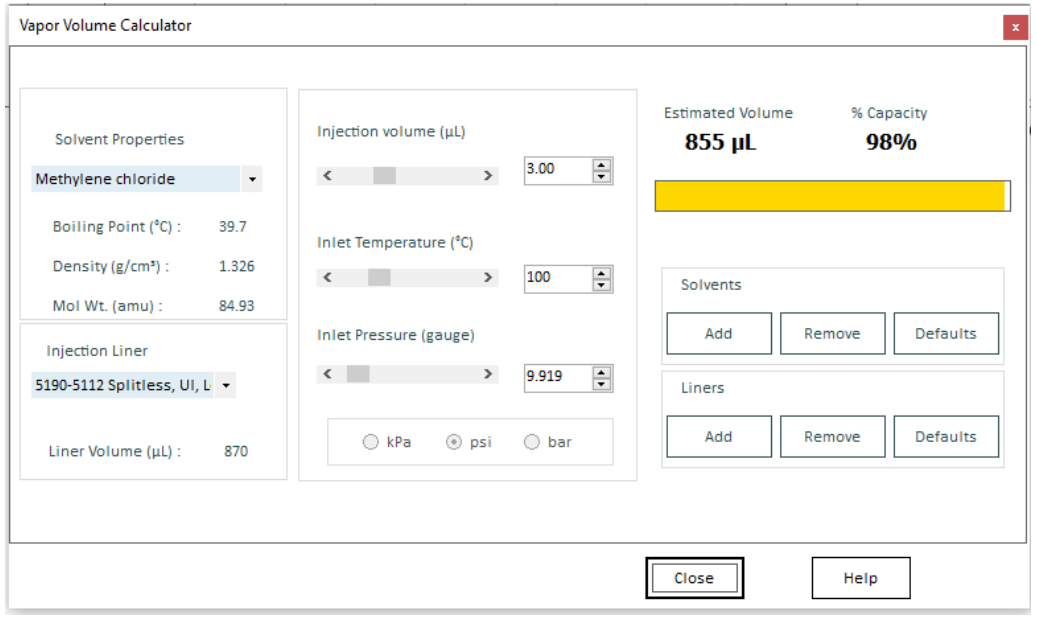
Why LVI over traditional splitless?

DCM overloads liner → move to MMI for cold splitless

3µL on SSL @ 260°C

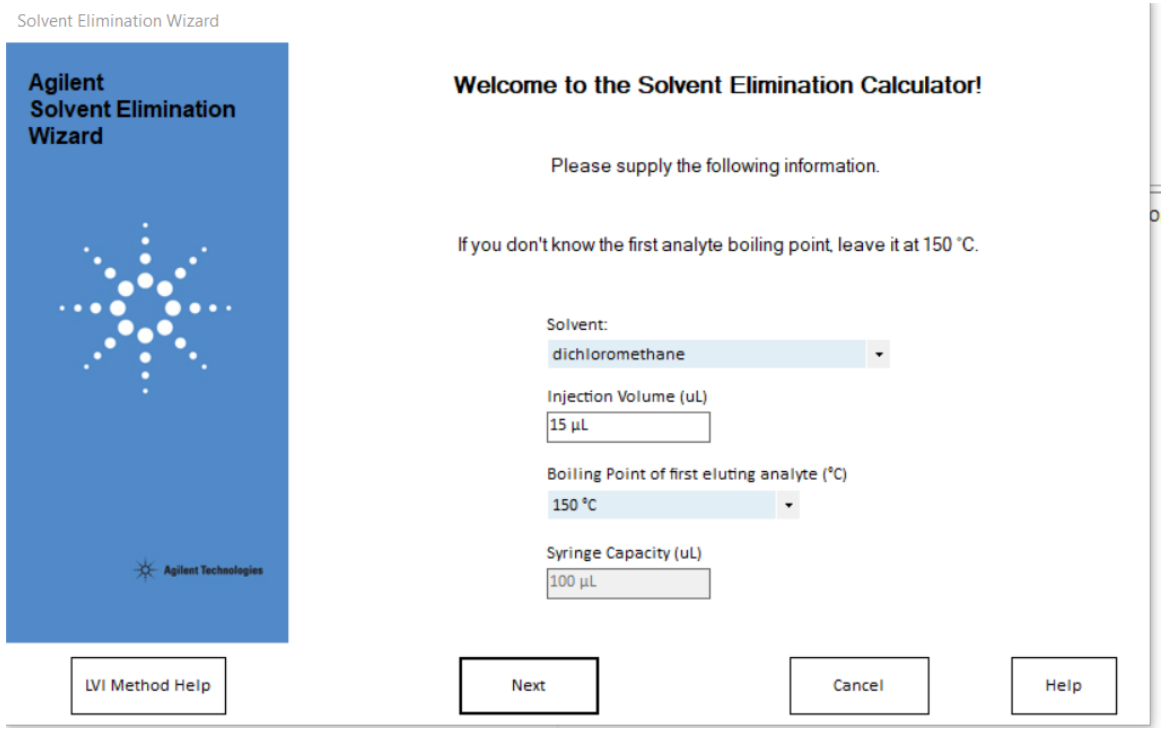


3µL on MMI @ 100°C



Why LVI over traditional splitless?

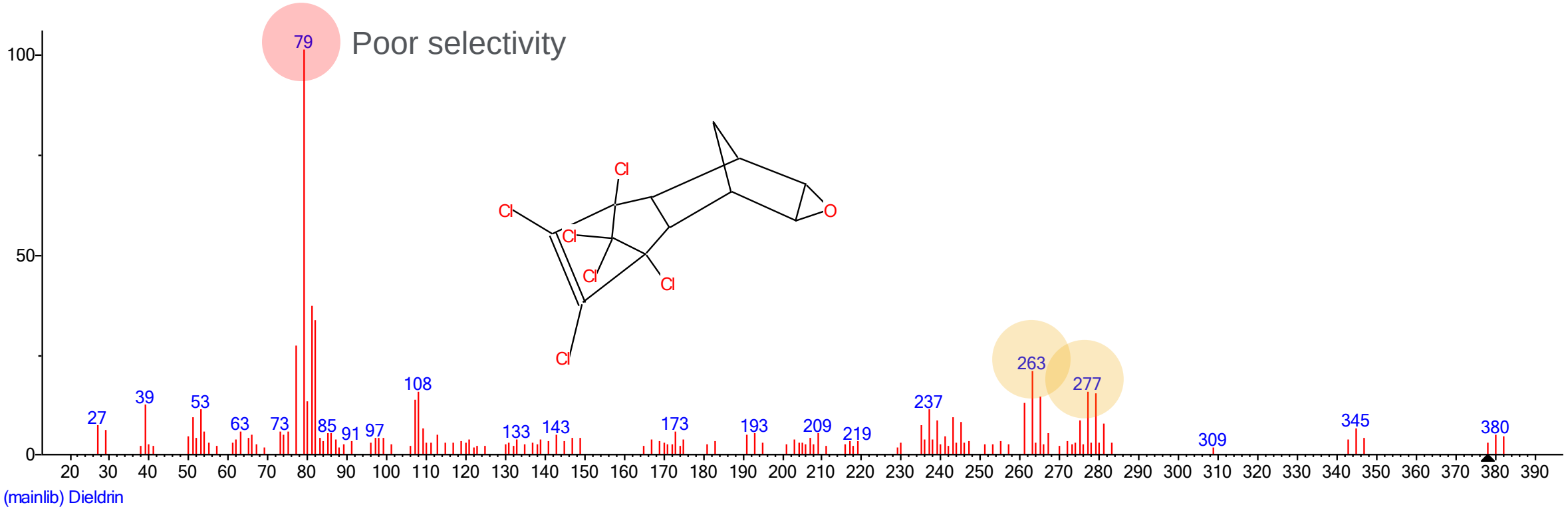
Advantages of the MMI in Solvent vent mode



- Allows for sample prep of smaller volumes
- Lower detection limits
- Reduces decomposition of thermally labile compounds
- A “gentler” introduction of samples into system
- Software comes with the LVI wizard to help with method setup

The difficulty with planar pesticides using TQ GCMS: Dieldrin

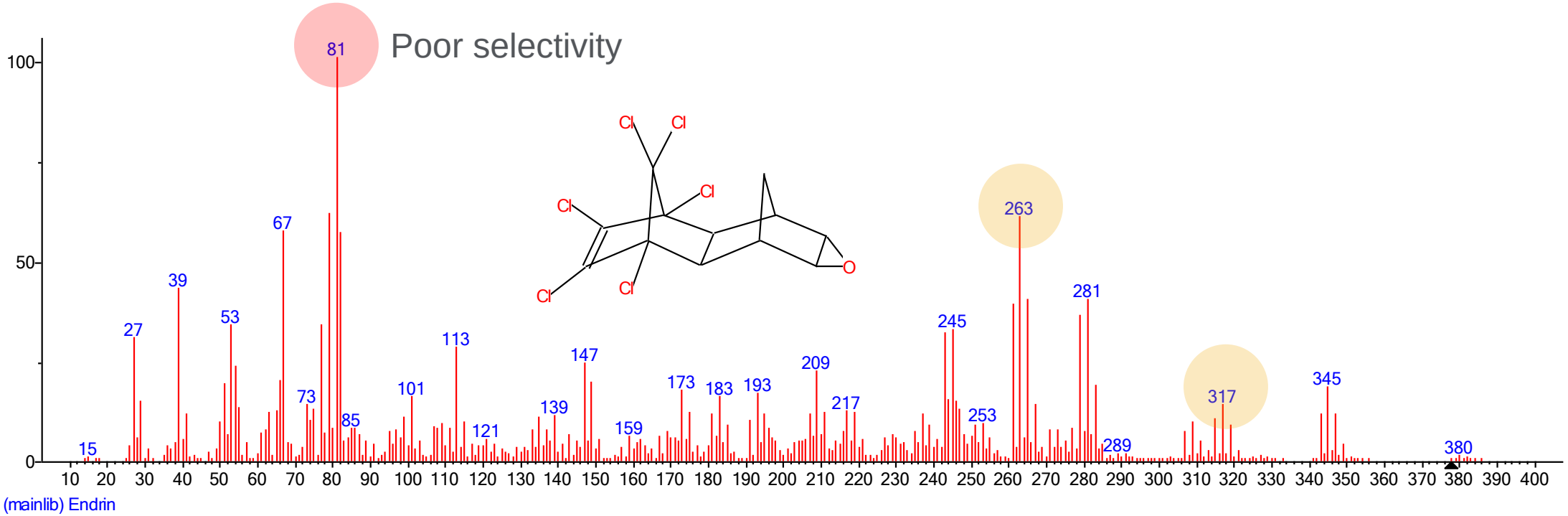
Little abundance of highly selective (aka high mass) precursor ions ⬆ LOD



Dieldrin		277	Widest	241	Widest	10.55	0.20	0.20	14.8	9
Dieldrin		262.9	Widest	193	Widest	10.55	0.20	0.20	14.8	45
Dieldrin		262.9	Widest	191	Widest	10.55	0.20	0.20	14.8	45

The difficulty with planar pesticides using TQ GCMS: Endrin

Little abundance of highly selective (aka high mass) precursor ions ⬆ LOD



Endrin		316.7	Widest	280.8	Widest	10.79	0.20	0.20	13.6	12
Endrin		316.7	Widest	100.8	Widest	10.79	0.20	0.20	13.6	15
Endrin		262.9	Widest	193	Widest	10.79	0.20	0.20	13.6	45

GC Method parameters: 8890/7010B

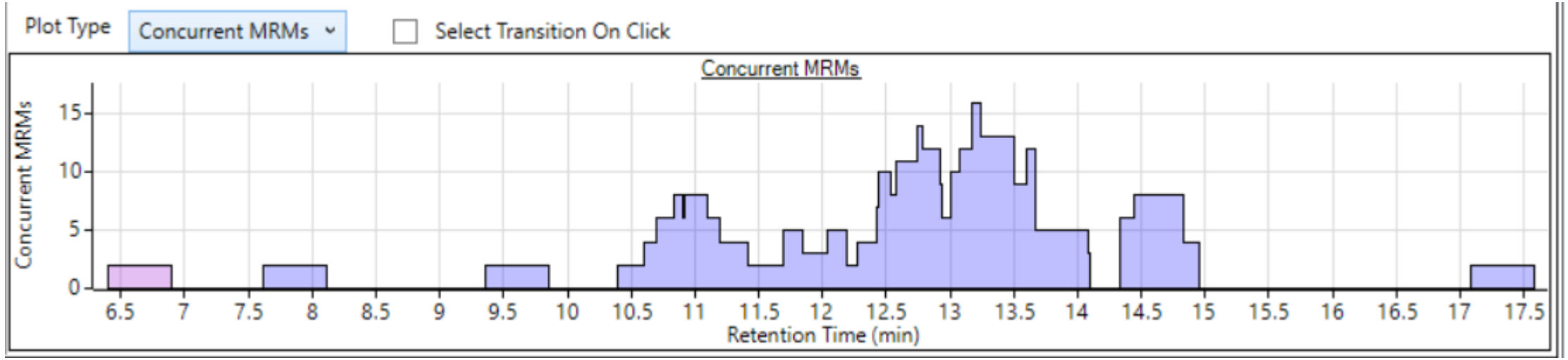
<18-minute method

Parameter	Value
Injection Volume	10uL or 15µL
Inlet	MMI @ 40°C solvent vent mode Temperature: Hold 0.32 min, ramp 600 °C/min to 325 °C Vent: 150mL/min @ 2.5psi for 0.32min Purge 60mL/min @ 2.52 min Septum Purge mode: Switched
Liner	Agilent Ultra Inert bottom frit liner (part #5190-5112)
Column	DB-UI 8270D Column (part #122-9732) 30m x 250µm, 0.25mm
Carrier gas	Helium @ ~1.25 mL/min constant flow Retention time locked to Acenaphthene-d10
Oven	40°C hold 2.52 Ramp 25°C/min → 260 Ramp 5°C/min → 280 Ramp 25°C/min → 320, hold 0.5 min
MSD Transfer Line	320°C

MS Method parameters: 8890/7010B

<18-minute method

Parameter	Value
Solvent Delay	6 minutes
Gain	10
Mode	dMRM
Temperatures	Source: 300°C Quads: 150°C
Total MRM's	65



Source cleaning in-between batches

JetClean in offline mode

To help prevent carryover & contamination:

Background contamination at such low ppb/ppt levels can occur.

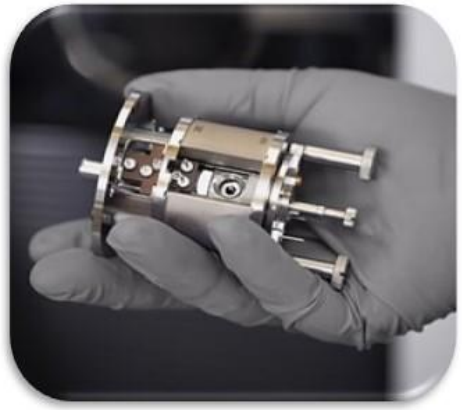
After each batch, 3 runs of JetClean was done for a duration of 5 minutes.

Quick and easy way to ensure system remained clean and ready to run.

HES Source with lenses exposed

Reduce GC/MS Downtime

JetClean Self-cleaning ion source



With innovative JetClean technology, your lab can:

- Increase instrument uptime. Fewer manual cleanings maximize productivity.
- Maintain data quality. A clean ion source ensures run-to-run reproducibility.
- Enhance operator convenience. Automated cleaning requires virtually no user intervention.

Without JetClean self-cleaning ion source

January X2	February X2	March X2
April X2	May X2	June X2
July X2	August X2	September X2
October X2	November X2	December X2

Twenty-four cleanings per year

With JetClean self-cleaning ion source*

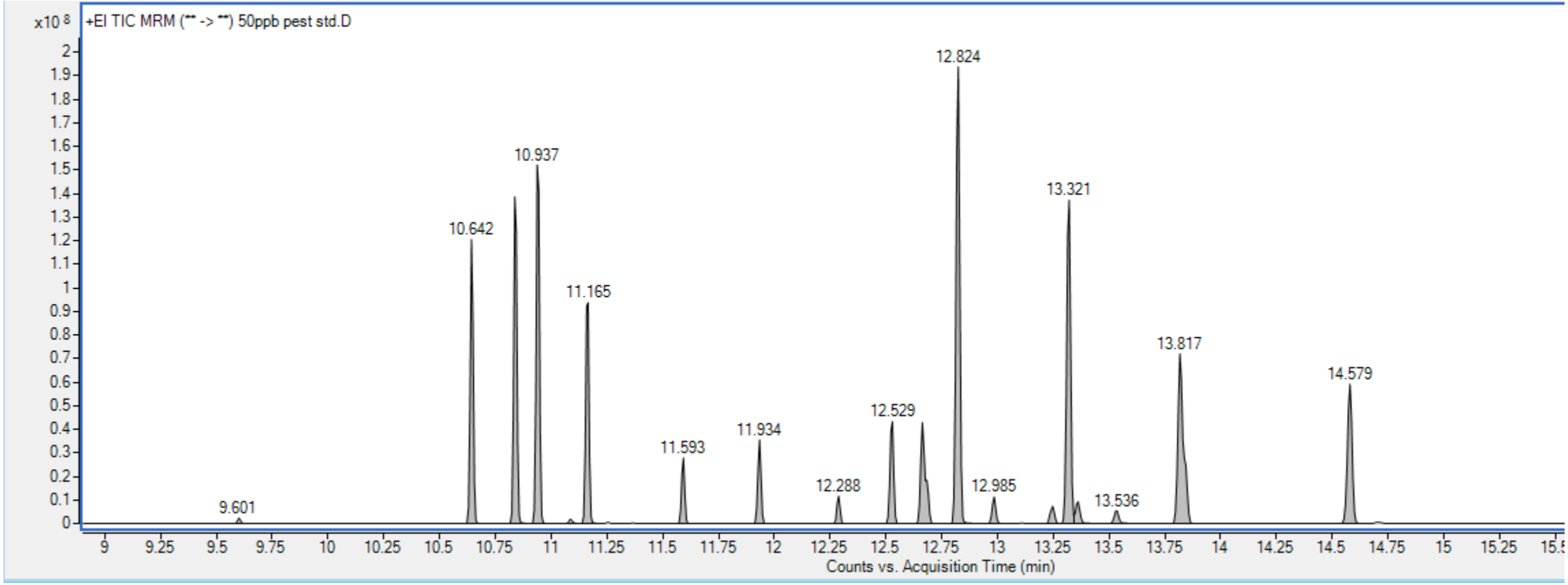
January	February	March
April	May	June
July	August	September X1
October	November	December

One cleaning per year

Cleaning frequency reduced by **up to 90%**

Example chromatogram

Pesticide analytes



Pesticides Calibrations using 15ul injection volume

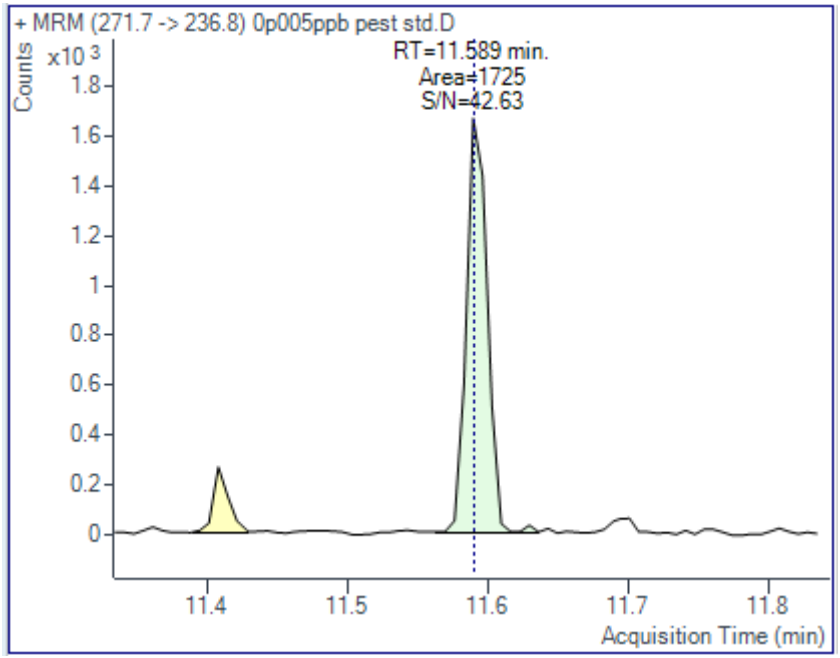
Original Method	CAS #	Analytes	Instrument LOD ug/L	Calibrated Range ug/L	Average RF
8081	72-54-8	4,4'-DDD	0.005	0.005-50	9.05
8081	72-55-9	4,4'-DDE	0.005	0.005-50	8.24
8081	50-29-3	4,4'-DDT	0.01	0.01-25	14.18
8081	309-00-2	Aldrin	0.005	0.005-50	6.09
8081	319-84-6	alpha-BHC	0.005	0.005-50	12.53
8081	5103-71-9	cis-Chlordane	0.005	0.005-50	7.88
8081	319-85-7	beta-BHC	0.005	0.01-50	12.04
8081	319-86-8	delta-BHC	0.005	0.005-50	7.10
8081	60-57-1	Dieldrin	0.01	0.025-50	4.76
8081	959-98-8	Endosulfan I	0.005	0.005-50	7.75
8081	33213-65-9	Endosulfan II	0.005	0.005-50	8.24
8081	1031-07-8	Endosulfan sulfate	0.005	0.005-25	10.39
8081	72-20-8	Endrin	0.015	0.025-50	6.96
8081	7421-93-4	Endrin aldehyde	0.005	0.005-50	10.74
8081	53494-70-5	Endrin ketone	0.005	0.01-50	8.51
8081	58-89-9	gamma-BHC (Lindane)	0.005	0.005-50	13.85
8081	5103-74-2	trans-Chlordane	0.005	0.005-50	4.75
8081	76-44-8	Heptachlor	0.005	0.005-50	7.81
8081	1024-57-3	Heptachlor epoxide	0.005	0.005-50	8.34
8081	72-43-5	Methoxychlor	0.005	0.005-25	13.28

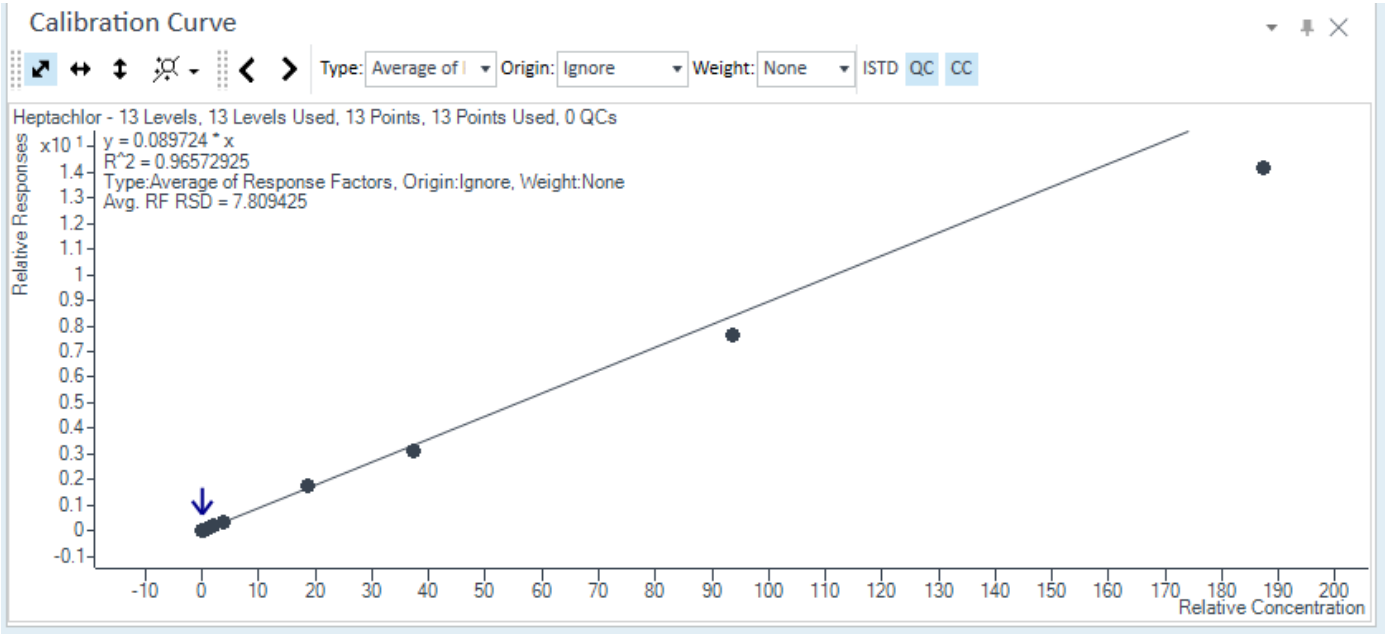
Pesticides Calibrations using 10ul injection volume

Original Method	CAS #	Analytes	Instrument LOD ug/L	Calibrated Range ug/L	Average RF
8081	72-54-8	4,4'-DDD	0.005	0.01-50	8.36
8081	72-55-9	4,4'-DDE	0.005	0.01-50	8.96
8081	50-29-3	4,4'-DDT	0.01	0.01-50	11.79
8081	309-00-2	Aldrin	0.005	0.005-50	8.28
8081	319-84-6	alpha-BHC	0.005	0.005-50	12.42
8081	5103-71-9	cis-Chlordane	0.005	0.005-50	15.9
8081	319-85-7	beta-BHC	0.005	0.01-50	11.37
8081	319-86-8	delta-BHC	0.005	0.01-50	10.37
8081	60-57-1	Dieldrin	0.025	0.050-50	10.56
8081	959-98-8	Endosulfan I	0.005	0.01-50	9.79
8081	33213-65-9	Endosulfan II	0.01	0.015-50	11.36
8081	1031-07-8	Endosulfan sulfate	0.005	0.005-25	16.91
8081	72-20-8	Endrin	0.05	0.050-50	10.18
8081	7421-93-4	Endrin aldehyde	0.01	0.015-50	10.78
8081	53494-70-5	Endrin ketone	0.015	0.05-50	6.93
8081	58-89-9	gamma-BHC (Lindane)	0.005	0.005-50	16.83
8081	5103-74-2	trans-Chlordane	0.005	0.01-50	8.85
8081	76-44-8	Heptachlor	0.005	0.005-50	11.35
8081	1024-57-3	Heptachlor epoxide	0.005	0.01-50	7.99
8081	72-43-5	Methoxychlor	0.005	0.005-25	18

Pesticides: Heptachlor 15ul injection

0.005ppb – 50ppb

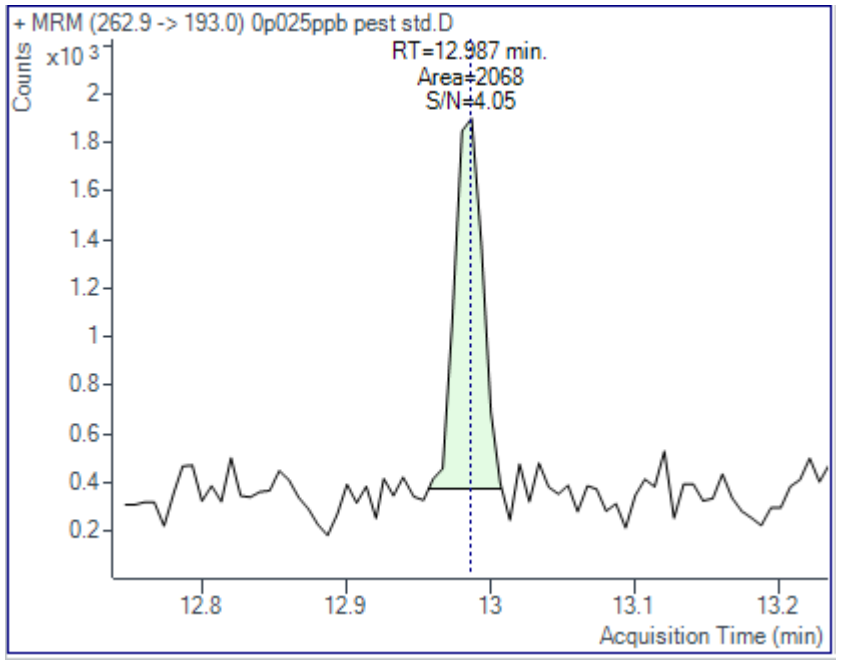


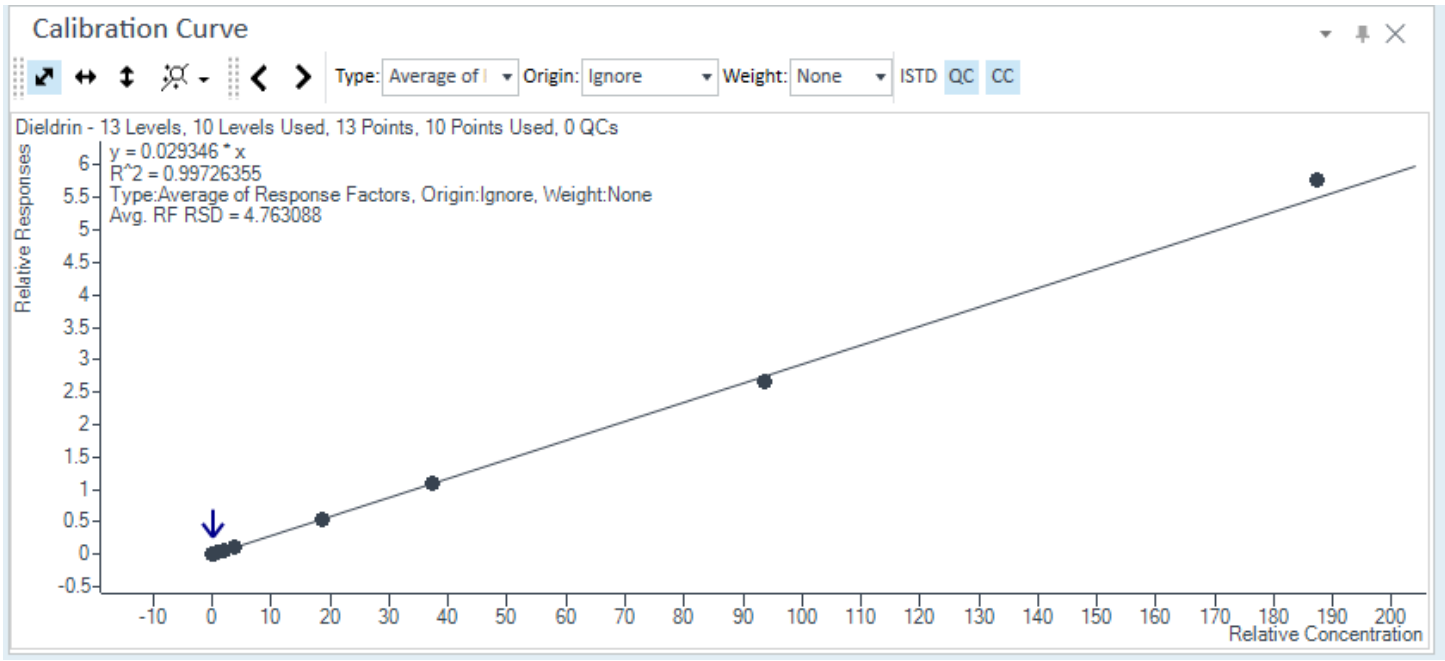


Signal to Noise: 42.63
Average RF: 7.80

Pesticides: Dieldrin 15ul injection

0.025ppb – 50ppb

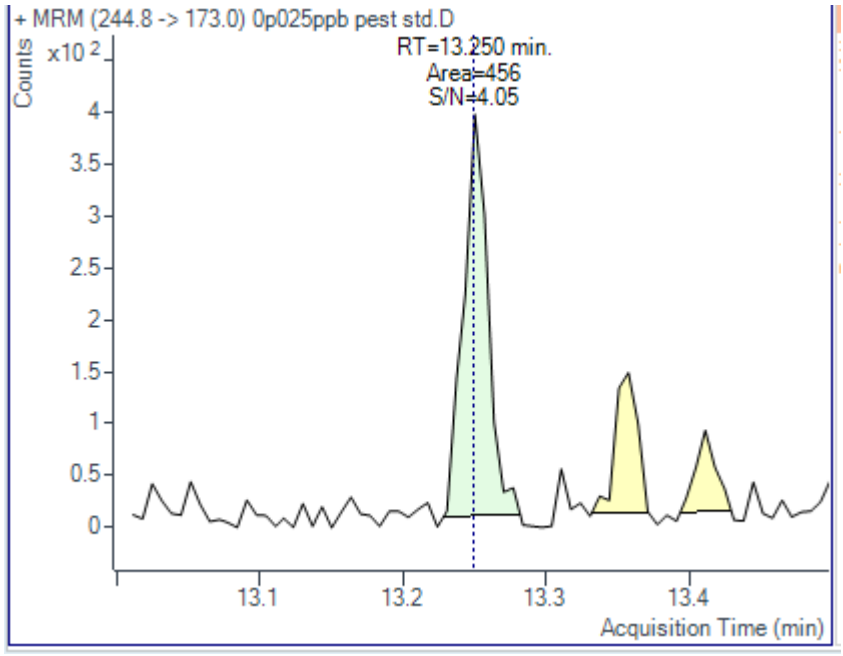


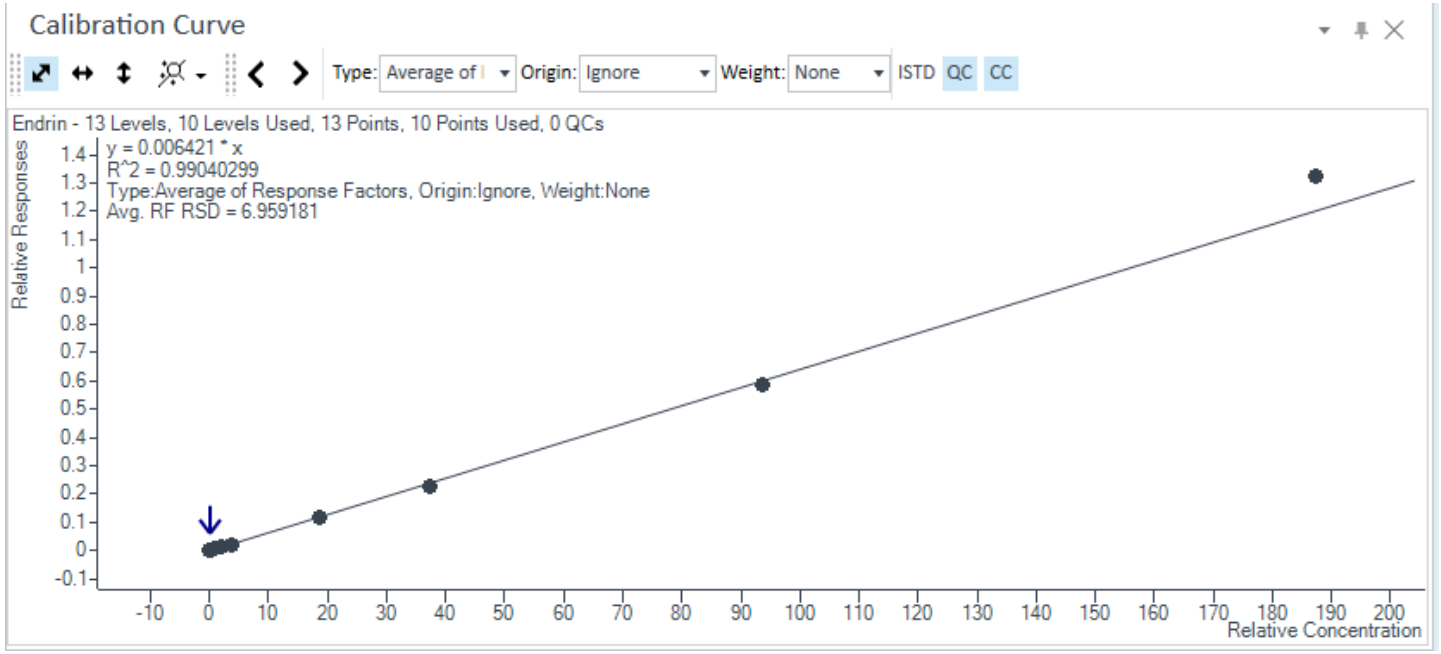


Signal to Noise: 4.05
Average RF: 4.76

Pesticides: Endrin 15ul injection

0.025ppb – 50ppb

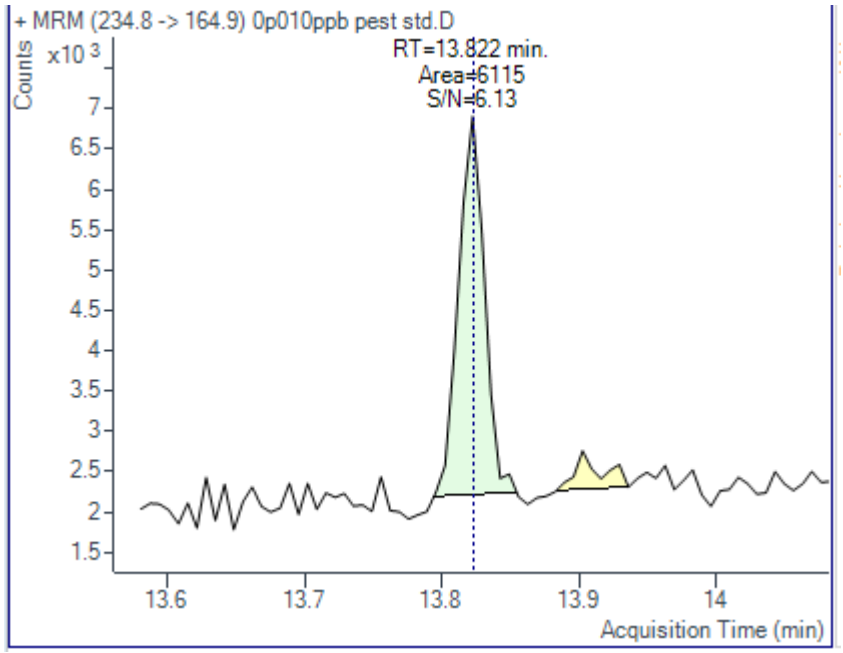


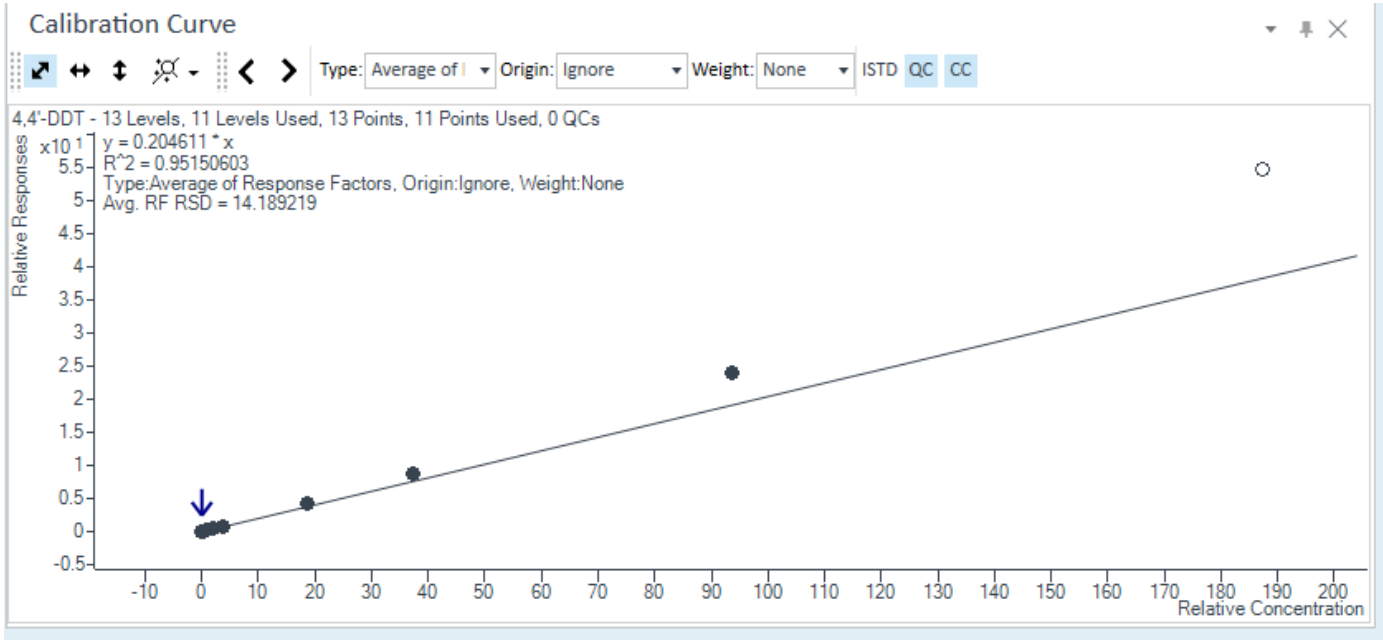


Signal to Noise: 4.05
Average RF: 6.95

Pesticides: 4,4 DDT

0.010ppb – 25ppb

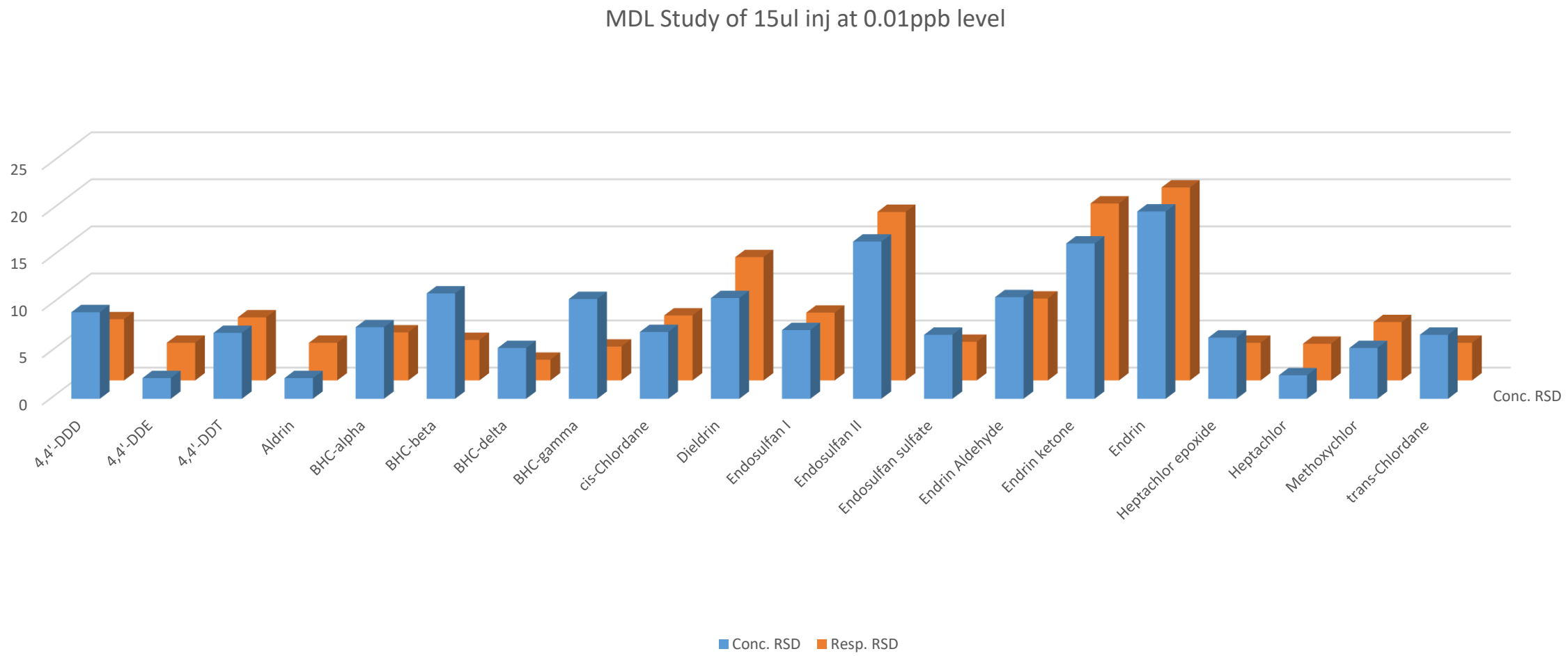




Signal to Noise: 6.13
Average RF: 14.18

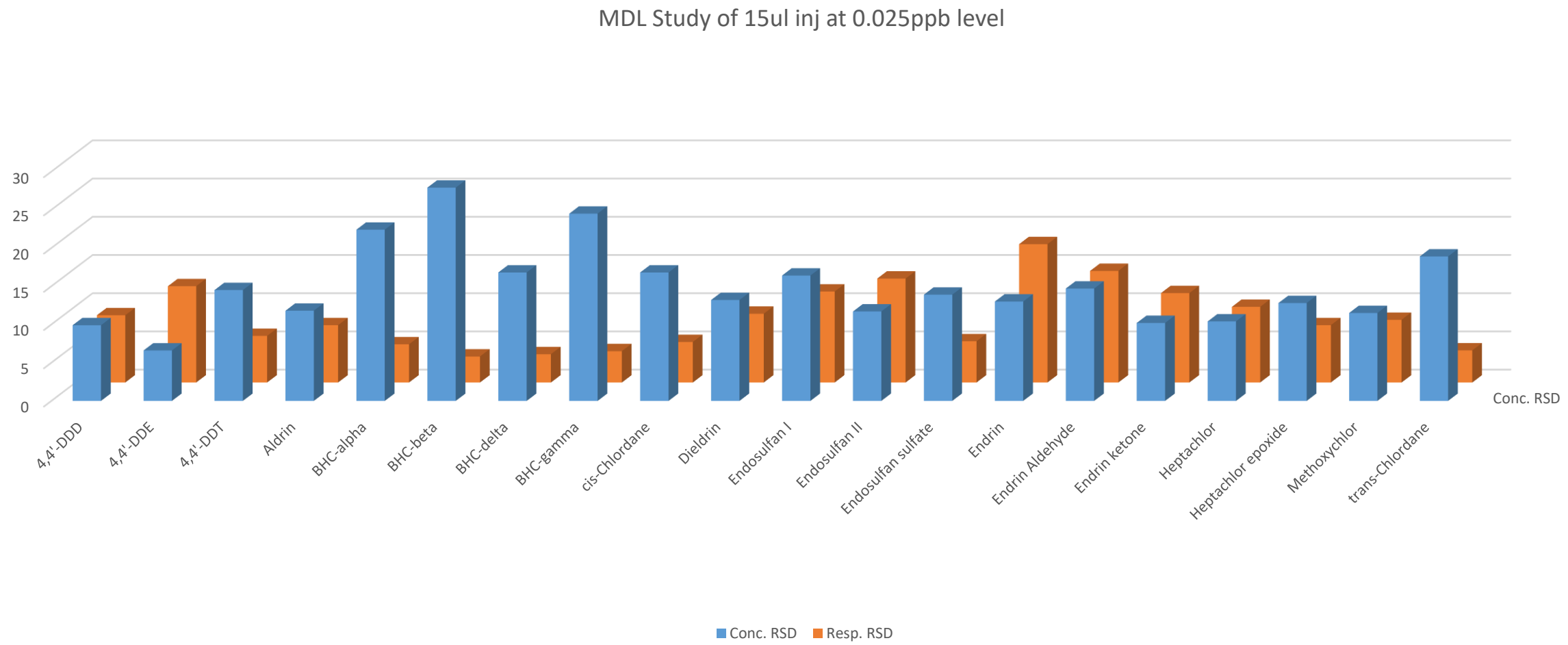
MDL Study using 15ul inj

0.01ppb conc level



MDL Study using 15ul inj

0.025ppb conc level



Conclusions of 8890/7010B OCP method

- Detection limits of 0.05ppb or better were achieved for all compounds.
- All OCP’s calibrated with an RF below 20
- Calibration range was low ppt up to 25-50ppb for all compounds.
- System remained clean and carryover free with use of JetClean in between batches.
- Issues of coelution, interferences, and compound breakdown were solved with use of lower inlet starting temperatures from the MMI.
- Large volume injection is a good option for getting more sample into system without the presence of a large solvent background.

Questions?

Thank you!

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