Semi-Volatiles in Drinking Water per EPA Method 525

Maintaining Optimal Analytical Performance

Angela Smith Henry, Ph.D.
Applications Chemist
Agilent Technologies Inc.,

Agilent
Trusted Answers

EPA 525: Semi-volatile compounds analysis in drinking water by GC/MS

Requirements of the method

- **Instrument Performance Checkout**
  - Pass DFTPP tuning check
  - Pass Endrin/DDT breakdown percentage
    - <20% total, 15% individual for EPA 525.2
    - <20% DDT breakdown for EPA 525.3
  - Isomer pair resolution

- **Calibration curve: 0.1 to 10ppm (0.1 to 5ppm for EPA 525.3)**
  - Achieve linearity and verify responses ±30%
  - Use average response factors, or linear regression fit, where necessary

8890 GC: Testing and Extending EPA 525

- Test ability of 8890 GC/MS system

- Instrument Performance Checkout
  - Pass DFTPP tuning check
  - Pass Endrin/DDT breakdown percentage (<20% total, 15% individual for EPA 525.2)
    - **What is the longevity of the Endrin/DDT breakdown? Can we run 300+ injections and remain below 20% breakdown?**
  - Isomer pair resolution

- Calibration curve: 0.1 to 10ppm (0.1 to 5ppm for EPA 525.3)
  - Achieve linearity and verify responses ±30%
  - Use average response factors, or linear regression fit, where necessary
- **Extended calibration curve: 0.02 to 15 ppm**

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Plan of work

- **Instrument Performance Checkout**
  - DFTPP tuning check
  - Endrin/DDT breakdown longevity

- **Calibration curves**
  - EPA 525.2: 0.1 to 10ppm
  - EPA 525.3: 0.1 to 5ppm
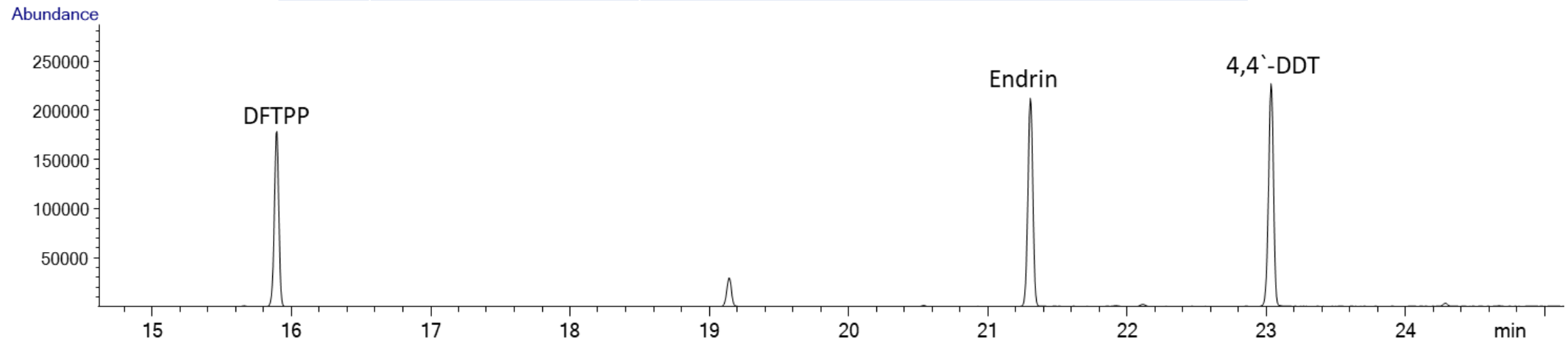 - Extended range: 0.02 to 15 ppm

Endrin/DDT testing parameters

Parameter	Value
Injection volume	1 µL
Inlet	Split/splitless 200 °C; Pulsed splitless 50 psi until 1 min; Purge 50 mL/min at 1 min; Standard septum purge
Inlet liner	Agilent Ultra Inert single taper splitless liner
Column temperature program	40 °C (hold for 1 minute), 25 °C/min to 160 °C (hold 3 min), 6 °C/min to 312 °C
Column	J&W DB-8270D: 30 m × 0.25 mm × 0.25 µm column
Carrier gas and flow rate	Helium at 1.2 mL/min, constant flow
MS parameters	
Transfer line temperature	270 °C
Ion source temperature	300 °C
Quadrupole temperature	180 °C

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Endrin/DDT testing parameters

Testing Sequence

Line	Number of runs	Sample
1	1	Ethyl acetate blank
2	5	Instrument Performance Check (IPC) solution
3	10	Ethyl acetate blank
4	3	IPC solution
Repeat lines 3 and 4 until 310 blank injections		
5	5	IPC solution

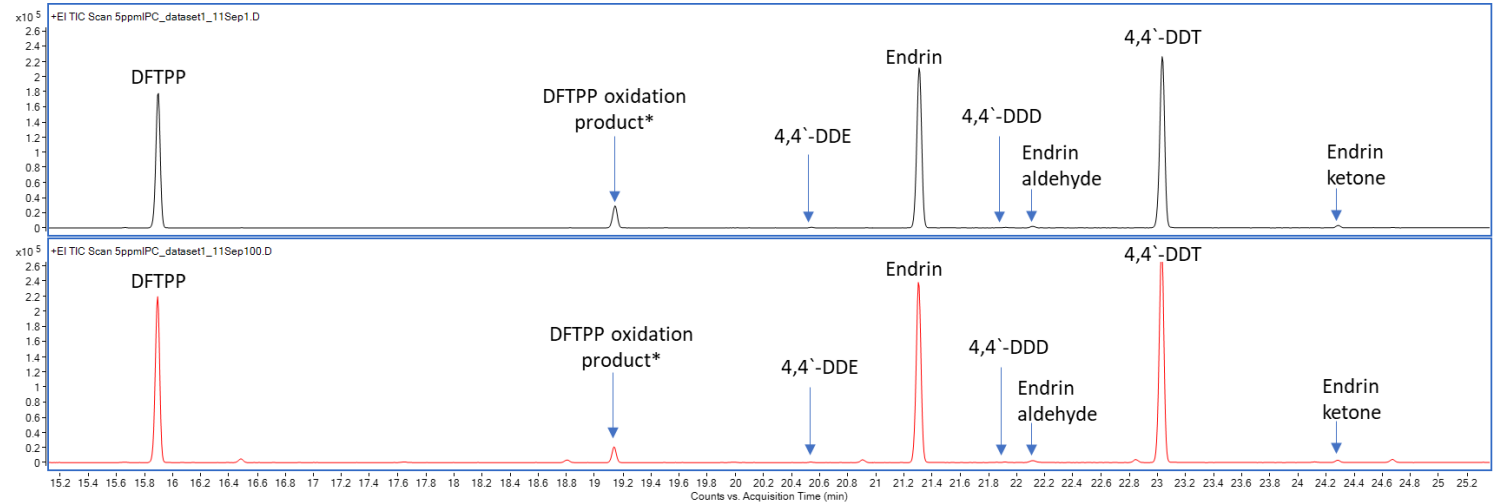TIC of Instrument Performance Check (IPC) solution

Instrument Performance Check: DFTPP tuning criteria
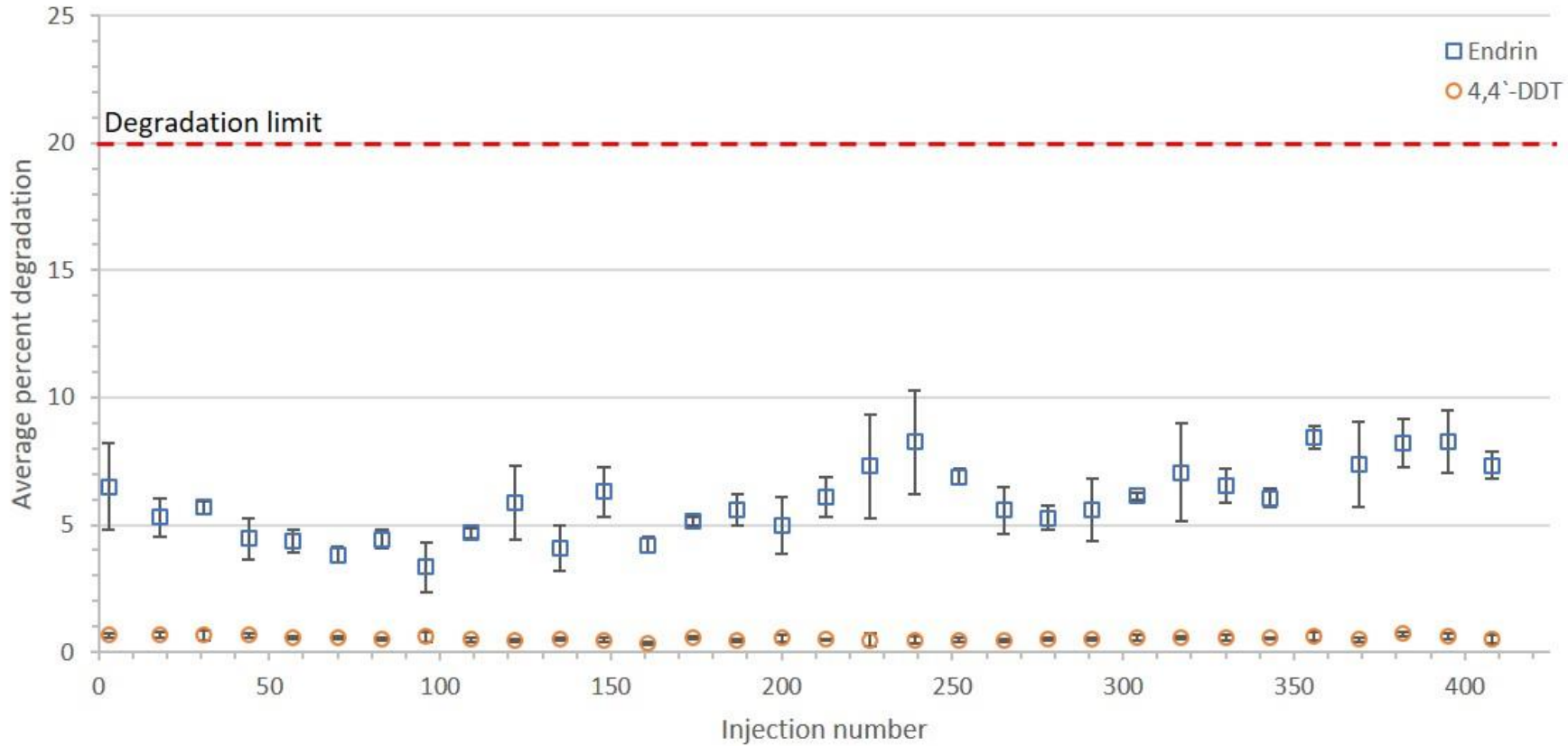
IPC Sample 100 (Run 412 in sequence)

+ Scan (rt: 15.830-15.985 min, 28 scans) 5ppmIPC_dataset1_11Sep100.D Average of Entire Peak Subtract None (Auto)
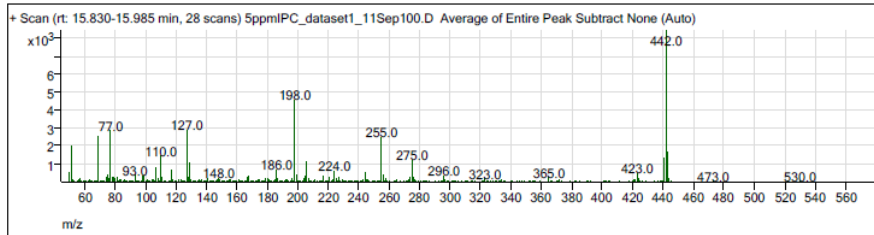
Target Mass	Rel. To Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn	Pass/Fail
51	198	10	80	43.1	1962	Pass
68	69	0	2	1.5	38	Pass
70	69	0	2	0.3	8	Pass
127	198	10	80	62.8	2862	Pass
197	198	0	2	0.0	1	Pass
198	198	100	100	100.0	4555	Pass
199	198	5	9	7.0	319	Pass
275	198	10	60	26.1	1188	Pass
365	198	1	100	4.4	199	Pass
441	443	1	99	79.5	1321	Pass
442	442	50	100	100.0	8480	Pass
443	442	15	24	19.6	1660	Pass

IPC Total Ion Chromatograms 1 (top – black) and 100 (bottom – red)

DFTPP tuning criteria passed for all 100 IPC solution injections

Endrin/DDT testing

Line	Number of runs	Sample
1	1	Ethyl acetate blank
2	5	Instrument Performance Check (IPC) solution
3	10	Ethyl acetate blank
4	3	IPC solution
Repeat lines 3 and 4 until 310 blank injections		
5	5	IPC solution

Over 400 injections, total % breakdown <11%

Avoid time loss and sequence re-runs due to inlet leaks

What if we could leak check the inlet before every run?

You can with Agilent Intuvo 9000 and Agilent 8890 GC

- Quick pressure/flow test
- Utilized in 412 run sequence
- No flow failures in sequence

Plan of work

- **Instrument Performance Checkout**
  - DFTPP tuning check ✓
 - Endrin/DDT breakdown longevity ✓

- **Calibration curves**
  - EPA 525.2: 100ppb to 10ppm
  - EPA 525.3: 100ppb to 5ppm
  - Extended range: 20ppb to 15 ppm

EPA 525 Calibration testing

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EPA 525 full method testing

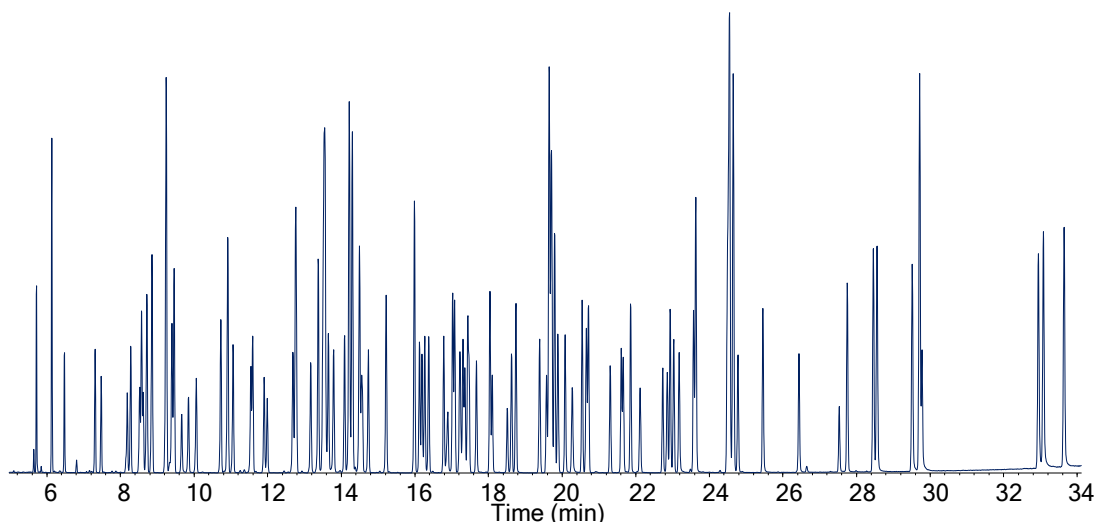| Parameter	Value
Injection volume	1 µL
Syringe	ALS syringe, Blue Line, 10 µL, PTFE-tip plunger
Inlet	Split/Splitless 250°C; Pulsed Splitless 50 psi until 1 min; Purge 50 mL/min at 1 min; Switched septum purge
Inlet Liner	Agilent Ultra Inert single taper with wool splitless liner
Column temperature program	40°C (hold for 1 minute), 25°C/min to 160°C (hold 3 min), 6°C/min to 312°C
Column	Agilent DB-UI 8270D, 30m x 0.25 mm x 0.25µm
Carrier gas and flow rate	Helium at 1.2 mL/min, constant flow
MS parameters	
Transfer line temperature	270°C
Ion source temperature	320°C
Quadrupole temperature	200°C
Drawout plate	9mm (G3870-20449)

- Verify Instrument performance check pass criteria
  - DFTPP ion ratios
  - Endrin/DDT % breakdown < 20%
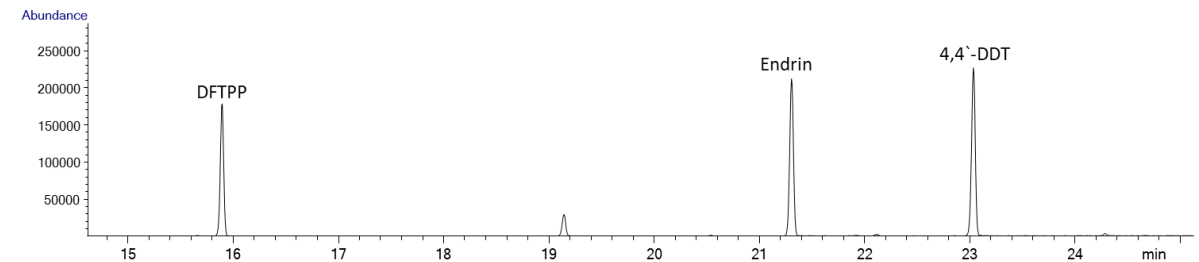
TIC of Instrument Performance Check (IPC) solution

EPA 525 full method testing

- Verify separation of isomer pairs: phenanthrene and anthracene; benz[a]anthracene and chrysene

- Calibration curve:
 - Minimum: 0.1 – 5 ppm (complies with 525.3)
  - Extended: 0.02 – 15 ppm

Full TIC of 2.5ppm target analytes, and 5ppm ISTDs and surrogates

Parameter	Value
Injection volume	1 µL
Syringe	ALS syringe, Blue Line, 10 µL, PTFE-tip plunger
Inlet	Split/Splitless 250°C; Pulsed Splitless 50 psi until 1 min; Purge 50 mL/min at 1 min; Switched septum purge
Inlet Liner	Agilent Ultra Inert single taper with wool splitless liner
Column temperature program	40°C (hold for 1 minute), 25°C/min to 160°C (hold 3 min), 6°C/min to 312°C
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Transfer line temperature	270°C
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Drawout plate	9mm (G3870-20449)

Instrument/Method verification: Separation of isomer pairs

Phenanthrene and anthracene = baseline resolution
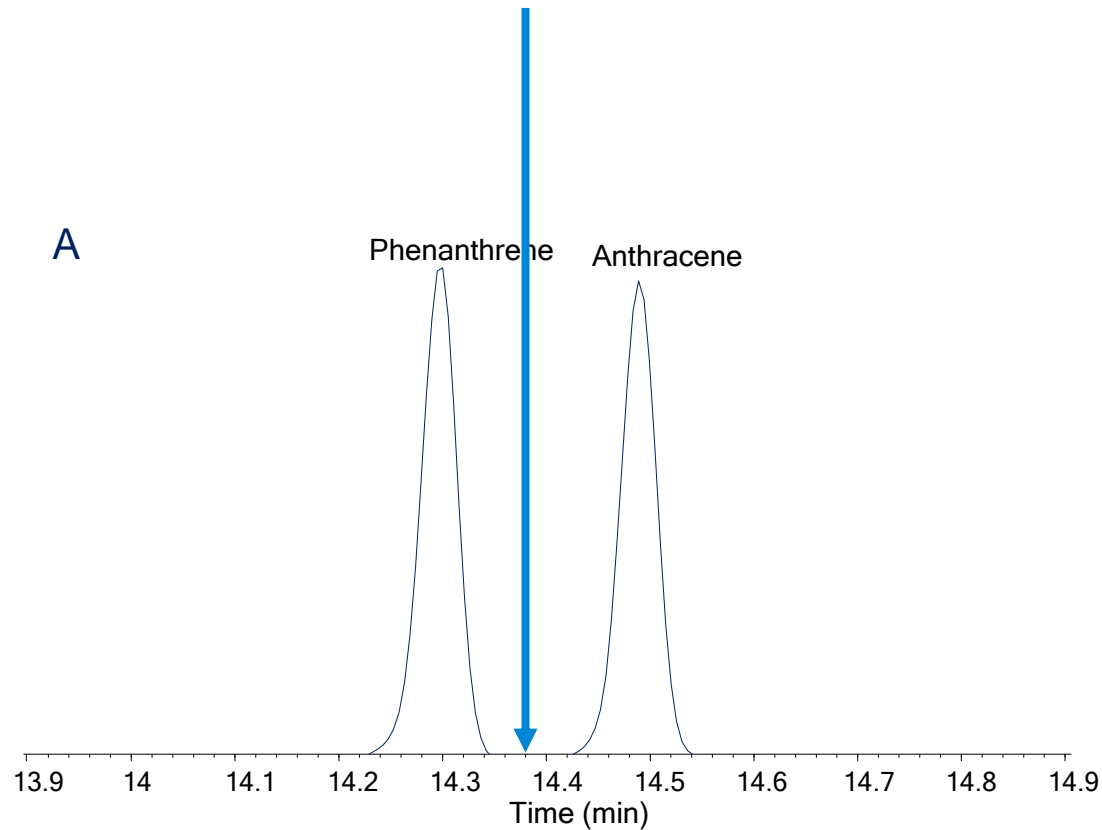
Benz[a]anthracene and chrysene >25% resolution
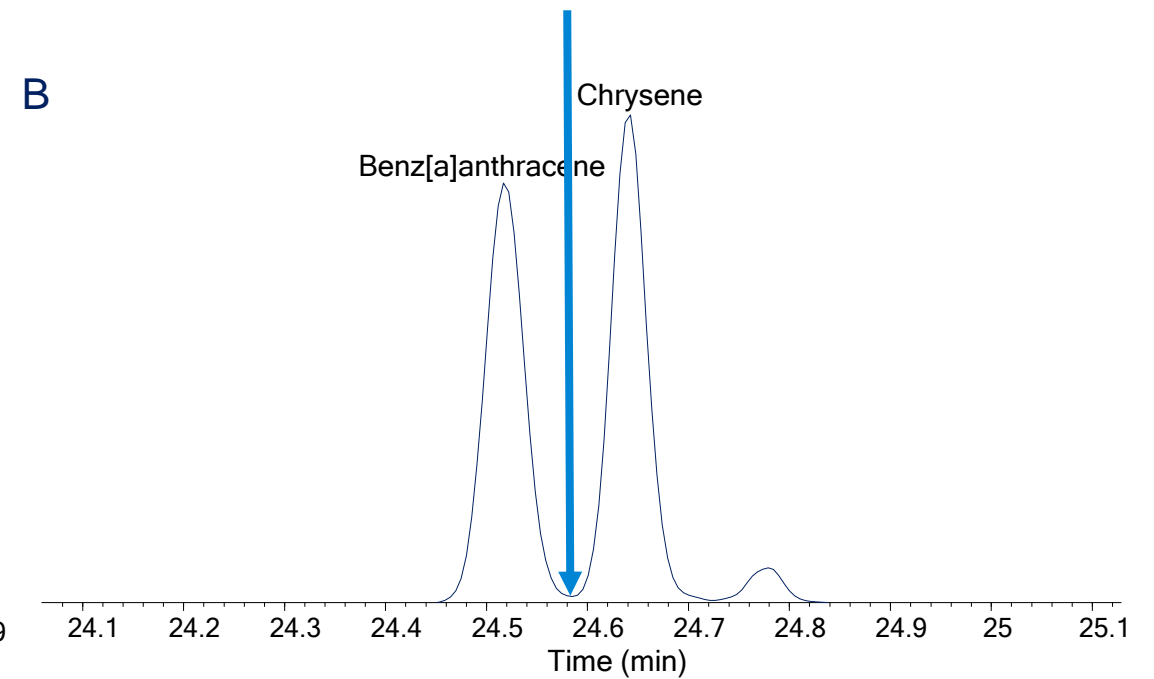
Isomer pairs pass EPA 525.2 and 525.3 criteria

Is the extended calibration range feasible for 102 semivolatile organic compounds?

Calibration Range (ng/µL)	Average RSD in RFs	Standard Deviations in Average RSD RFs	Targets Requiring Linear Regression
0.02 to 15	12.71	6.60	Chlorothalonil, endosulfan I, endosulfan sulfate
0.1 to 10	8.97	4.46	
0.1 to 5	8.96	4.45	

All 102 compounds (response factors) are <30% RSD for EPA 525.2 and 525.3 ranges
- EPA 525 Calibration ranges = pass

Only 3 compounds required linear regression for extended range
- Linear regression are allowable in EPA 525 methods

In all three calibration range cases, calibration was successfully achieved

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Is the extended calibration range feasible 102 semivolatile organic compounds?
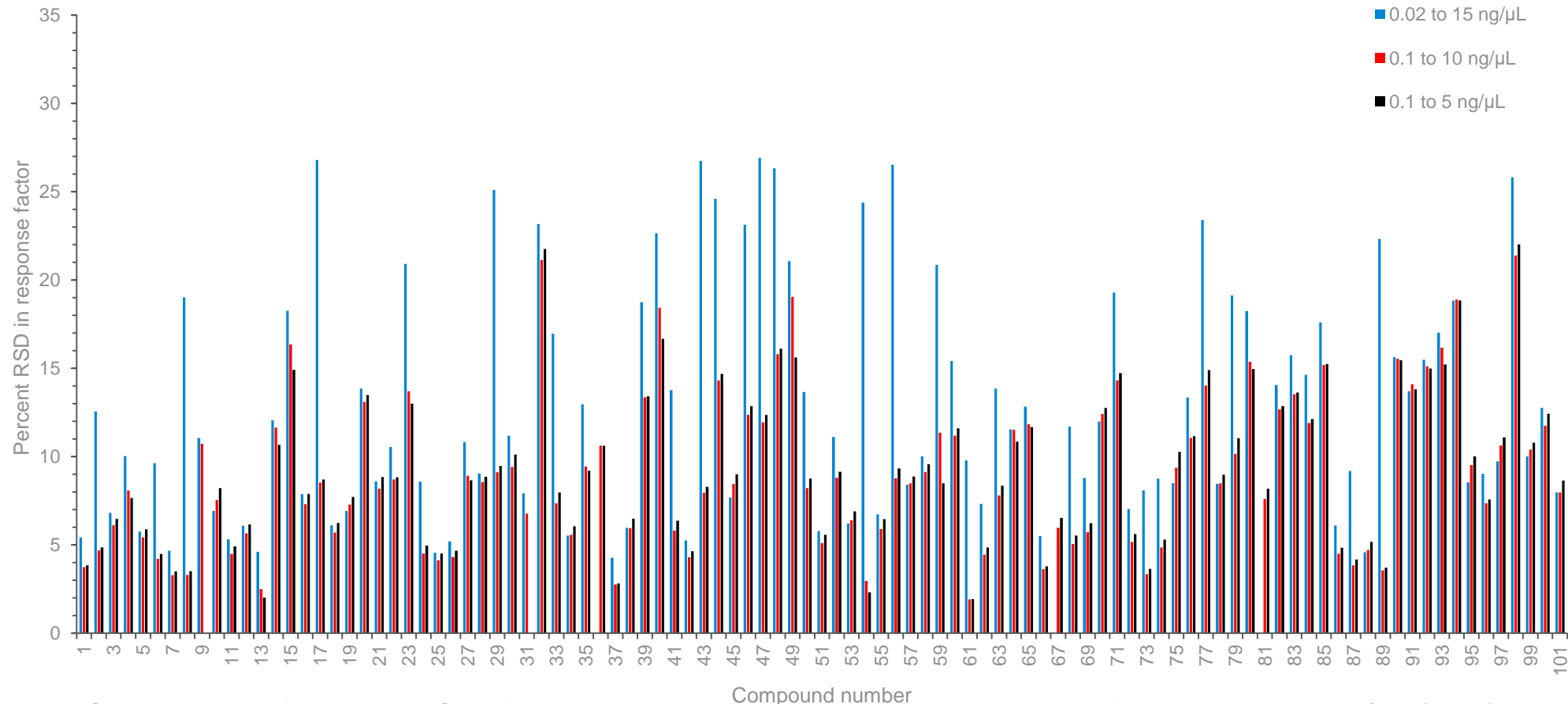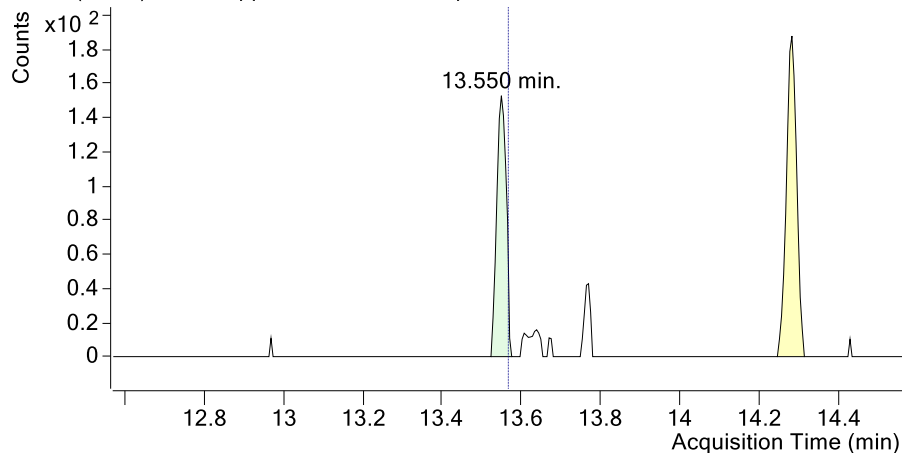

Comparison of percent RSDs for calibration ranges of the target analytes from 0.02 to 15 ng/µL (blue), 0.1 to 10 ng/µL (orange), and 0.1 to 5 ng/µL (green).

Extended range calibration achieved for 99 compounds with average response factors (0.02-15 ng/µL); 3 compounds required weighted linear regression.
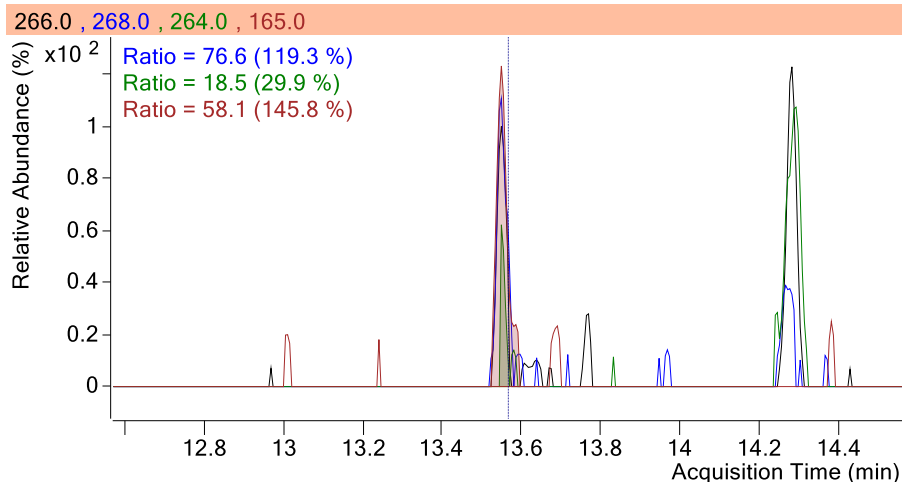
Pentachlorophenol: Low level detection
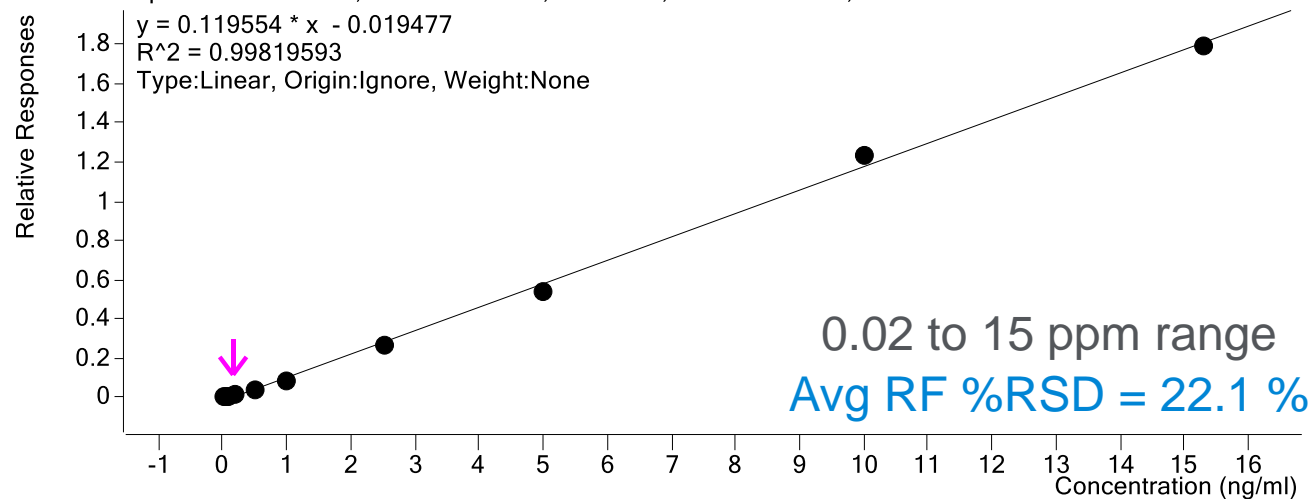
Quant Ion at 0.02 ppm

+ EIC (266.0) Scan 20ppb_525mixes_26Sept_curve2.D

Counts ×10^2

13.550 min.

Acquisition Time (min)

Qualifier ions at 0.02 ppm

266.0 , 268.0 , 264.0 , 165.0

Relative Abundance (%) ×10^2

Ratio = 76.6 (119.3 %)
Ratio = 18.5 (29.9 %)
Ratio = 58.1 (145.8 %)

Acquisition Time (min)

Pentachlorophenol - 10 Levels, 10 Levels Used, 10 Points, 10 Points Used, 0 QCs

Relative Responses

$y = 0.119554 * x - 0.019477$
$R^2 = 0.99819593$
Type:Linear, Origin:Ignore, Weight:None

Concentration (ng/ml)

0.02 to 15 ppm range
Avg RF %RSD = 22.1 %

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Chlorpyrifos

Quant Ion at 0.02 ppm

+ EIC (97.0) Scan 20ppb_525mixes_26Sept_curve2.D

17.298 min.

Counts ×10^2

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1

16.4 16.6 16.8 17 17.2 17.4 17.6 17.8 18 18.2

Acquisition Time (min)

Qualifier ions at 0.02 ppm

97.0 , 197.0 , 199.0 , 314.0

Ratio = 87.3 (101.9 %)
Ratio = 90.7 (109.9 %)
Ratio = 34.3 (78.1 %)

Relative Abundance (%) ×10^2

1
0.8
0.6
0.4
0.2
0

16.4 16.6 16.8 17 17.2 17.4 17.6 17.8 18 18.2

Acquisition Time (min)
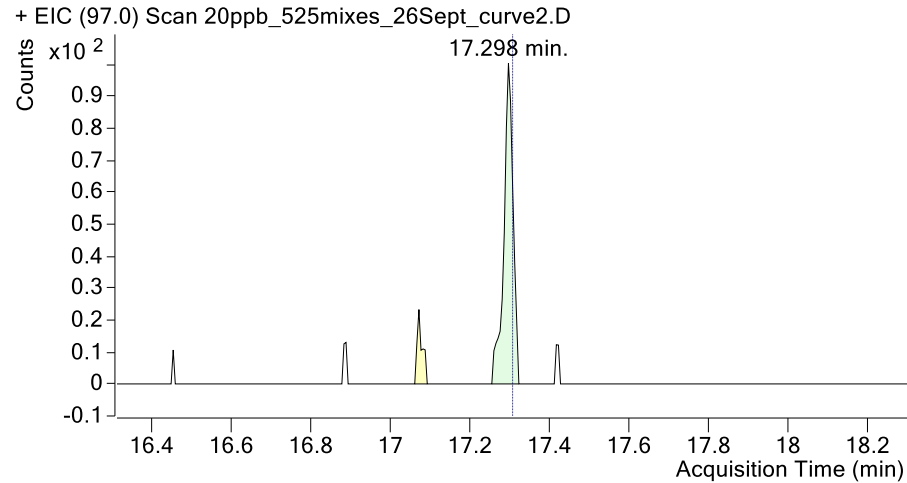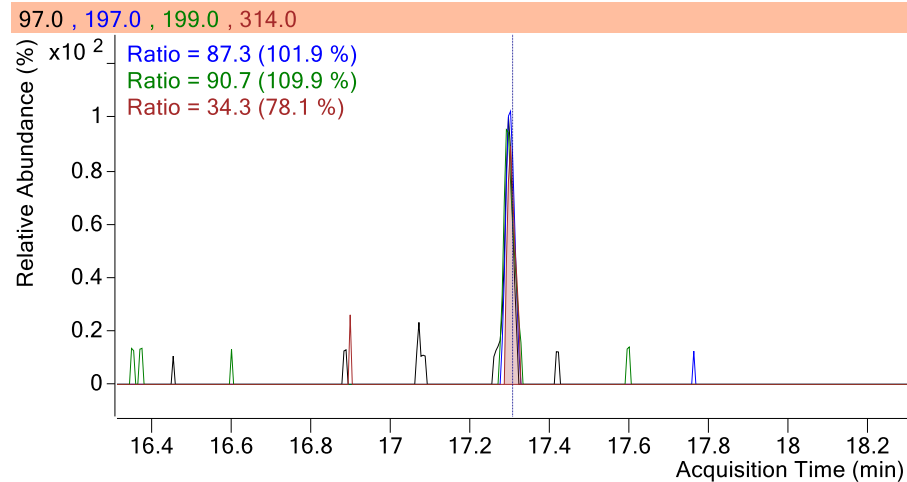
Chlorpyrifos - 10 Levels, 10 Levels Used, 10 Points, 10 Points Used, 0 QCs

Relative Responses ×10^{-1}

$y = 0.030207 * x - 7.621796E-004$
$R^2 = 0.99868913$
Type:Linear, Origin:Ignore, Weight:None

4
3.5
3
2.5
2
1.5
1
0.5
0

-1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Concentration (ng/ml)

0.02 to 15 ppm range
Avg RF %RSD = 6.2 %

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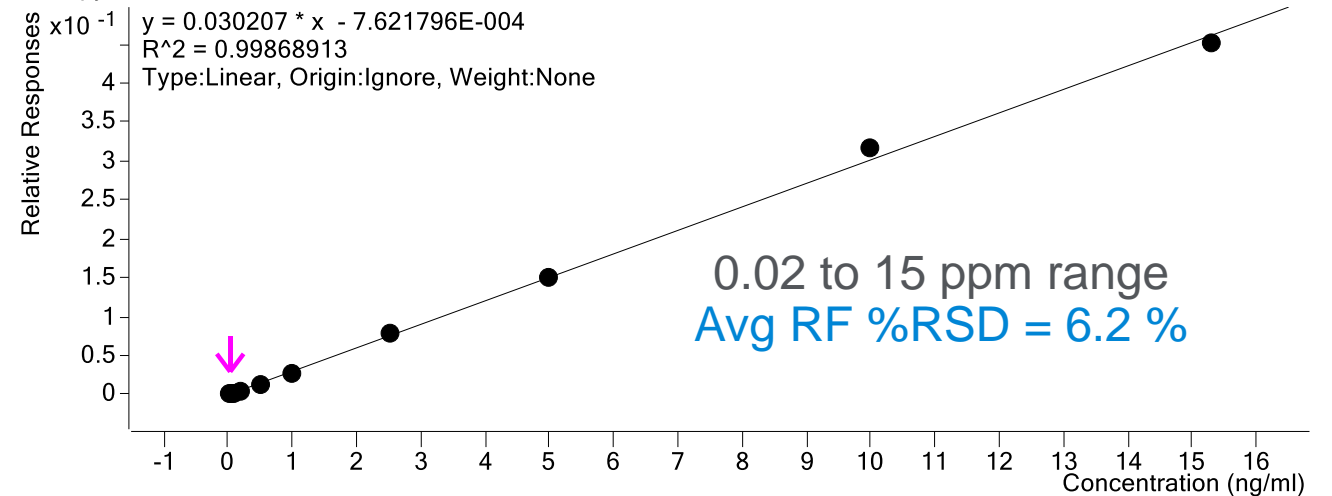
α-chlordane: Low level detection

Quant Ion at 0.02 ppm

+ EIC (373.0) Scan 20ppb_525mixes_26Sept_curve2.D

Counts ×10 ^{1}

19.804 min.

Acquisition Time (min)

Qualifier ions at 0.02 ppm

373.0 , 375.0 , 377.0 , 371.0

Relative Abundance (%) ×10 ^{2}

Ratio = 135.9 (142.0 %)
Ratio = 35.7 (69.7 %)
Ratio = 63.5 (140.6 %)

Acquisition Time (min)
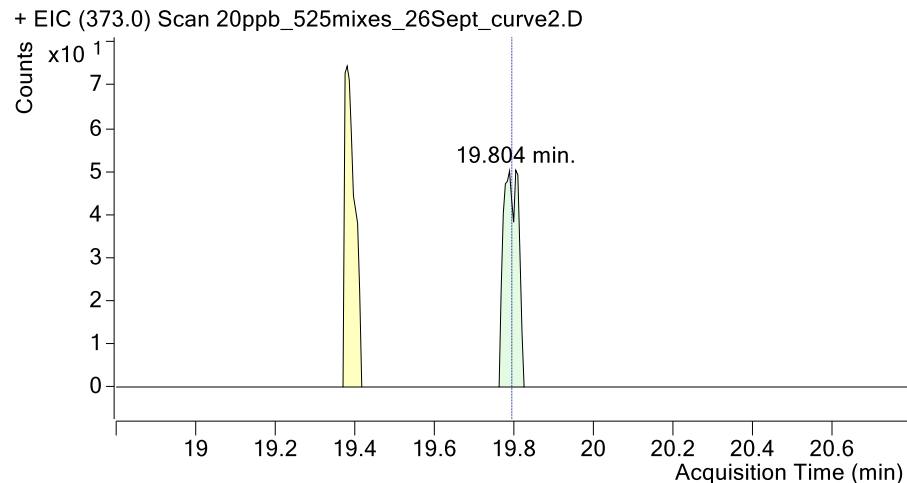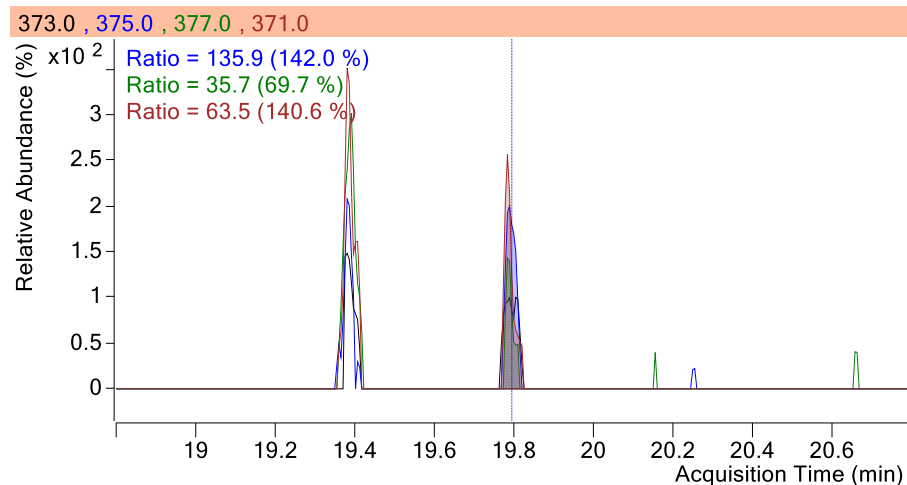
alpha-Chlordane - 10 Levels, 10 Levels Used, 10 Points, 10 Points Used, 0 QCs

Relative Responses ×10 $^{-1}$

$y = 0.025708 * x + 9.223430E\text{-}004$
$R^2 = 0.99907610$
Type:Linear, Origin:Ignore, Weight:None

Concentration (ng/ml)

0.02 to 15 ppm range
Avg RF %RSD = 11.7 %

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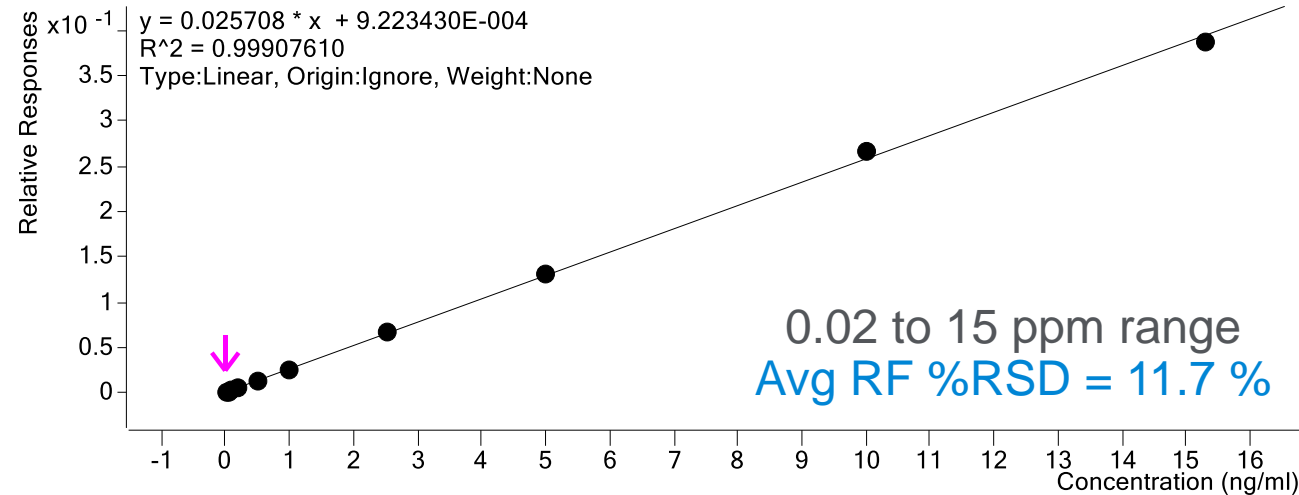
Plan of work completed

Switched septum purge
320°C source
200°C quad
9mm drawout lens
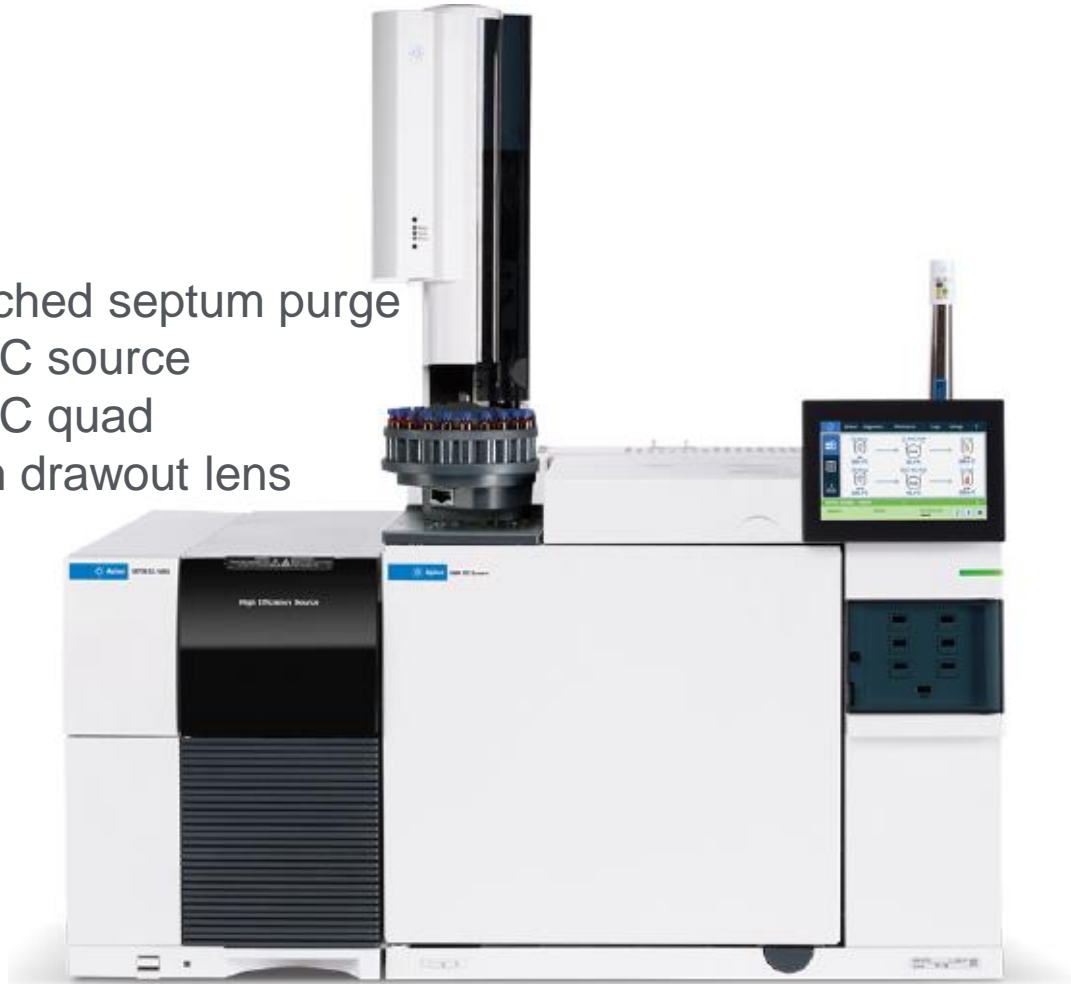
- Instrument Performance Checkout
  - DFTPP tuning check ✓
  - Endrin/DDT breakdown longevity ✓

- Calibration curves
  - Pass isomer baseline resolution ✓
  - EPA 525.2: 0.1 to 10ppm ✓
    - All compounds pass Avg. RFs
  - EPA 525.3: 0.1 to 5ppm ✓
    - All compounds pass Avg RFs
  - Extended range: 0.02 to 15 ppm ✓
    - Only 3 compounds require linear regression

Thank you for your attention!

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