Retain Your Spectral Fidelity: Using H_2 Carrier Gas and a Novel EI Source for EPA 8270 With GC/MS and GC-MS/MS Systems

NEMC 2022

New Organic Monitoring Techniques (Session 2)

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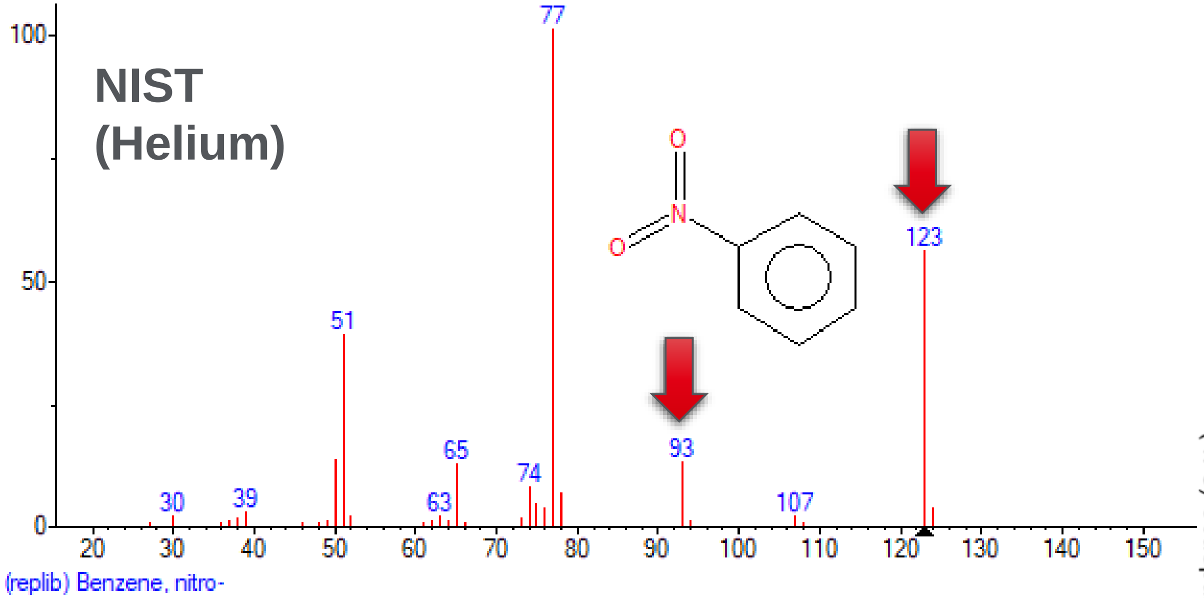
Reasons to use Hydrogen Carrier Gas

- Readily available (H_2 already used for FID and other detectors)
- Sustainable
- Lower Cost
- Cleans source during use
- Available on-demand (H_2 generator) or by cylinder
- Faster analysis
- Lower temperature separation possible
- Move to “more efficient” columns
  - 30 m x 0.25 mm x 0.25 µm → 20m x 0.18 mm x 0.18 µm

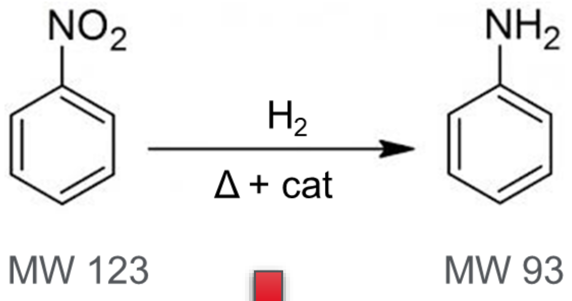
But….

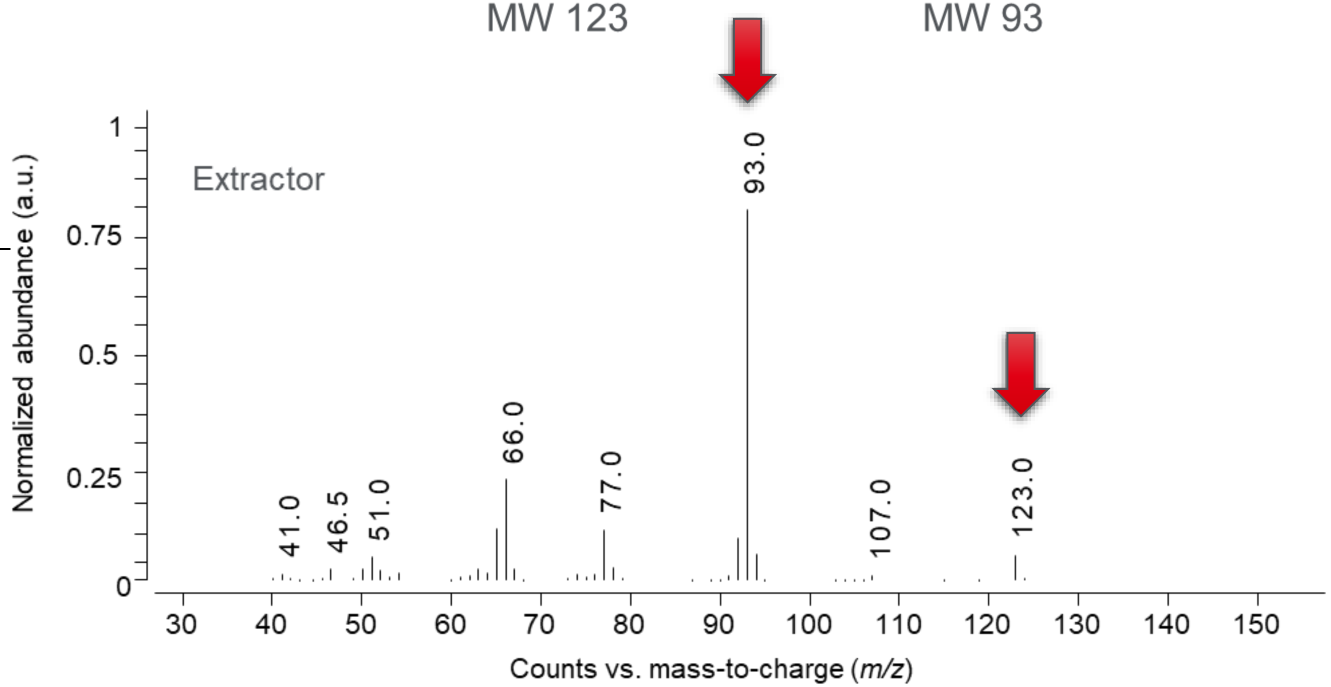
Source-Induced Problems with Hydrogen Carrier Gas: Nitrobenzene Conversion

Expected Mass Spectrum



What really happens with H_2





Conversion of nitrobenzene to aniline with H_2 carrier gas

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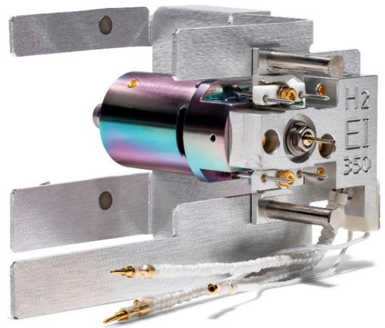
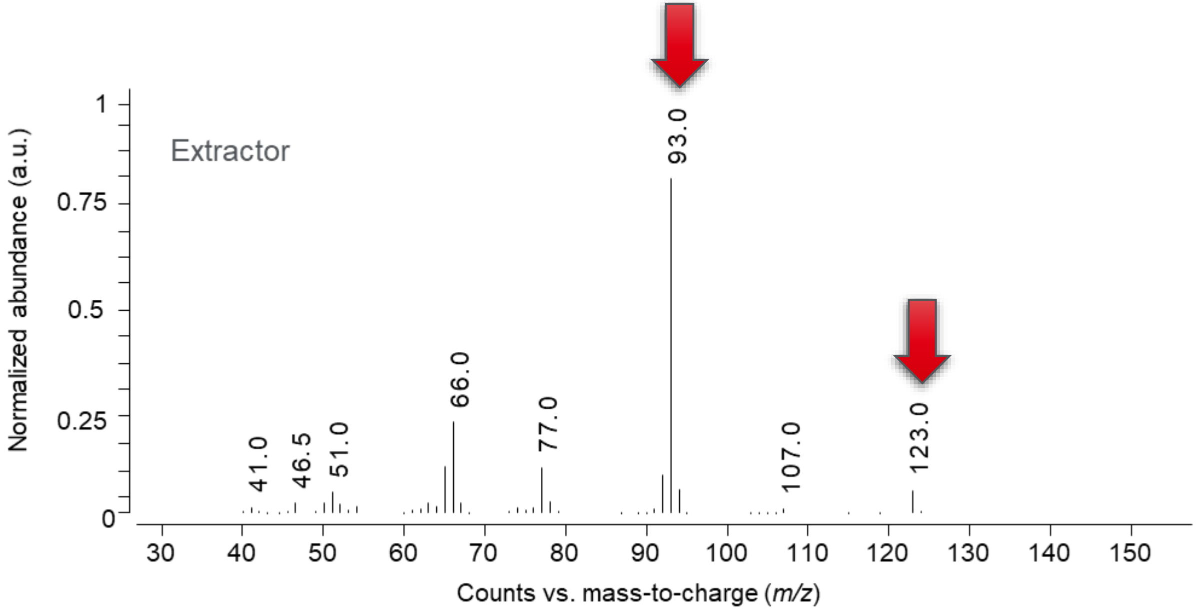
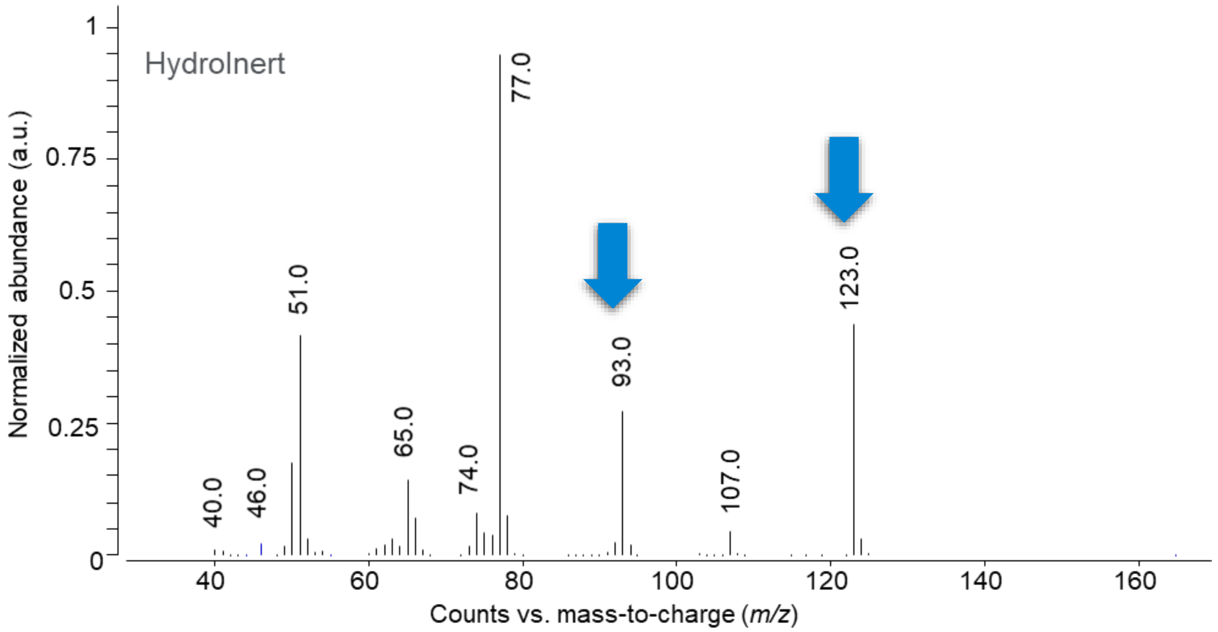
Back to nitrobenzene and H_2 carrier gas



Conventional source



Novel source



The novel source prevents hydrogenation!

Agenda

EPA 8270 on GC/MS SQ with H_2

- Development Challenges
- Successful Method
- Additional Method

EPA 8270 on GC/TQ with H_2

- Development Challenges
- Successful Method

Summary

Challenges in method development with H_2

Where did we start?

20 m x 0.18 mm x 0.18 µm

Method Parameters	
Injection Volume	1 µL
Inlet (Split-splitless Inlet)	230 °C **Split 20:1**
Column	**DB-5ms UI 20 m x 0.18 mm x 0.18 µm**
Column Temperature Program	40 °C (0 min hold) 30 °C/min to 320 °C (hold 2 min)
Carrier Gas and Flow Rate	H_2, 1.2 mL/min constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Scan	40–540 m/z
Tune	**atune.u**
Gain Factor	0.5
Threshold	0
A/D Samples	4

Why?

- Inlet pressure ≥ 5 psi
- Reasonable flow rate
- Existing column size/style

Major differences:

- Split injection to avoid overload
- Less capacity than “normal” 30 m x 0.25 mm x 0.25 µm

Evaluating methods with EPA 8270 short mix @ 10ppm

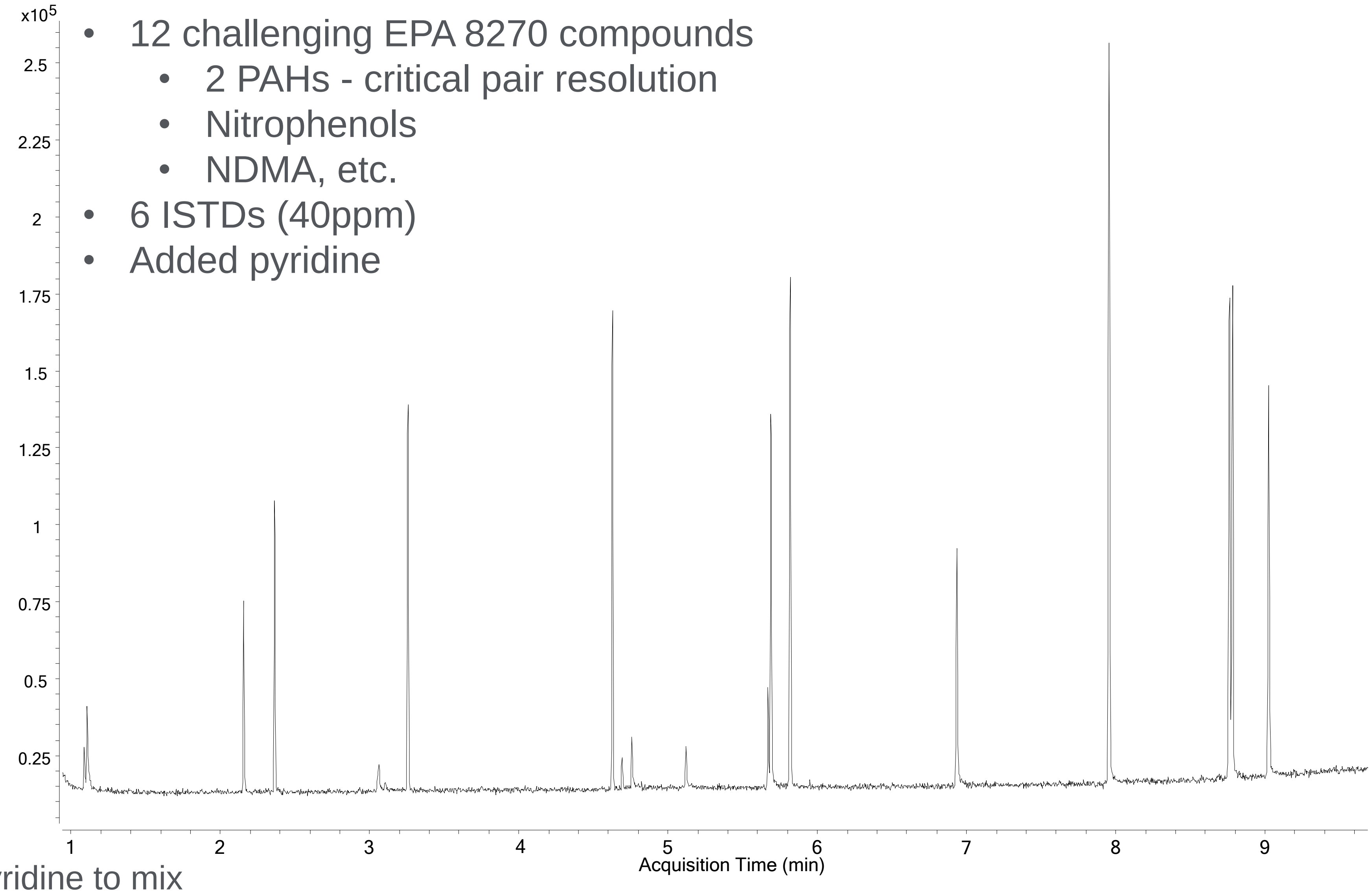
Why use the short mix?

- Contains the “difficult” compounds
- Quick decisions on method changes

Questions

- Does the 20:1 split work best?
- Can we do a pulsed splitless injection instead?
- **Can we reach 0.1 µg/mL with this method/format?**

- 12 challenging EPA 8270 compounds
    - 2 PAHs - critical pair resolution
    - Nitrophenols
    - NDMA, etc.
- 6 ISTDs (40ppm)
- Added pyridine



EPA short mix: p/n 5191-3905; added pyridine to mix
Internal standards: p/n ISM-560

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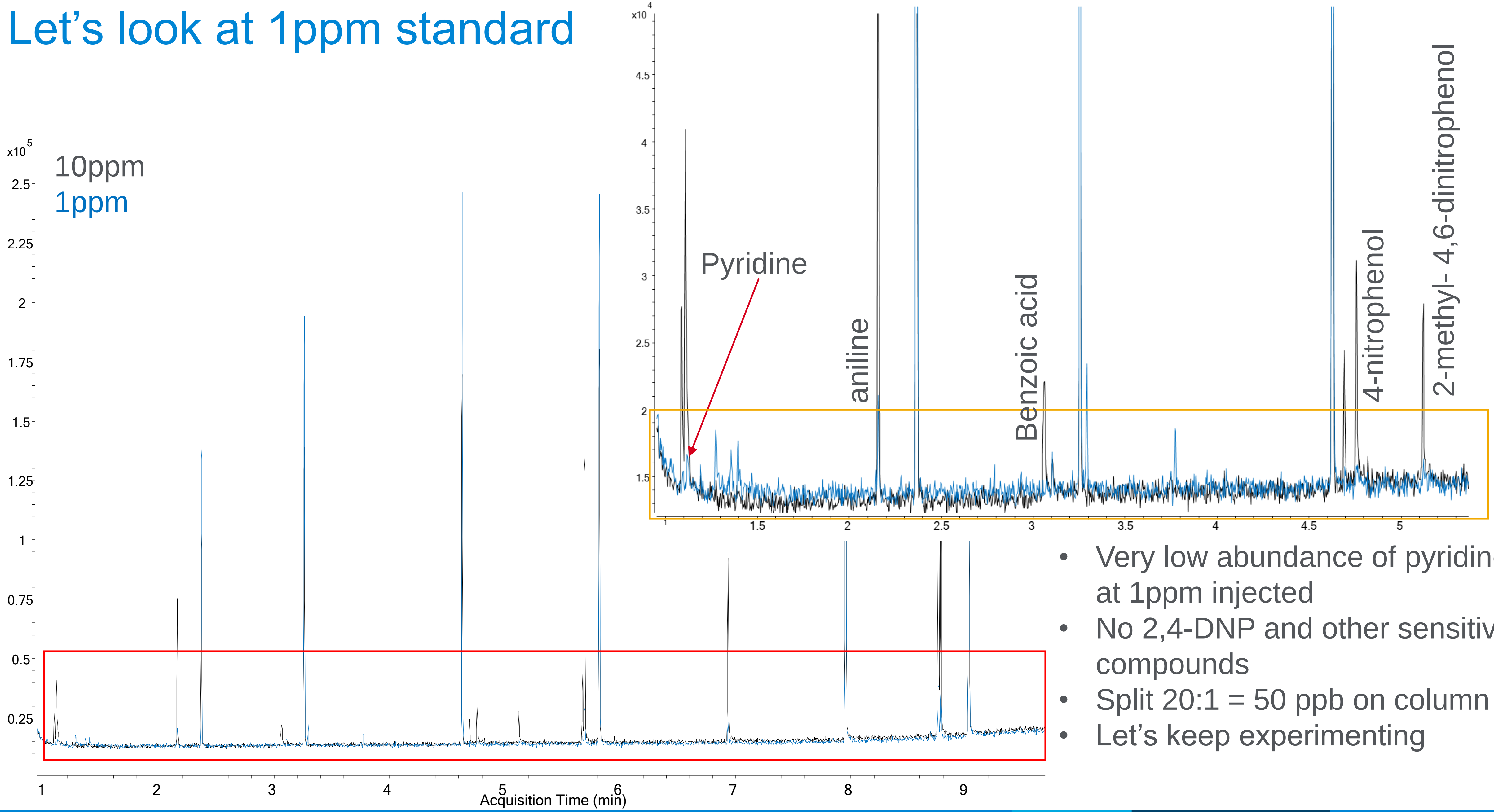
Let’s look at 1ppm standard



- Very low abundance of pyridine at 1ppm injected
- No 2,4-DNP and other sensitive compounds
- Split 20:1 = 50 ppb on column
- Let’s keep experimenting

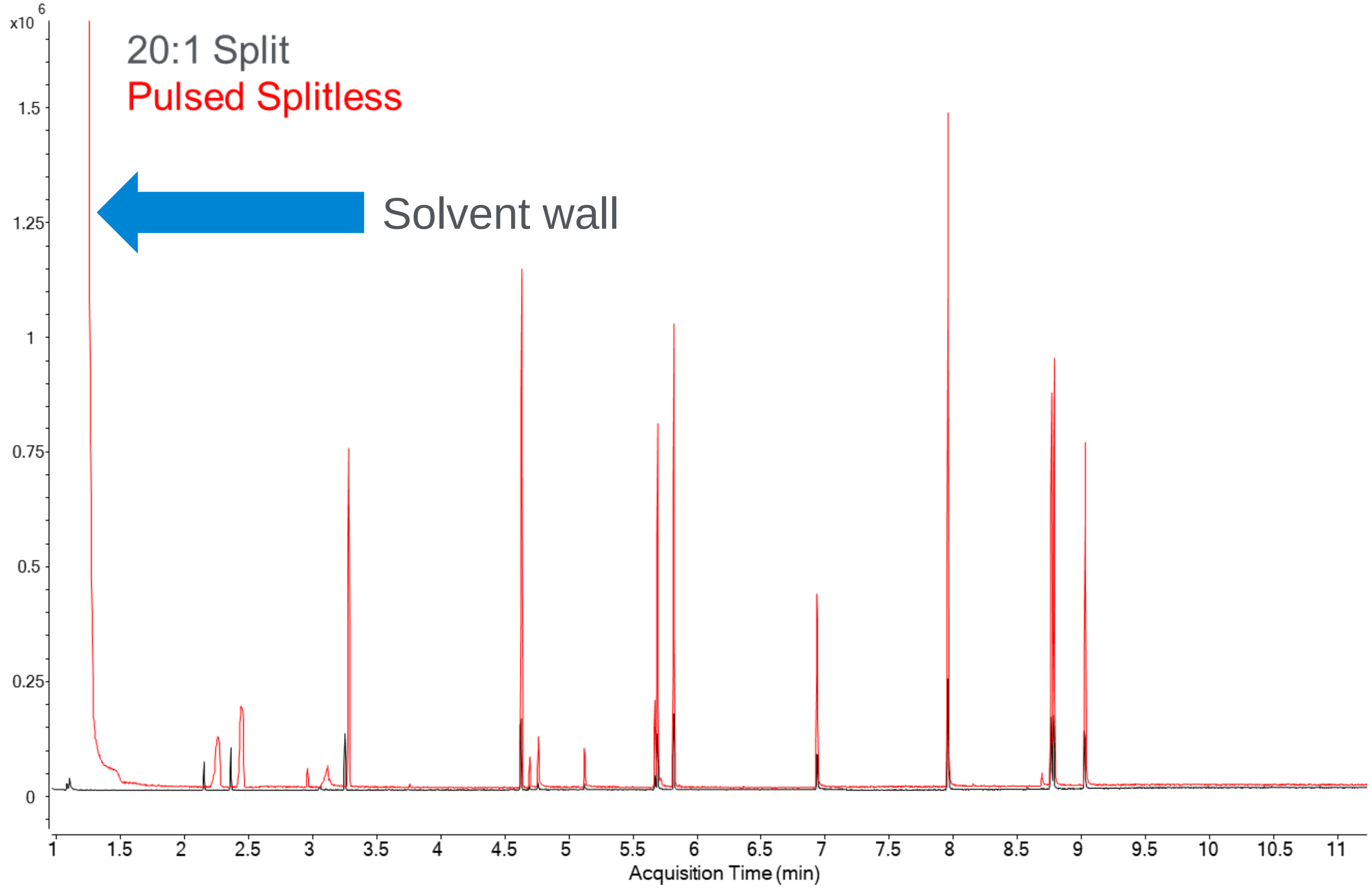
Method development: Injection parameter optimization attempts

10ppm EPA short mix: Focused on NDMA and pyridine

Pulsed splitless?

Lower split ratio?

Pulsed split?



Method development: Injection parameter optimization attempts

10ppm EPA short mix: Focused on NDMA and pyridine

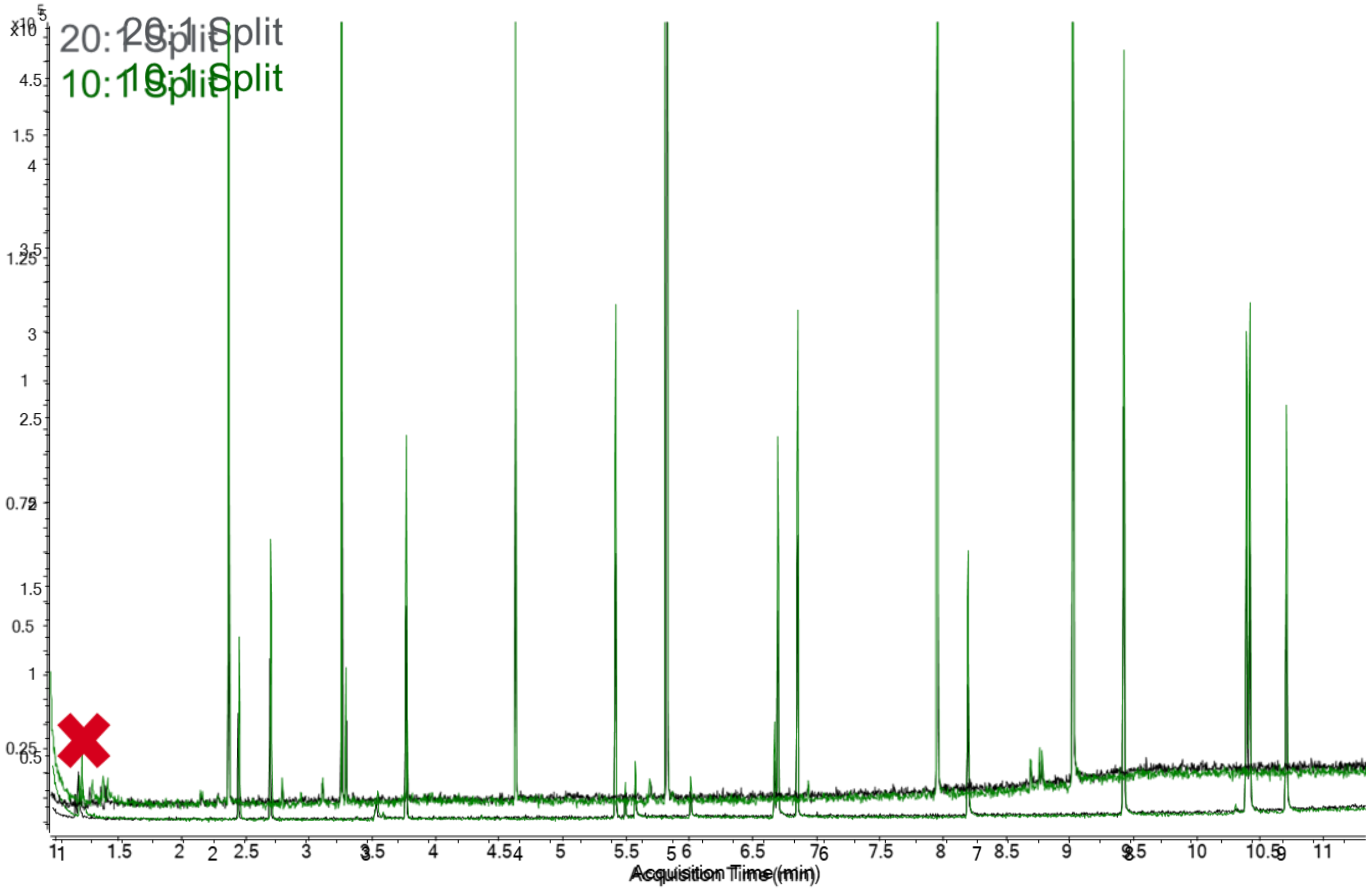
Pulsed splitless? ✖

Lower split ratio?

- Looks promising at 10 ppm
- But no NDMA or pyridine at 100ppb

Pulsed split?

Etune?



Method development: Injection parameter optimization attempts

10ppm EPA short mix: Focused on NDMA and pyridine

Pulsed splitless? ✗

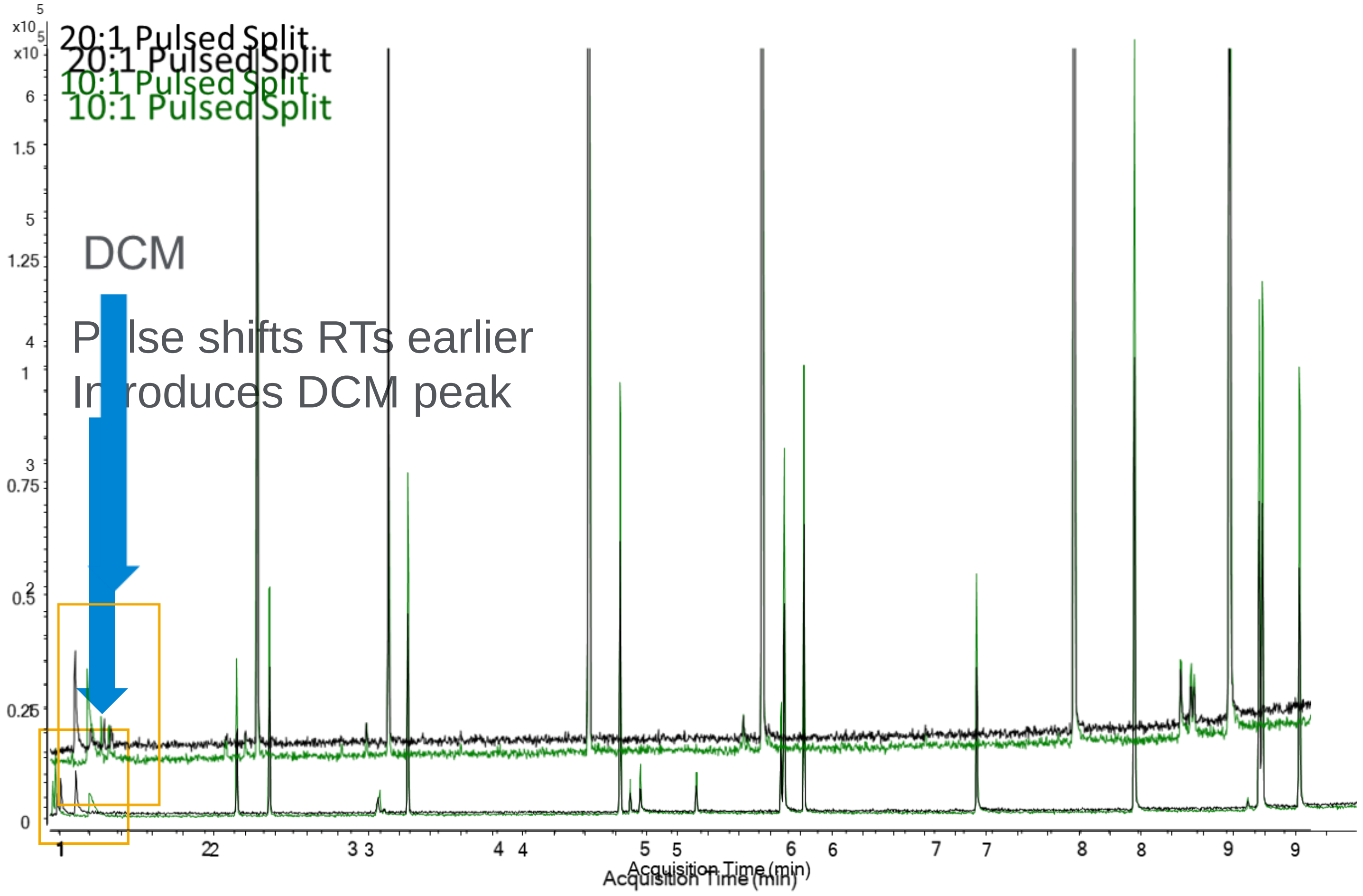
Lower split ratio? ✗

- Looks promising at 10 ppm
- But no NDMA or pyridine at 100ppb

Pulsed split?

- Looks promising at 10 ppm
- But no NDMA or pyridine at 100ppb

Etune? No better….



Transition to the 0.36 µm DB-5ms UI column

20 m x 0.18 mm x 0.18 µm

Method Parameters	
Injection Volume	1 µL
Inlet (Split-splitless Inlet)	230 °C **Split 20:1**
Column	**DB-5ms UI 20 m x 0.18 mm x 0.18 µm**
Column Temperature Program	40 °C (0 min hold) 30 °C/min to 320 °C (hold 2 min)
Carrier Gas and Flow Rate	H_2, 1.2 mL/min constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Scan	40–540 m/z
Tune	**atune.u**
Gain Factor	0.5
Threshold	0
A/D Samples	4

20 m x 0.18 mm x 0.36 µm

Method Parameters	
Injection Volume	1 µL
Inlet (Split-splitless Inlet)	230 °C **Split 10:1**
Column	**DB-5ms UI 20 m x 0.18 mm x 0.36 µm**
Column Temperature Program	40 °C (0 min hold) 30 °C/min to 320 °C (hold 2 min)
Carrier Gas and Flow Rate	H_2, 1.2 mL/min constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Scan	40–540 m/z
Tune	**etune.u**
Gain Factor	0.5
Threshold	0
A/D Samples	4

Can you pass DFTPP ion ratios with etune?

Target Mass (m/z)	Ion Abundance Criteria	Measured Relative Abundance	Pass/Fail
51	*10–80% of 198 m/z	38.5 %	Pass
68	<2% of 69 m/z	1.0 %	Pass
69	Present	36.5 %	Pass
70	<2% of 69 m/z	0.4 %	Pass
127	*10–80% of 198 m/z	54.4 %	Pass
197	<2% of 198 m/z	0.0 %	Pass
198	Base peak or present *or >50% of 442 m/z	51.6 %	Pass
199	5–9% of 198 m/z	5.0 %	Pass
275	10–60% of base peak	30.4 %	Pass
365	>1% of base peak	4.9 %	Pass
441	<150% of 443 m/z *present, but <24% of 442	83.1% *15.7%	Pass
442	Base peak or present *or >50% of 198 m/z	100% (base peak)	Pass
443	15–24% of 442 m/z	18.9 %	Pass

* EPA 8270D criteria

Yes, it can pass!

What about atune?

Yes, it passes, but….

- Calibration range for majority of compounds would be ≥0.2 – 100 µg/mL

What about atune with the 0.36 µm or other split ratios?

What did we try?

Atune

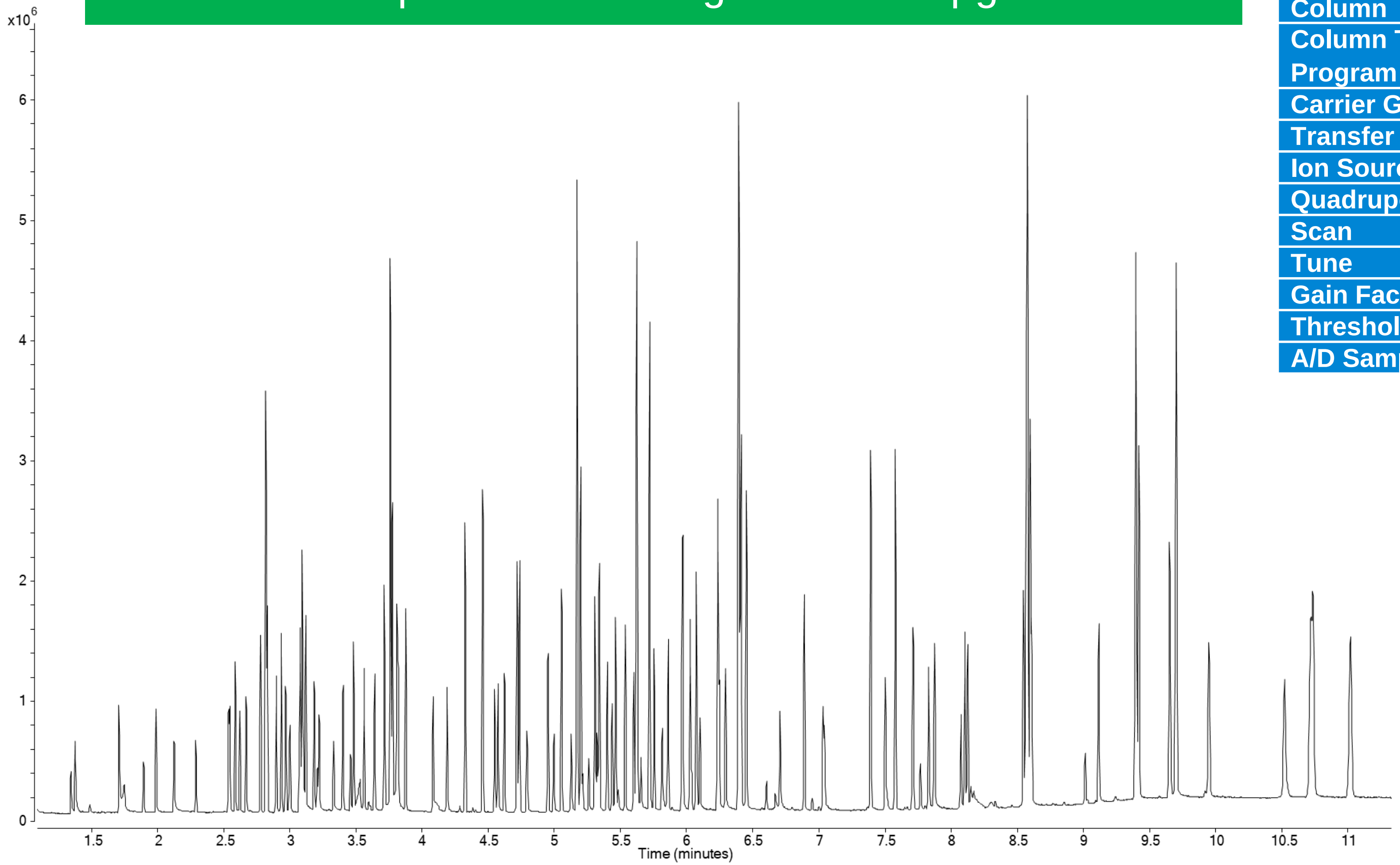
- Split 20:1 → Issues < 1ppm for NDMA, pyridine, 2,4-DNP, etc.
- Split 10:1 → Issues < 1ppm for “ ” “ ” “ ”
- Split 5:1 → Issues < 1ppm for “ ” “ ” “ ”
- Pulsed Split 10:1 → Issues ≤ 0.5 ppm
- Pulsed Split 5:1 → Issues ≤ 0.5 ppm

Etune

- Split 20:1 → Issues ≤ 0.5ppm
- Split 5:1 → Saturation issues at higher concentrations
- Pulsed Split 10:1 → Cal curve results not as good as Split 10:1

EPA 8270 GC/MS (Single Quad) Method Parameters: H_2 and a novel source

119 target analytes and surrogates
<13% require a curve fit
95 compounds: Full range 0.1 – 100 µg/mL

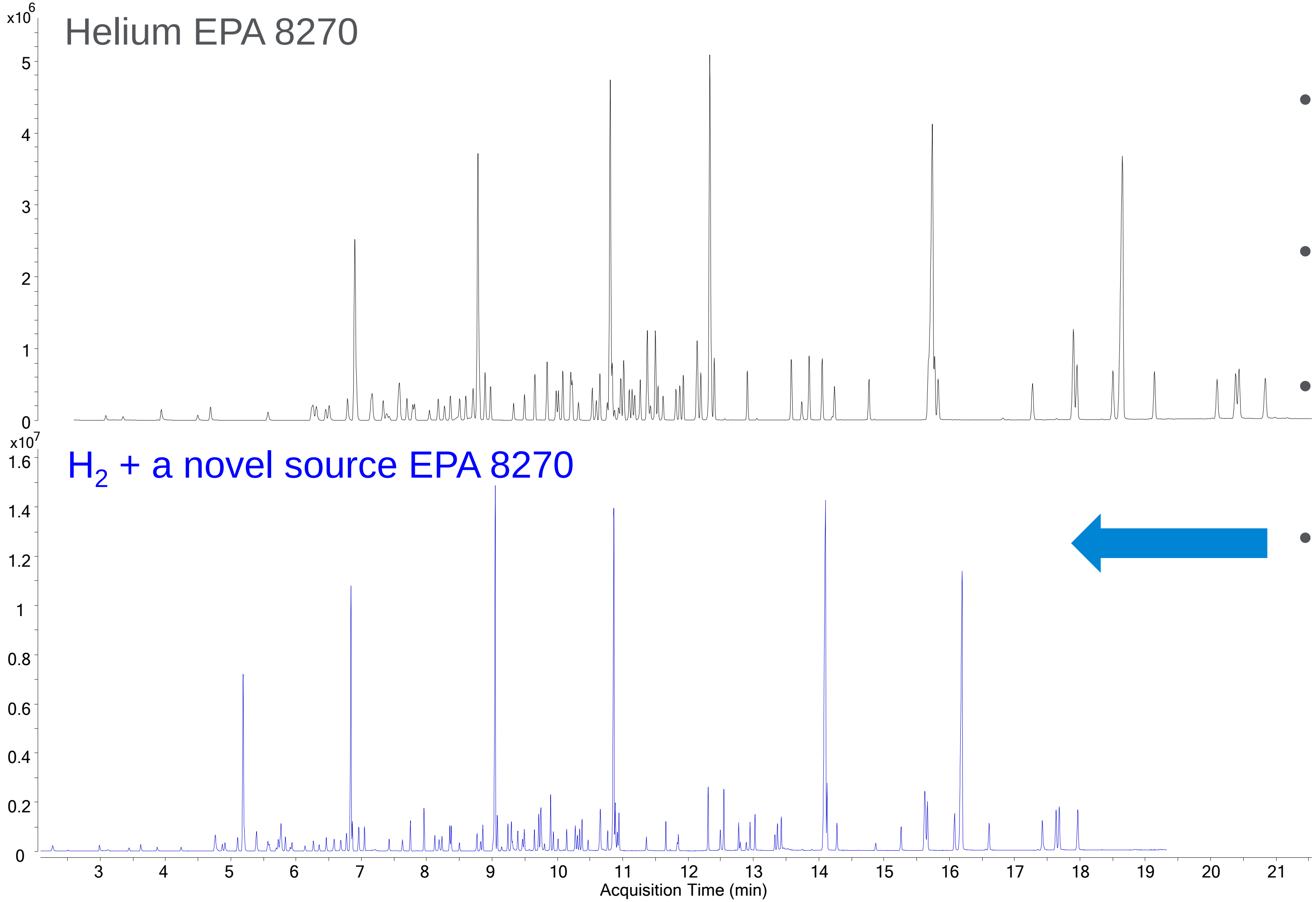


Method Parameters	
Injection Volume	1 µL
Inlet (Split-splitless Inlet)	230 °C **Split 10:1**
Column	**DB-5ms UI 20 m x 0.18 mm x 0.36 µm**
Column Temperature Program	40 °C (0 min hold) 30 °C/min to 320 °C (hold 2 min)
Carrier Gas and Flow Rate	H_2, 1.2 mL/min constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Scan	35–500 m/z
Tune	**etune.u**
Gain Factor	0.5
Threshold	0
A/D Samples	4

Calibration Curve Passing Criteria for EPA 8270E

	Number of compounds
Average RF %RSD <20%	104
Linear fit	14
Quadratic fit	1 (Sulfotep)

Do I have similar responses between "normal" helium data and H_2 source data?



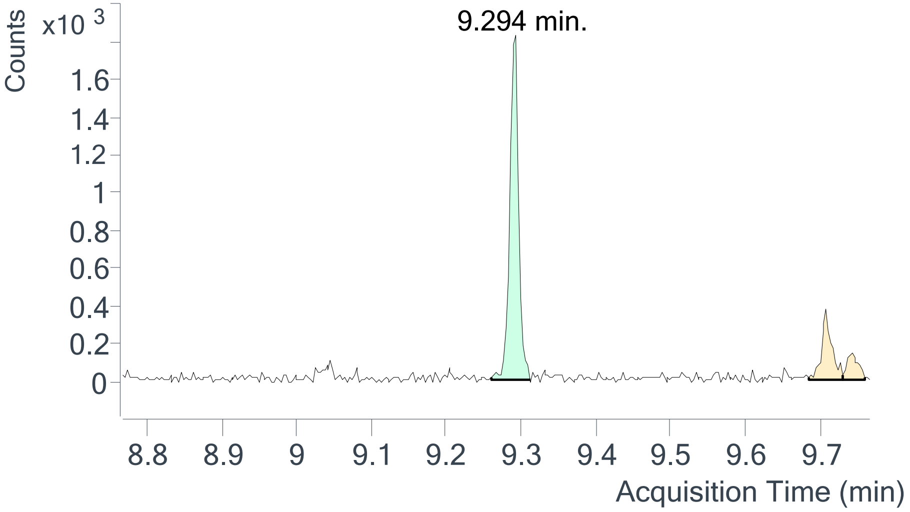
- Using the same column, injection parameters and tune (atune.u)
- Faster constant flow rate with H_2
- Benefits of H_2
  - Narrower peaks
  - Increased resolution
- Retained sensitivity!

Could I stay with a 30m column?

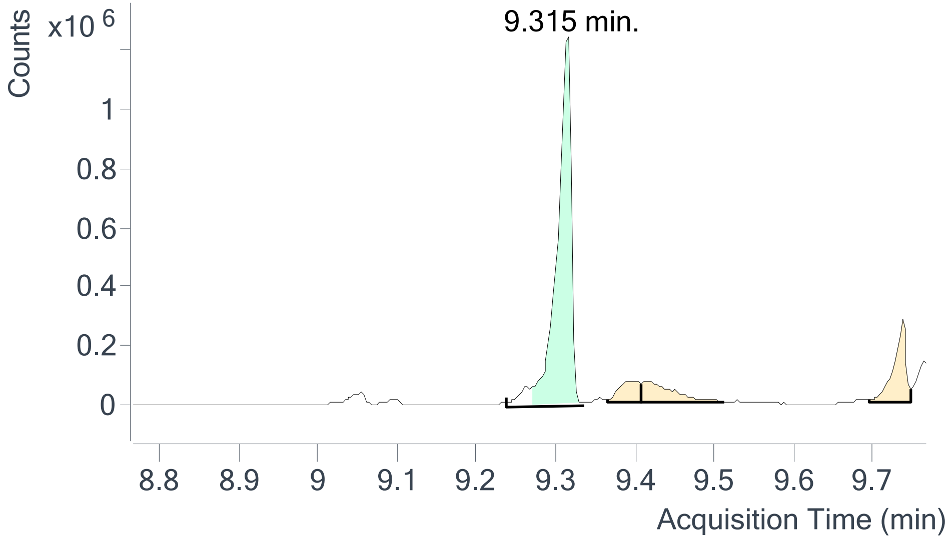
4-nitrophenol

0.1 ppm is great!
≥50ppm can have overloading issues

0.1 ppm

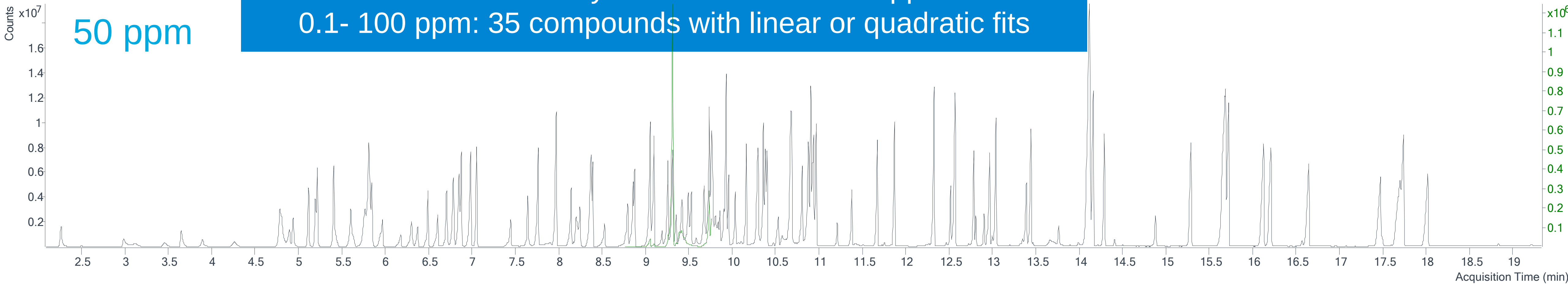


50 ppm



30m column may work best for 0.1 - 40ppm
0.1- 100 ppm: 35 compounds with linear or quadratic fits

50 ppm

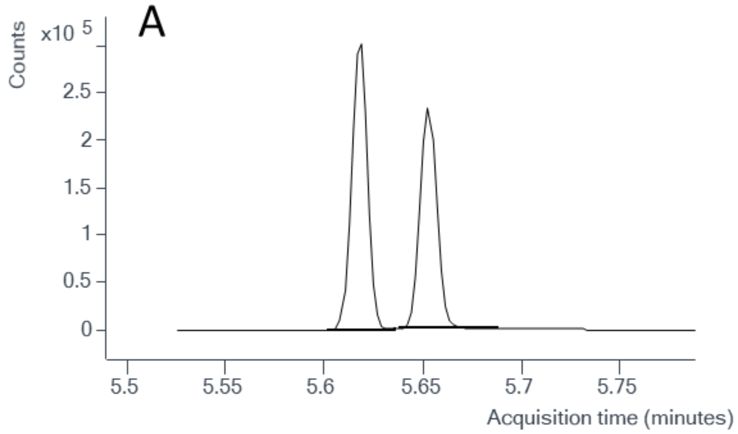


GC-TQ EPA 8270E

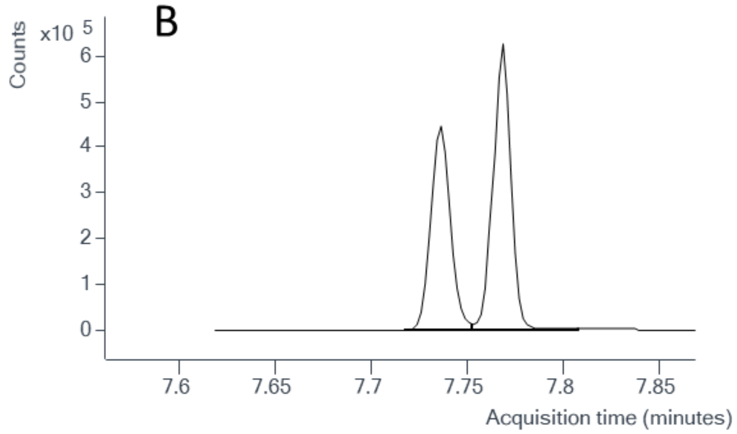
With H_2 carrier gas

Retain resolution of critical PAH pairs with H_2 for GC/TQ

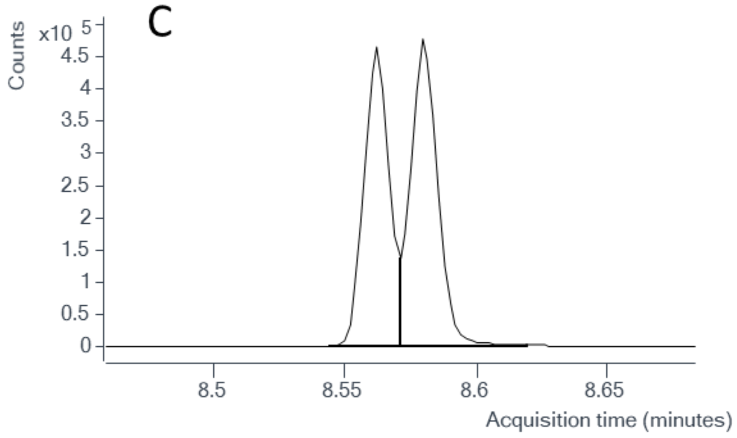
Phenanthrene and Anthracene



Benz[a]anthracene and chrysene



Benzo(b)fluoranthene and benzo(k)fluoranthene

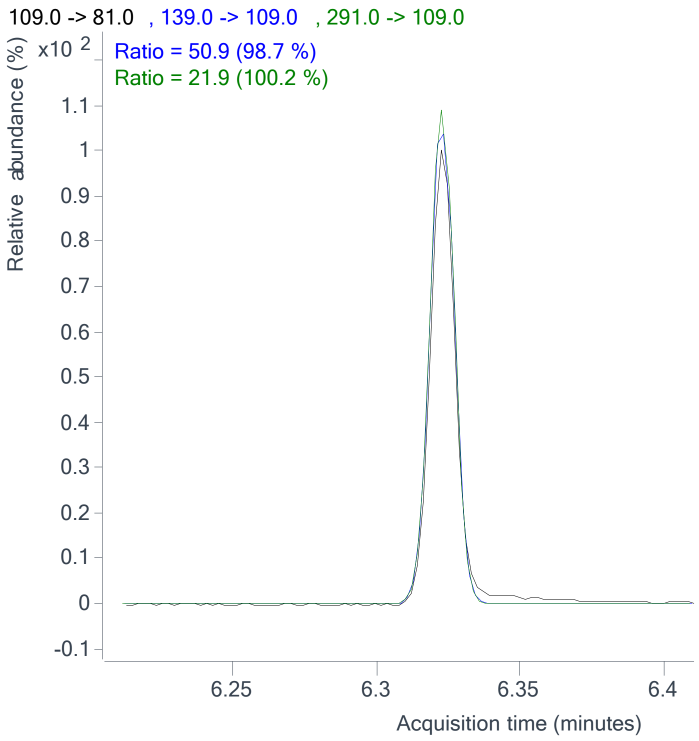


>50% resolution

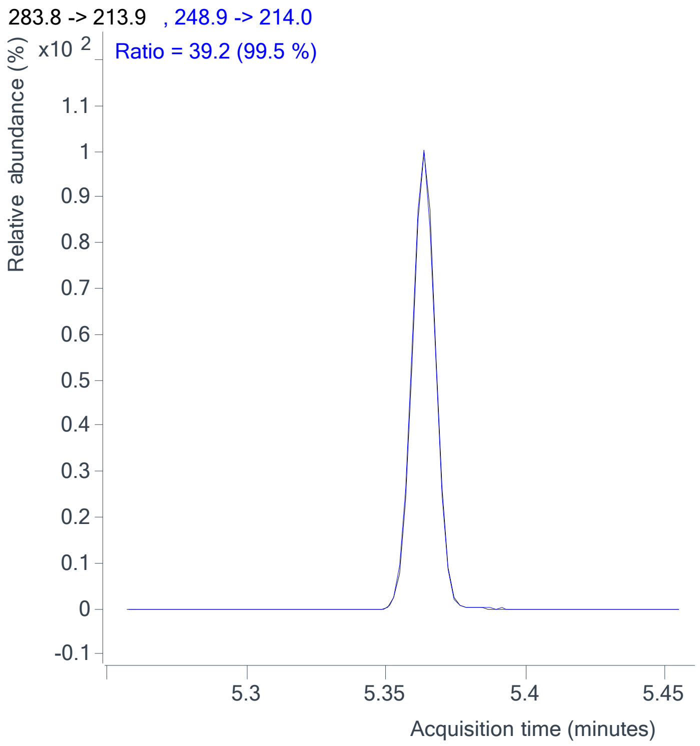
Retain your MRM transitions with H_2 and a novel source

MRM transitions are from helium generated data!

Parathion



Hexachlorobenzene



Remember to update/optimize collision energies!

Inlet method development with GC/TQ

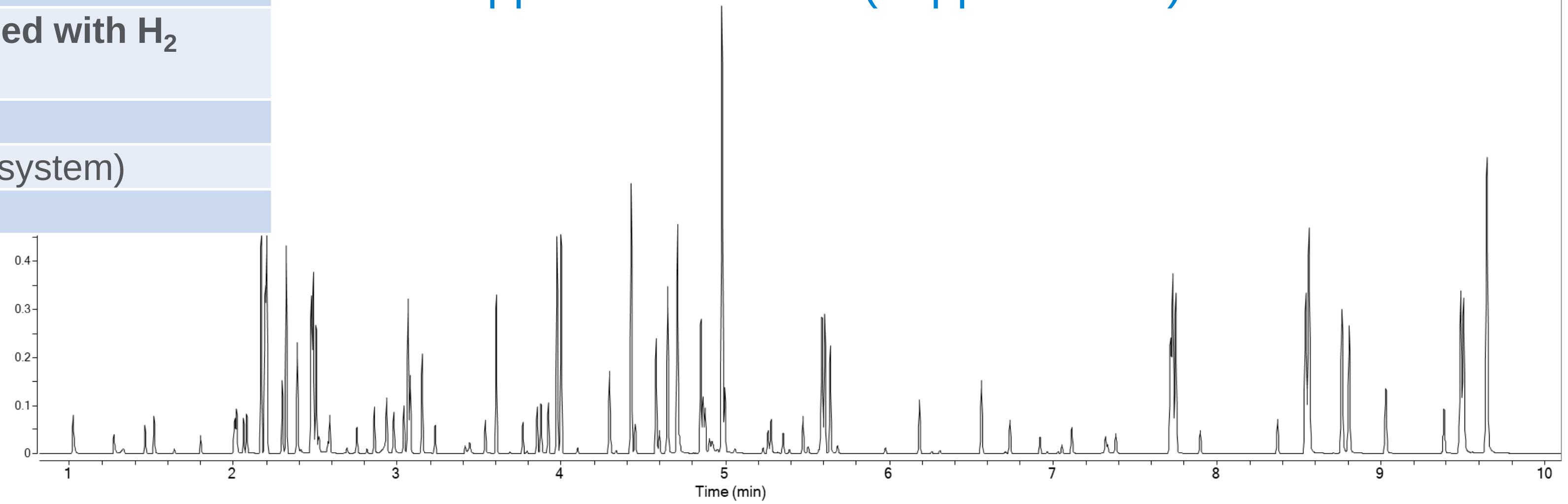
Should we use split/splitless or temperature programmable inlet?

GC/TQ Method Parameters	
Injection Volume	1 µL
Inlet	**Split 20:1**
Column	**DB-5ms UI 20 m x 0.18 mm x 0.18 µm**
Column Temperature Program	40 °C (hold 0 min), 30 °C/min to 320 °C (hold 2-2.7 min*) Post run: 320 °C hold for 2 min
Carrier Gas and Flow Rate	H_2 at 1.2 mL/min**, constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Collision Gas and Flow Rate	Nitrogen, 1.5 mL/min
Quench Gas	**No quench gas is used with H_2 carrier gas**
EMV Mode	Gain factor
Gain Factor	1 (optimized for each system)
Scan Type	dMRM

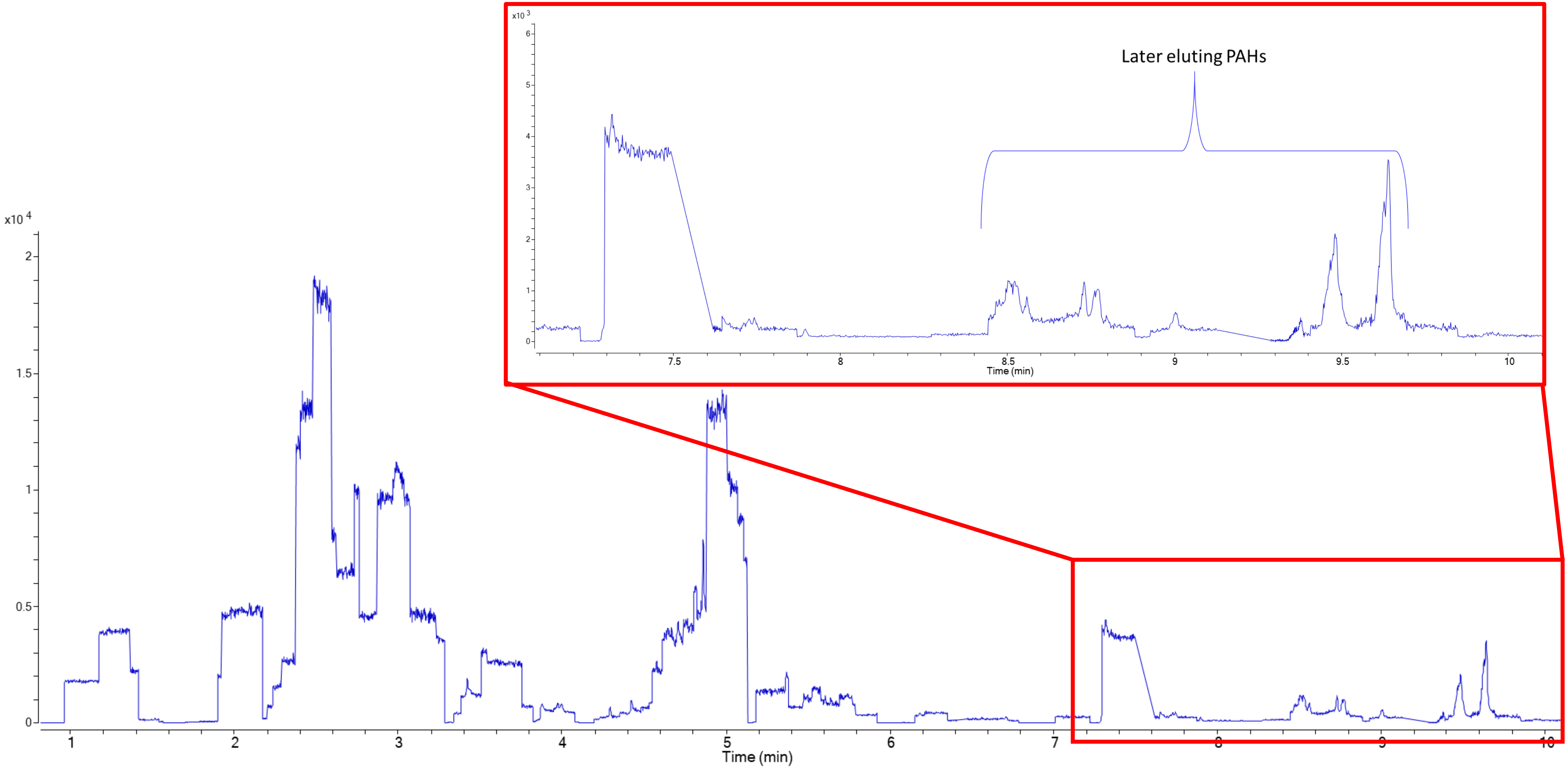
Similar run time to He GC/TQ method

- Start with split/splitless inlet
- 230 °C temperature

20 ppm EPA mixture (40ppm ISTDs)



DCM blank run after 20ppm EPA mixture run



Can we remove carryover…and still reach our 20 ppb extended range?

What can we try to optimize?

Liner

- Low pressure drop liner with wool
- Mid-frit liner

Inlet temperature

Pulsed Split injection

Split ratio

Results

When we changed liners….

- Carry over
- Carry over

When we tried 250 °C? Carry over

When we tried pulsed split injections? Carry over

When we tried 50:1 split ratio?

- No carryover!
- Could work for 0.1 – 100ppm, but we want the extended range

Switch to the Multimode Inlet

GC/TQ Method Parameters	
Injection Volume	1 µL
Multimode Inlet	250 °C (hold 0.3 min) ramp 200 °C/min to 350 °C (hold for run length) Postrun: 350 °C/min with 100 mL/min split flow **Split 20:1**
Column	**DB-5ms UI 20 m x 0.18 mm x 0.18 µm**
Column Temperature Program	40 °C (hold 0 min), 30 °C/min to 320 °C (hold 2-2.7 min*) Post run: 320 °C hold for 2 min
Carrier Gas and Flow Rate	H_2 at 1.2 mL/min**, constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Collision Gas and Flow Rate	Nitrogen, 1.5 mL/min
Quench Gas	**No quench gas is used with H_2 carrier gas**
EMV Mode	Gain factor
Gain Factor	1 (optimized for each system)
Scan Type	dMRM

Tested different:

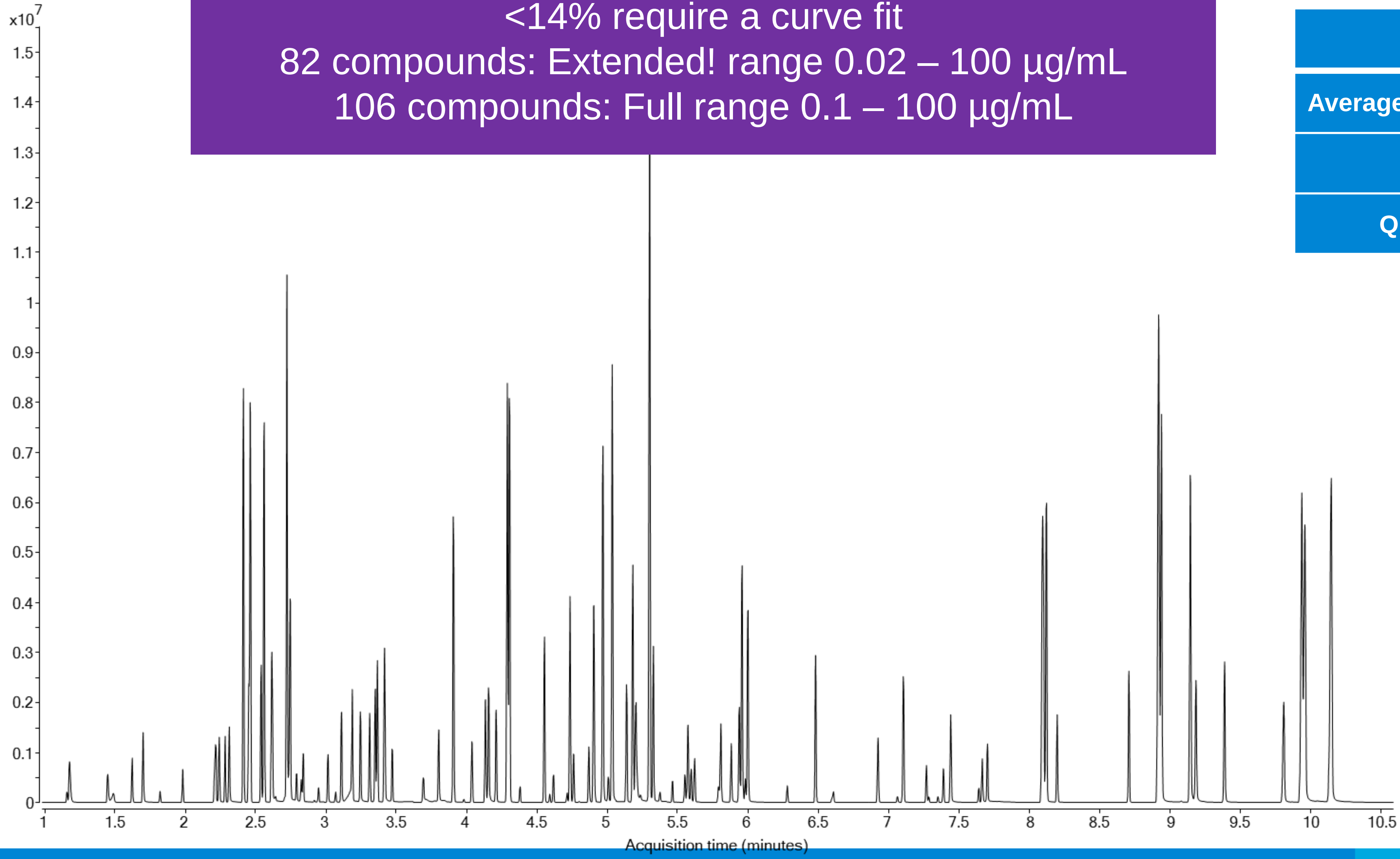
- Starting inlet temps
- Hold times of starting and final inlet temps
- Final inlet temp

Best conditions

- Start at 250 °C, ramp to 350 °C and hold for run length
- **Sample prep MUST include water removal step with the elevated inlet temp**

EPA 8270 GC/TQ Method Parameters: H_2 and a novel source

120 target analytes and surrogates
<14% require a curve fit
82 compounds: Extended! range 0.02 – 100 µg/mL
106 compounds: Full range 0.1 – 100 µg/mL



Calibration Curve Passing Criteria for EPA 8270E

	Number of compounds
Average RF %RSD <20%	104
Linear fit	6
Quadratic fit	10

Summary

- Retained mass spectral fidelity with H_2 carrier
- Demonstrated viable methods for EPA 8270E on GC/MS and GC/TQ with H_2 carrier gas and a novel source
  - Passed DFTPP (injected sample) check on both GC/MS AND GC/TQ
  - Full calibration range for GC/MS (0.1 – 100 ppm)
  - Extended calibration range for GC/TQ (0.02 – 100 ppm)

Sample prep is critical with H_2 and DCM → Requires water removal “drying” step

Method translation and development takes time; plan accordingly!

Determine:

- Critical compounds to see
- Preferred calibration range (full, extended or smaller than EPA 8270 method?)
- How much or is any carryover ok?

Acknowledgements

Thanks to:

Bill Mock at Pace Analytical National Center for Testing Innovation Laboratory

Agustin Pierri at Weck Labs

Thank you!

Any Questions?

Agilent

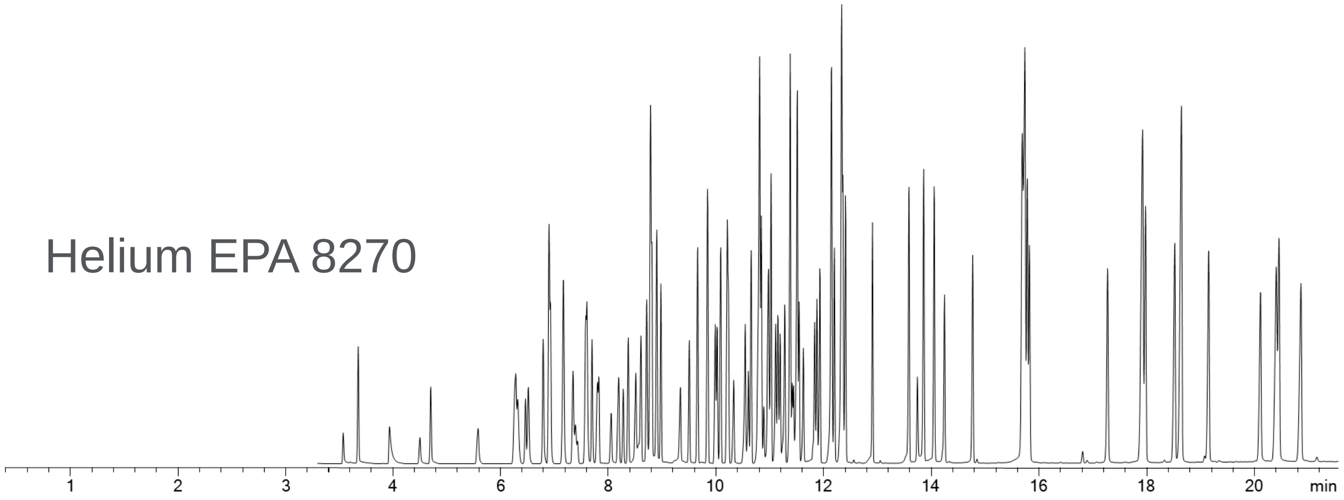
Appendix

Agilent HydroInert Source for Hydrogen Carrier Gas on GC/MS

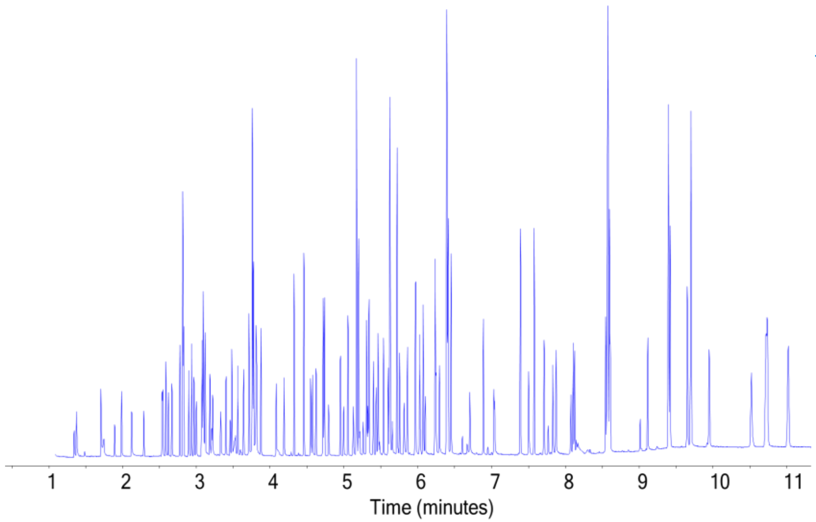
- Allows for the use of Hydrogen Carrier Gas with better supply and reduced cost
- Faster, shorter Separations
- Reduces loss of sensitivity and spectral anomalies
- Reduced source cleanings and maintenance

Comparing Helium and H_2 results

Helium EPA 8270



H_2 + a novel source EPA 8270



Shortened run time by ~1/2

Compound	Response Factor (RF) from EPA Method 8270E	RF He GC/MS	RF H_2 HydroInert GC/MS
Acenaphthene	0.9	1.3	1.1
Acenaphthylene	0.9	1.9	1.4
Acetophenone	0.01	1.2	0.4
Anthracene	0.7	1.1	1.0
Benzo(a)anthracene	0.8	1.4	1.5
Benzo(a)pyrene	0.7	1.2	0.9
Benzo(b)fluoranthene	0.7	1.4	1.2
Benzo(g,h,i)perylene	0.5	1.1	1.0
Benzo(k)fluoranthene	0.7	1.2	1.2
Bis(2-chloroethoxy)methane	0.3	0.4	0.3
62 compounds		**3% low**	**11% low**

Majority of RFs match to EPA 8270 RF guidelines

Agilent

HydroInert + H_2 results for response factors

Compound	Response Factor (RF) from EPA Method 8270E	RF He GC/MS	RF H_2 HydroInert GC/MS	RF H_2 HydroInert GC/MS/MS
Acenaphthene	0.9	1.3	1.1	0.2
Acenaphthylene	0.9	1.9	1.4	0.1
Acetophenone	0.01	1.2	0.4	1.0
Anthracene	0.7	1.1	1.0	0.9
Benzo(a)anthracene	0.8	1.4	1.5	1.0
Benzo(a)pyrene	0.7	1.2	0.9	0.9
Benzo(b)fluoranthene	0.7	1.4	1.2	1.2
Benzo(g,h,i)perylene	0.5	1.1	1.0	1.3
Benzo(k)fluoranthene	0.7	1.2	1.2	1.3
Bis(2-chloroethoxy)methane	0.3	0.4	0.3	0.7
62 compounds		**3% low**	**11% low**	**19% low**

Compound	Response Factor (RF) from EPA Method 8270E	RF He GC/MS	RF H_2 HydroInert GC/MS	RF H_2 HydroInert GC/MS/MS
Diethyl phthalate	0.01	1.4	1.0	0.6
4-Nitroaniline	0.01	0.3	0.21	0.13
Nitrobenzene	0.2	0.3	0.2	0.3
2,6-Dinitrotoluene	0.2	0.3	0.2	0.03
2,4-Dinitrophenol	0.01	0.2	0.1	0.02
4-Nitrophenol	0.01	0.2	0.14	0.05
N-Nitroso-di-n-propylamine	0.5	0.4	0.4	0.03
N-Nitrosodiphenylamine	0.01	2.05	0.9	2.3
Pentachlorophenol	0.05	0.18	0.1	0.1
2,3,4,6-Tetrachlorophenol	0.01	0.36	0.17	0.07

Majority of RFs match to EPA 8270 RF guidelines