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GC/MS/MS Determination of Semivolatiles Using Nitrogen Carrier, Reagent and CID Gas

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NATIONAL ENVIRONMENTAL MONITORING CONFERENCE
NEMC

Hurdles and Highlights for Helium Carrier Gas

- Non-renewable
- Petroleum production by-product
- **Supply instability**
- **Pricing instability**

- **Inertness**
- Chromatographic resolving power
- Compatibility with MS vacuum
- Compatibility with MS ionization
- Broad applications/publications

Will I be able to deliver results on time?

Alternatives to Helium

- **Nitrogen**

- Local generation possible
- **Inertness**
- **Slower optimum linear velocity**
- Requires column scaling
- Adverse effects on sensitivity for EI

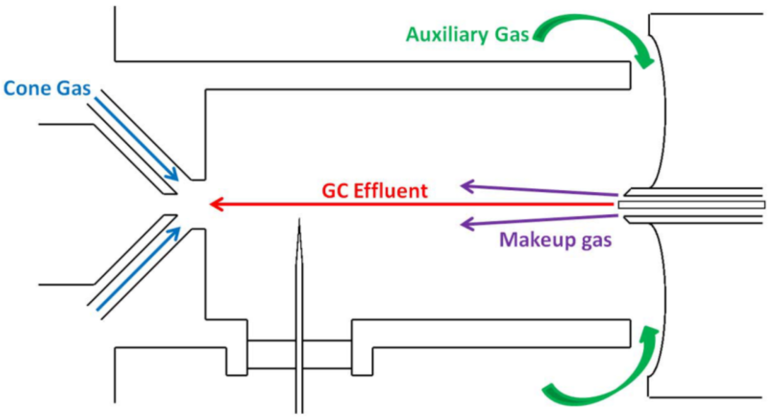
- **How does N_2 effect GC-APCI?**

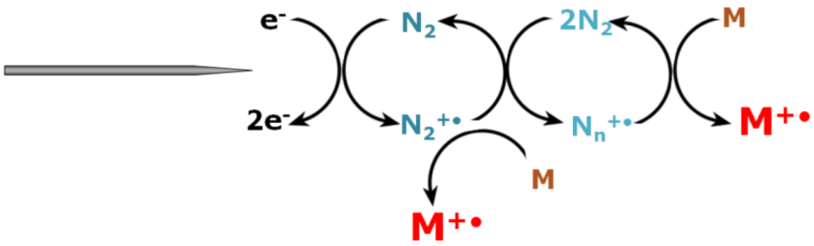
- **Hydrogen**

- Local generation possible
- **Undesirable reactivity**
- **Higher optimum linear velocity**
- Requires column scaling
- Adverse effects on sensitivity for EI

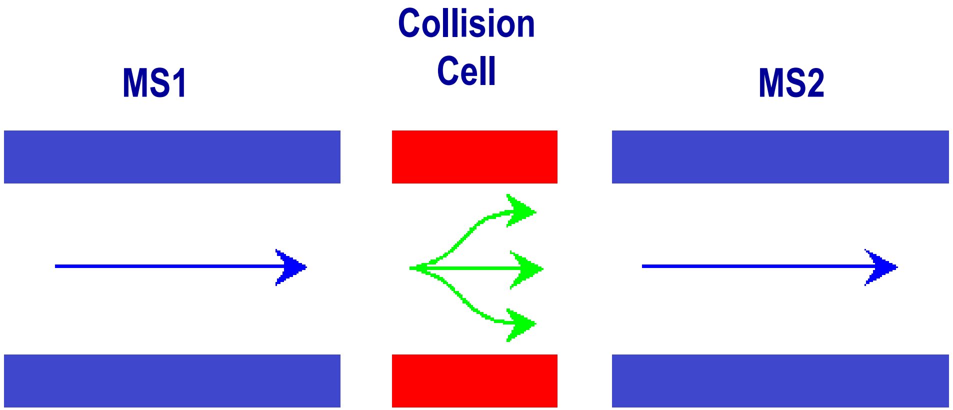
- **Not supported for GC-APCI**

GC-APCI MS: Gas Chromatography Atmospheric Pressure Chemical Ionization Mass Spectrometry





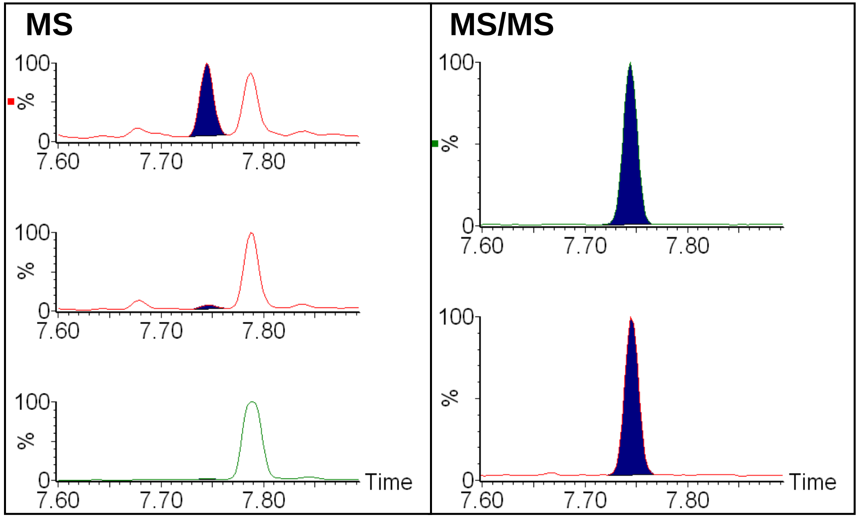
Multiple Reaction Monitoring: MRM (aka SRM)



- **MS1 filters precursor ions**
- **Gas filled cell with fragmenting voltage applied**
- **Ions undergo collision induced dissociation (CID)**
- **MS2 passes only specific product ions**

Why MS/MS?

- Higher confidence
  - Decrease/eliminate false positives/negatives
- Ease of integration
  - Easier to automate
  - Less manual reprocessing
- Time Savings
  - Allows faster run times
  - Reduce/eliminate sample clean up steps
- Reduced/eliminated chemical noise
  - Increases accuracy
  - Improves precision
  - Improves dynamic range

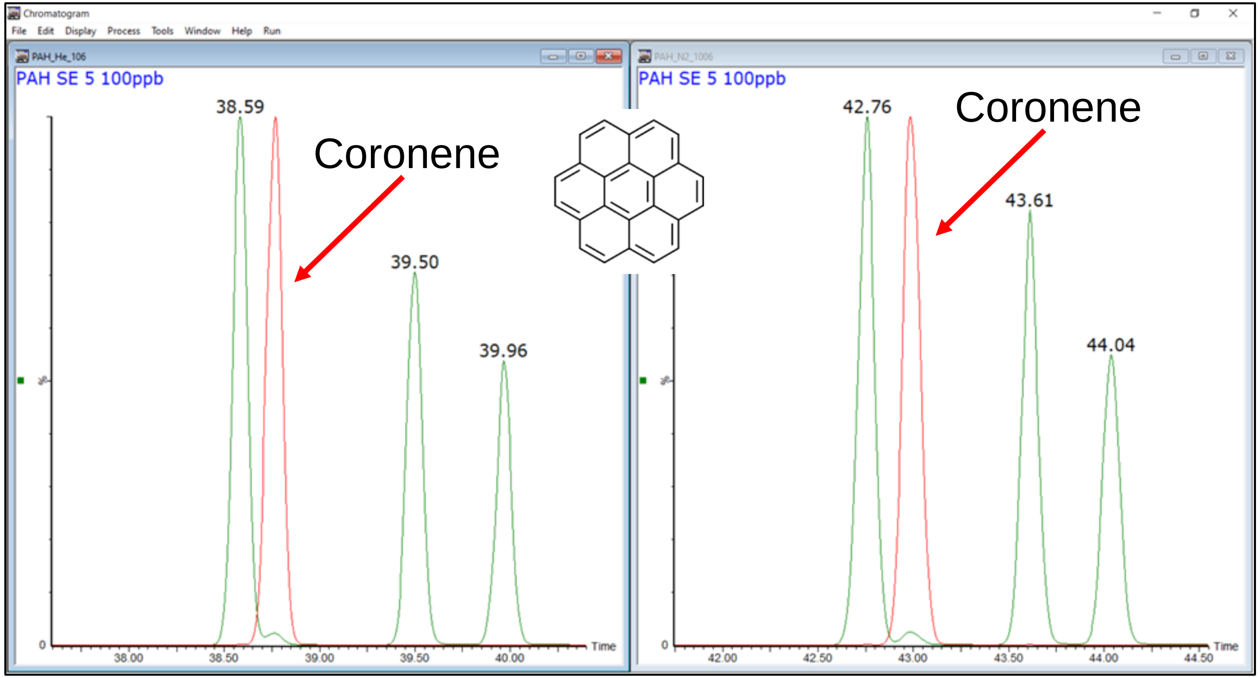


Specificity & Sensitivity

PAHs: N_2 v He, Without Column Scaling

- N_2 ~10% longer runtime
- He v. N_2 functionally equivalent separation
- Rxi-35Sil MS 30m x .25 x.25
  - No commercially available scaled column

- Nitrogen Carrier Gas White Paper, 2023



Helium

Nitrogen

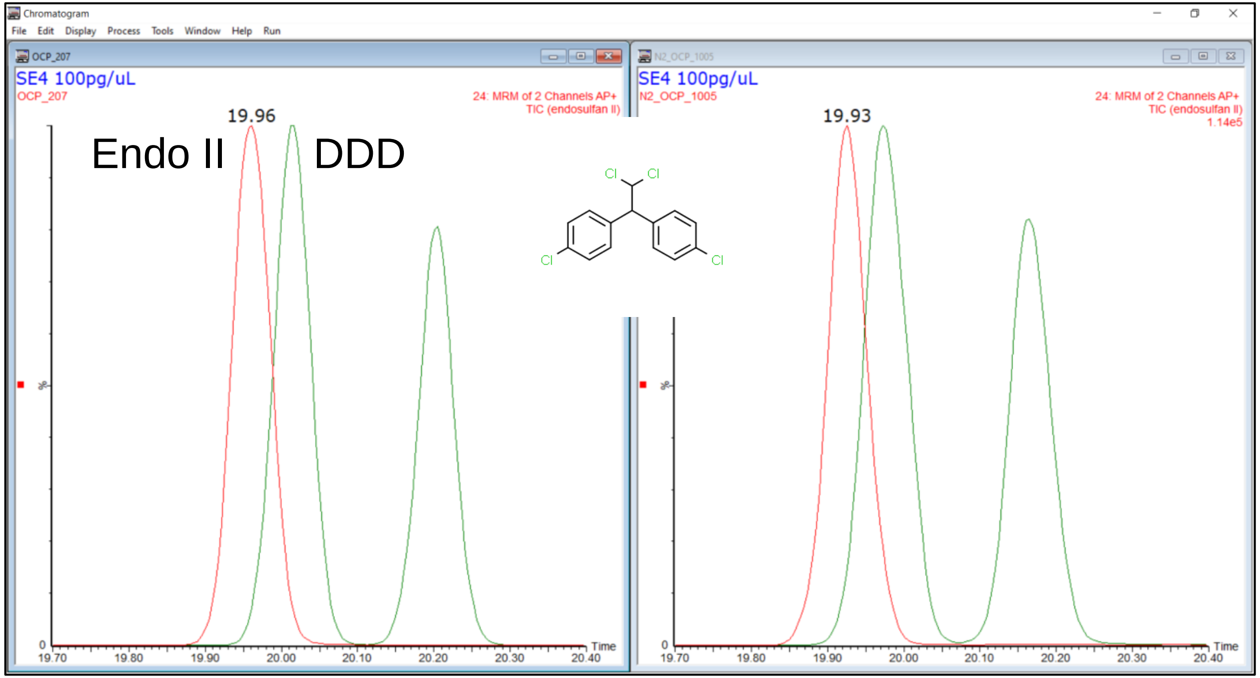
Translating Methods from He to N_2 Carrier Gas

- Define gas type
- Scale column dimensions
  - Keep phase ratio constant
- Outlet Pressure for APGC (Atm) or EI (Vacuum)

- Link to EZGC Method Translator, (Restek)

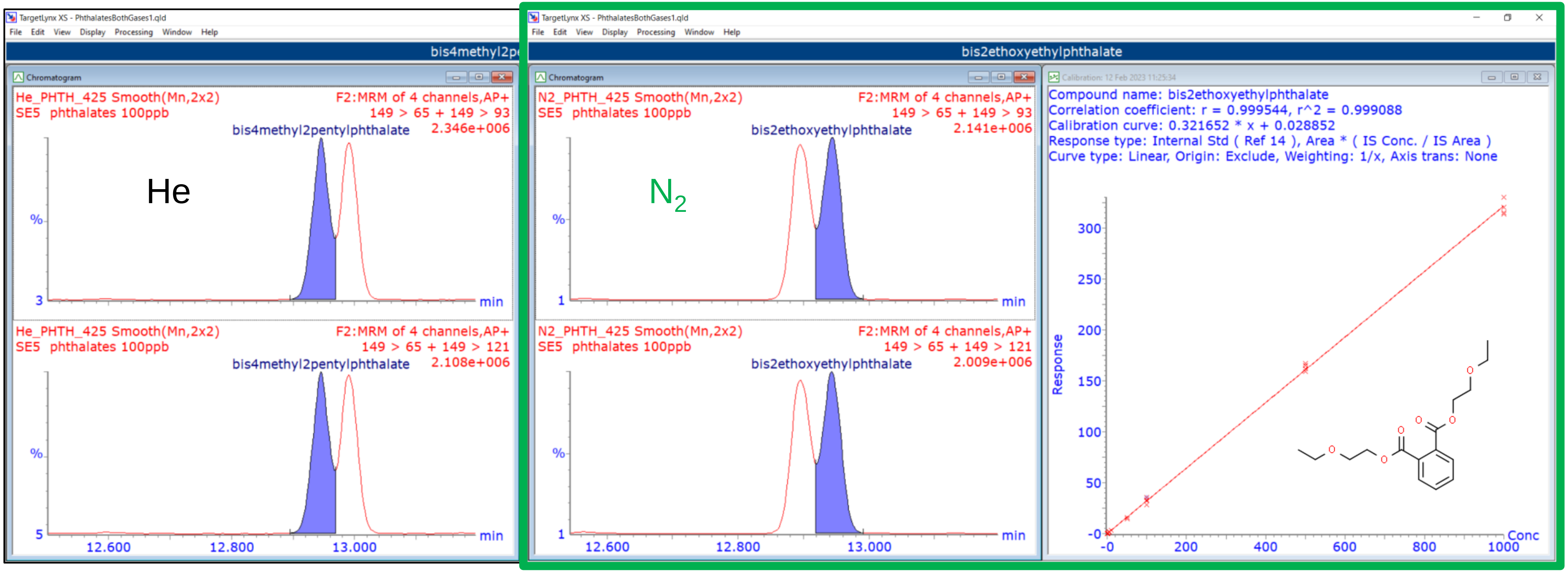
OCPs: N_2 v He, Scaled Column

- **N_2 40m** x .18 x .18 Rxi-5Sil MS
- **He 60m** x .25 x .25 Rxi-5Sil MS
- 50 peaks (39/11)
- +/- 1.1s average
- He at 1.5 mL/min
- N_2 at 0.45 mL/min



Helium Nitrogen

Phthalates: N_2 v He, Scaled Column



Rxi-5Sil MS **30 m** x 0.25 mm x 0.25 µm for **He** and **20 m** x 0.15 mm x 0.15 µm for **N_2**

Average r^2 0.996 for 16 of 17 analytes. Method includes 11 IS/Surr.

Multi-Class Semivolatiles (SVOCs)

- Single class SVOC analyses successfully translated to N_2 carrier GC-APCI

- Multi-class SVOC methods present additional challenges
  - Wider range of ionization characteristics
  - Different, specific requirements for long term stability assessment

- With the change to N_2 carrier, evaluation of N_2 collision gas in place of Ar was performed

GC/MS Conditions

MS	Xevo™ TQ-Absolute
Source Type	APGC™, dry source
Source Temp	150°C
Transfer Line Temp	320°C
Corona Current	2.0 µA
Auxiliary Gas	200 L/hr
Cone Gas	270 L/hr
Make Up Gas	350 mL/min
CID Gas	**N_2, 0.4 mL/min**

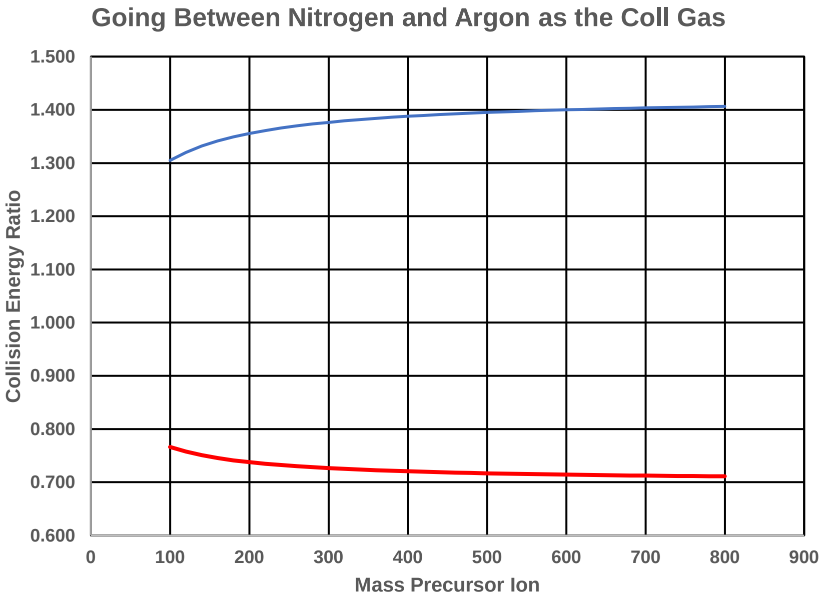
GC	Agilent 8890
Column	Rxi®-SVOCms **20m x 0.15 x 0.15**
Outlet	Atm
Injection	SSL, 310°C, Split 10:1, 4 mm pkd liner
Carrier Gas	**N_2, 0.25 mL/min**
Temp Program	40°C 1min, to 120°C at 15°C/min, to 335°C at 30°C/min hold 7 min. 20.5min run time

Translating From Ar CID Gas to N_2

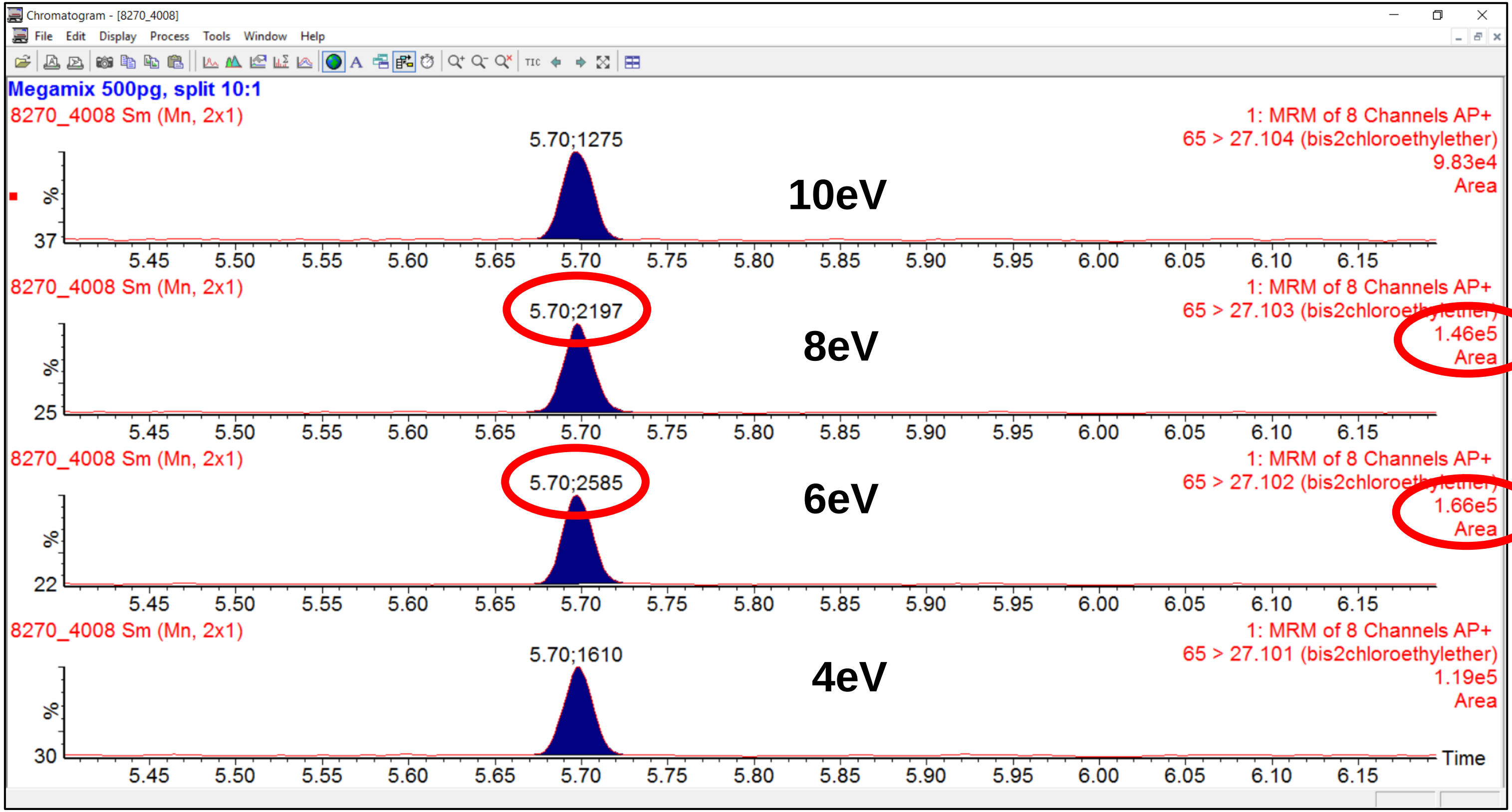
- Dry source APGC method **developed on TQ 2** and **transferred to TQ 1**

- **TQ 2,** N_2 carrier gas and **N_2 CID gas**
- **TQ 1,** He carrier gas and **Ar CID gas**
- Identical MRM Transitions

- **TQ 2 N_2 CEs modified for Ar on TQ 1**
  - Based on guidance in graph



Estimated v. Optimized, N_2 CID to Ar CID Gas

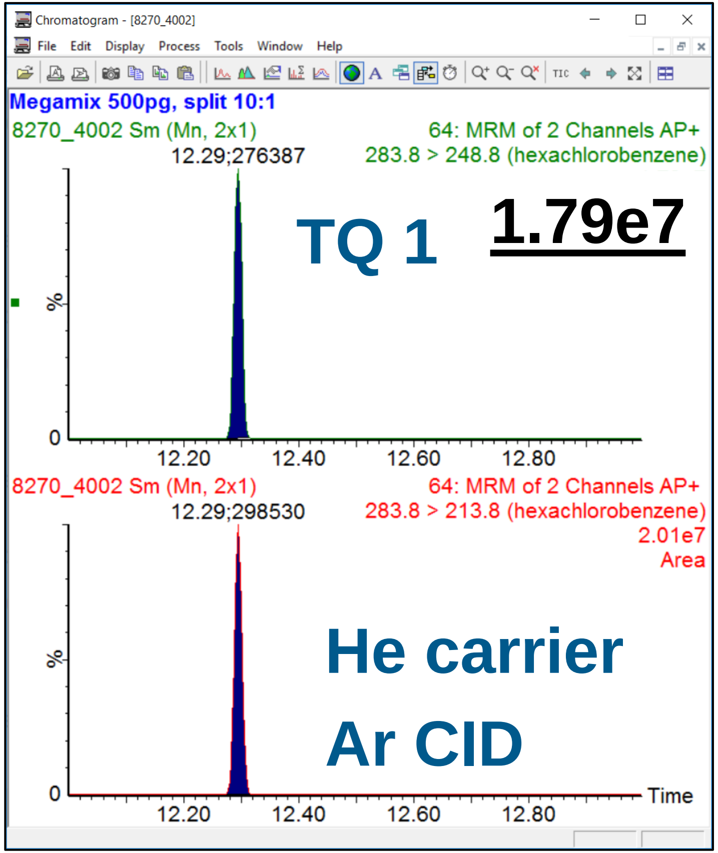


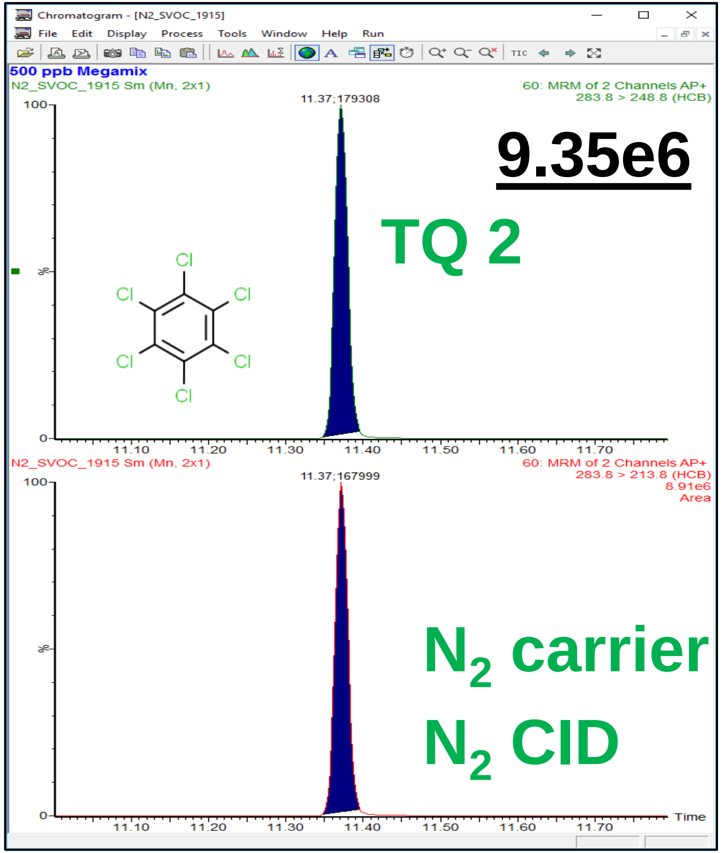
CE estimate from graph = 8eV

Optimized CE = 7eV

Multiple analytes classes showed similar agreement

Comparison Between Different Configurations



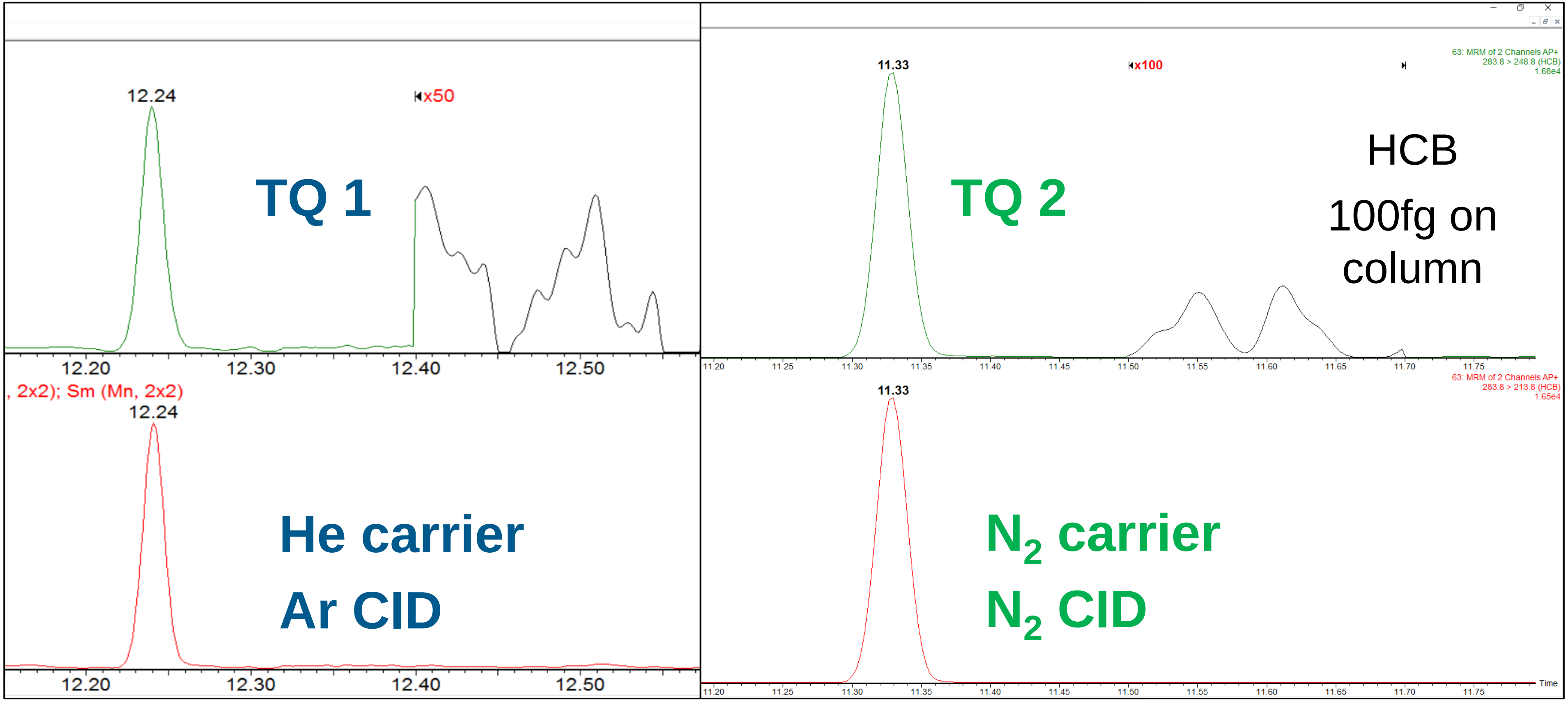


76 analytes in 8270 Megamix were within +/- 2X

500pg in-vial

50pg on column

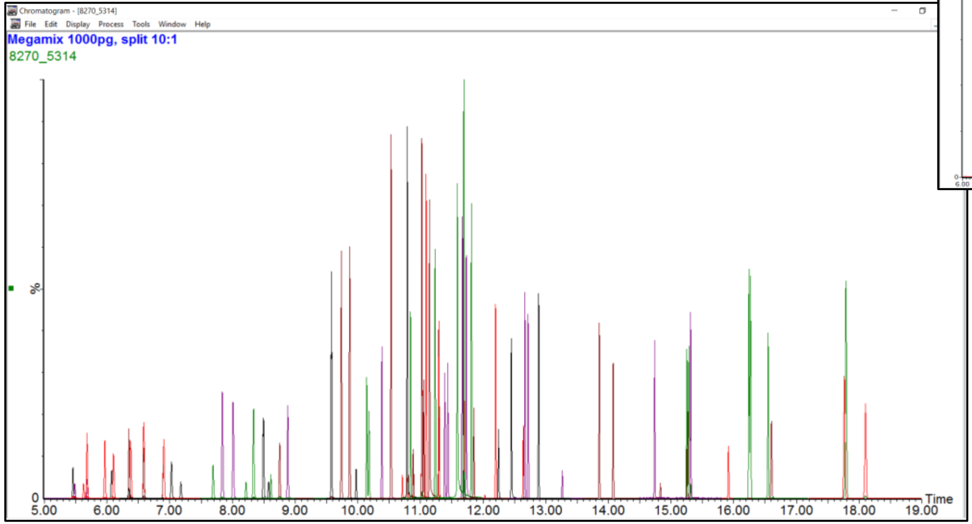
Comparison Between Different Configurations

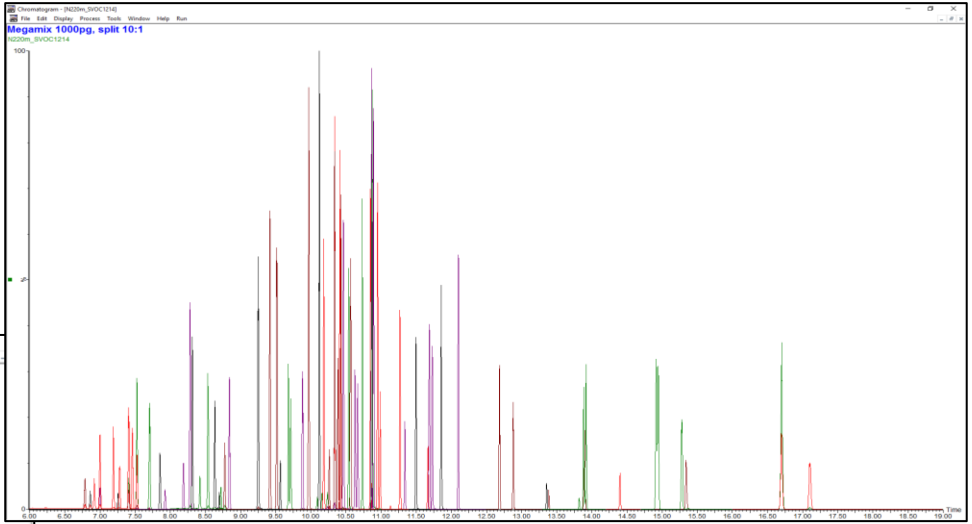


Comparison Between Different Configurations

He carrier

Ar CID

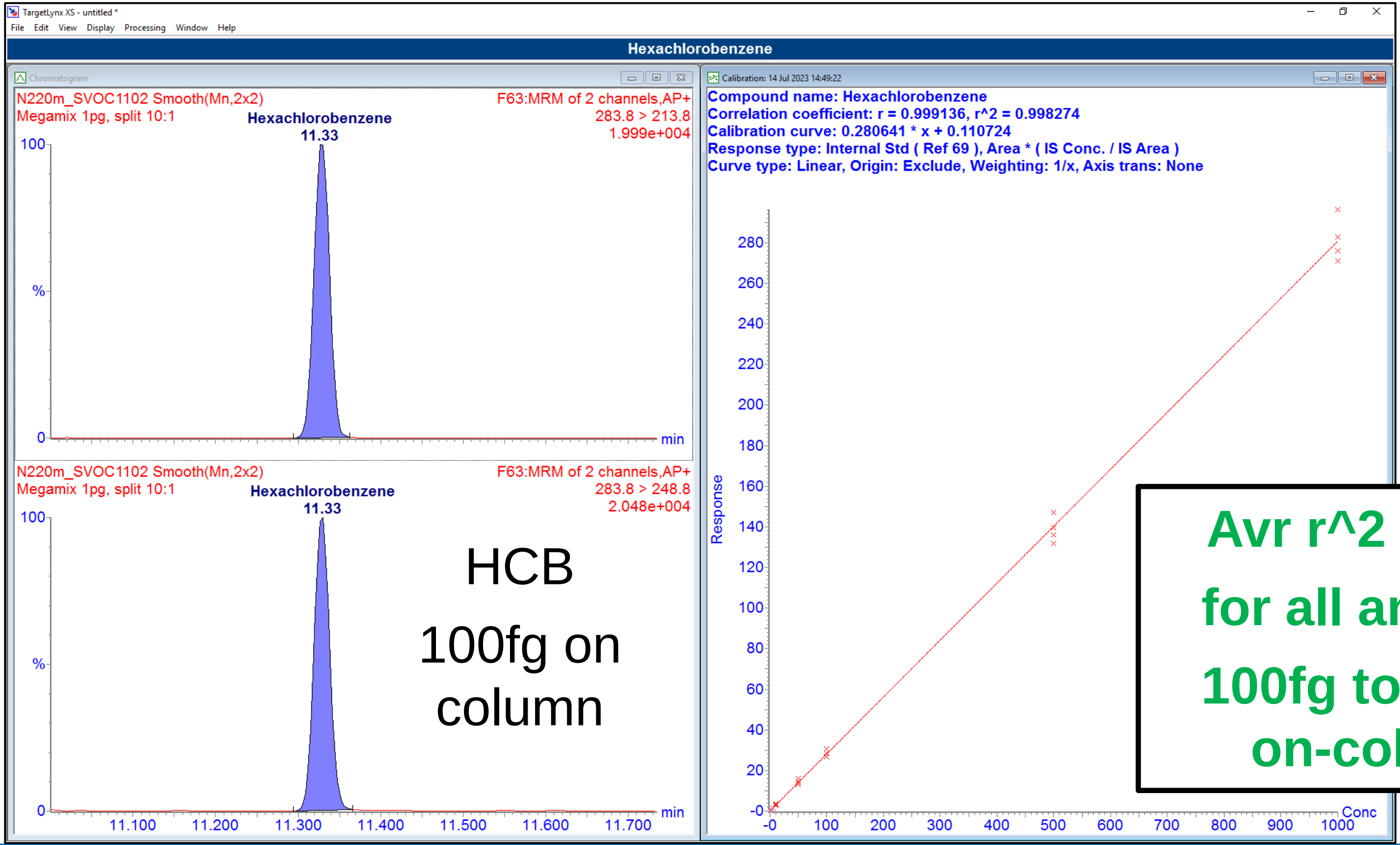




N_2 carrier

N_2 CID

All N_2 System Quantitation, TQ2



HCB

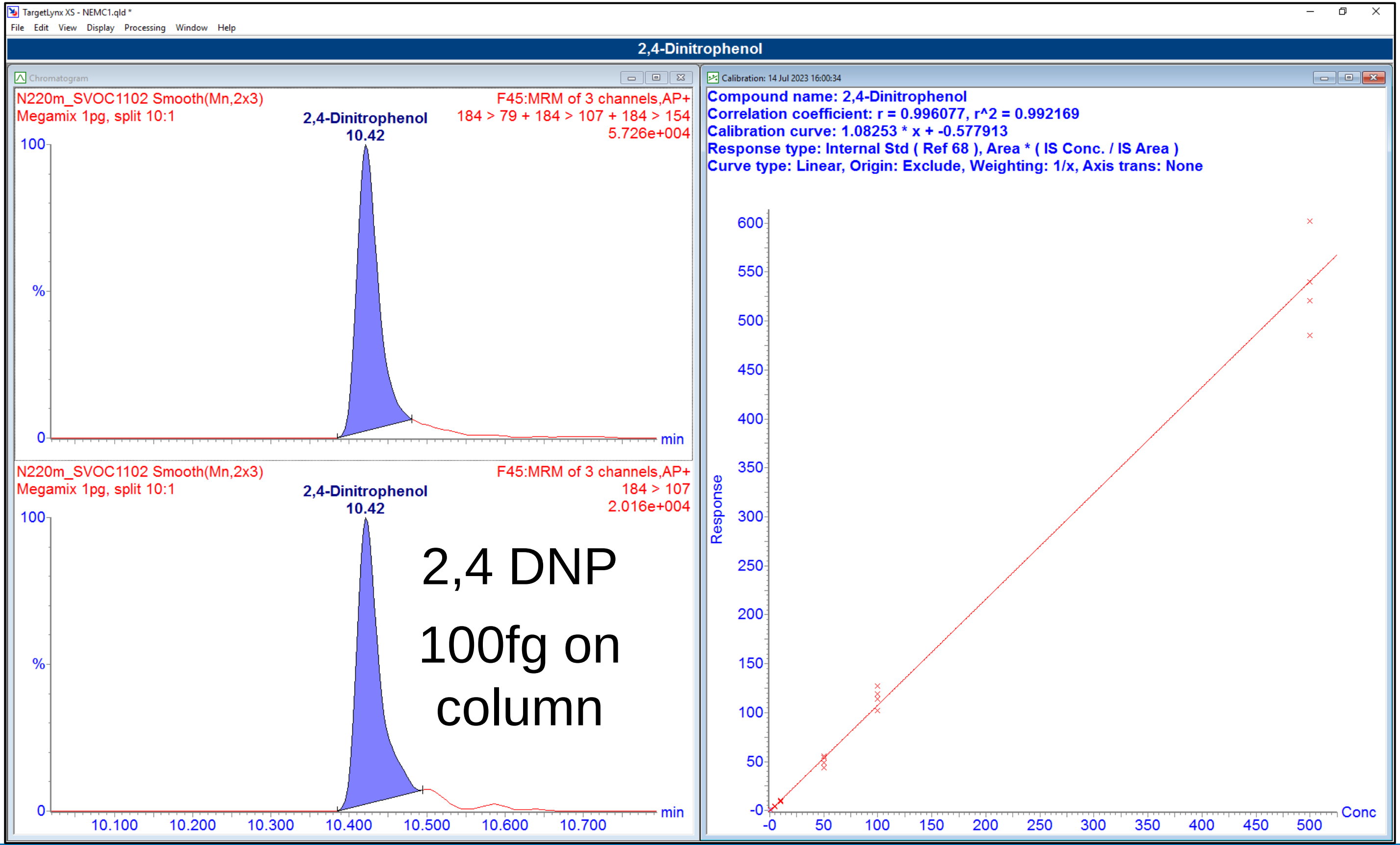
100fg on column

Avr r^2 >0.992

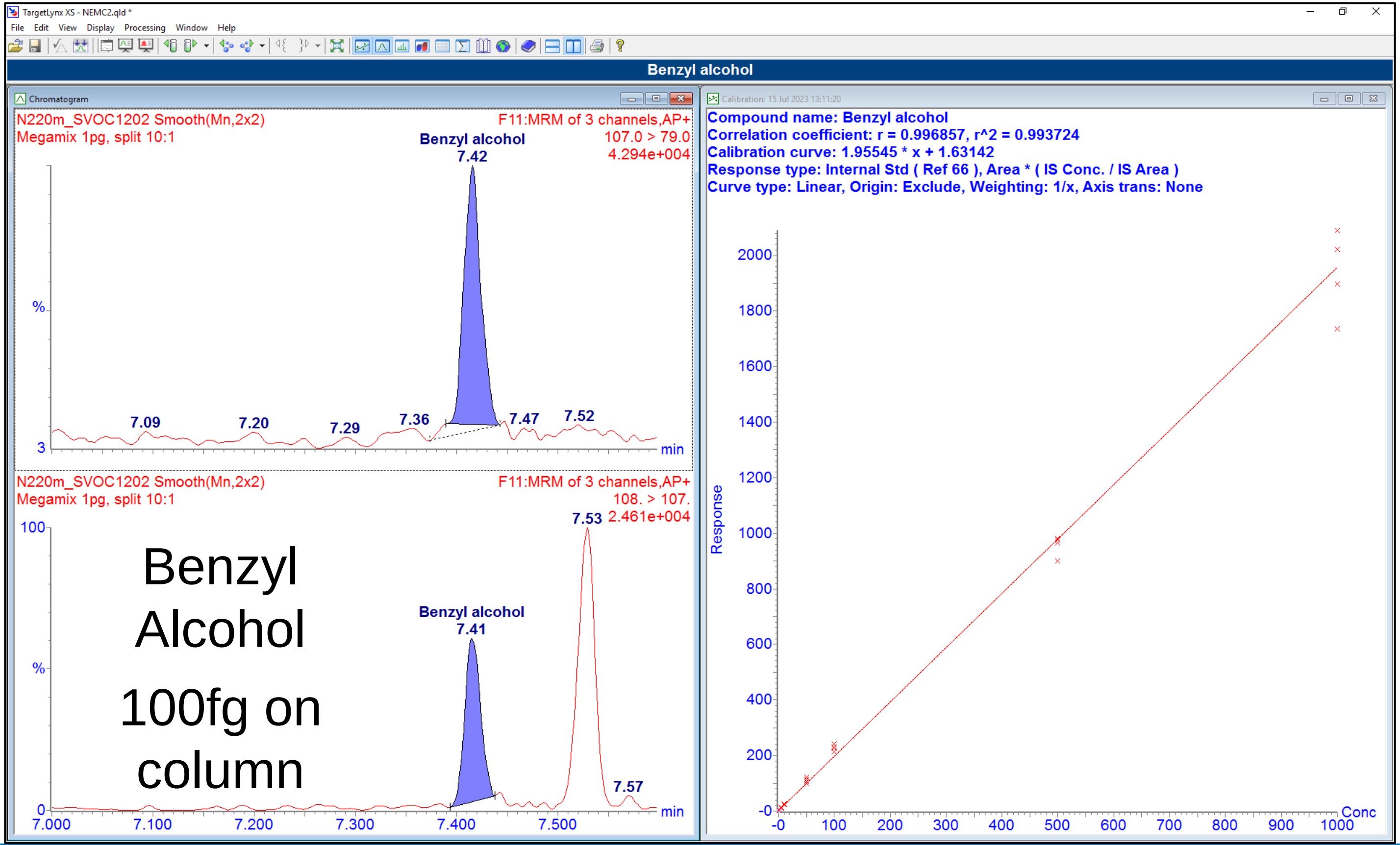
for all analytes

100fg to 100pg on-column

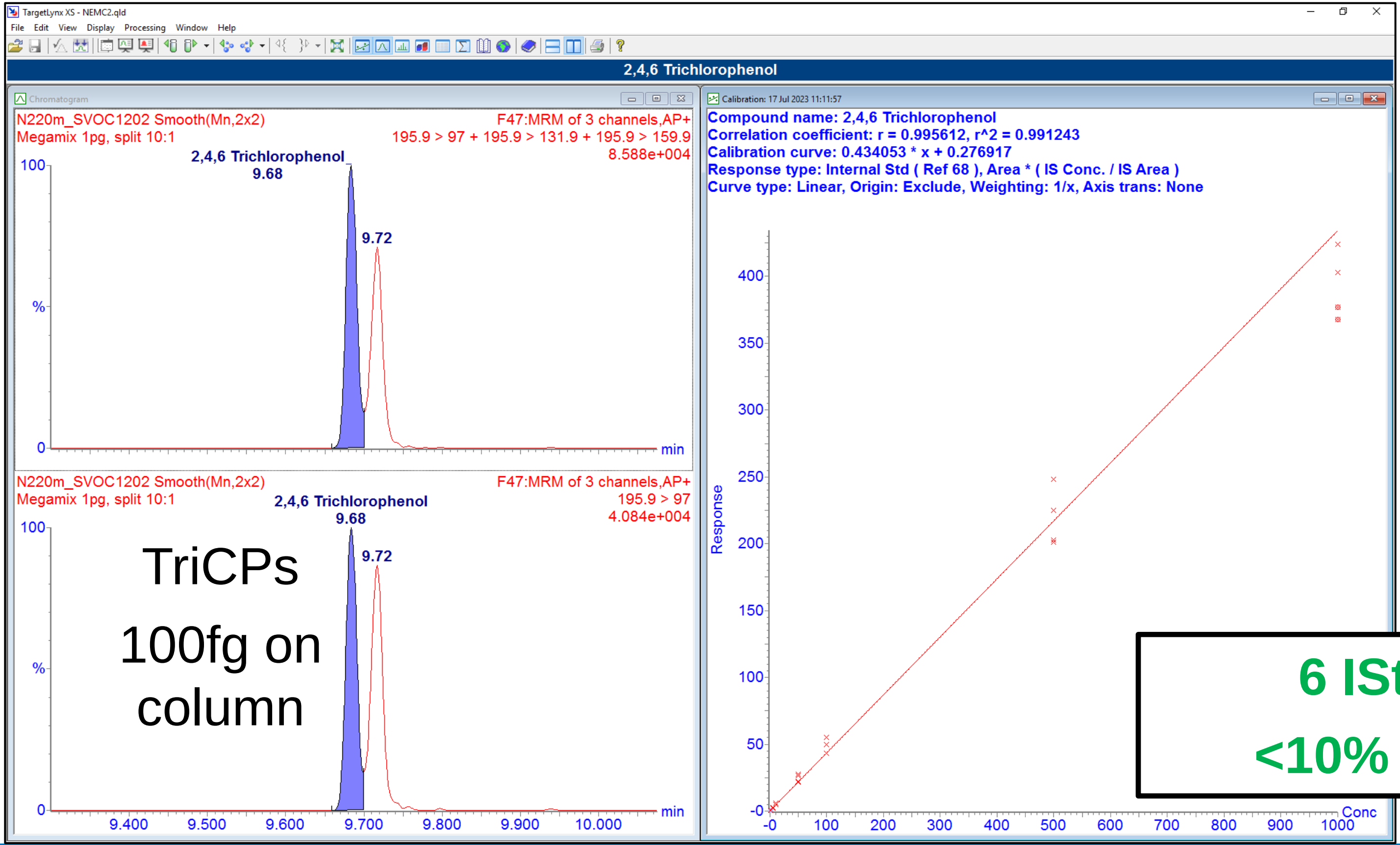
All N_2 System Quantitation, TQ2



All N_2 System Quantitation, TQ2



All N_2 System Quantitation, TQ2

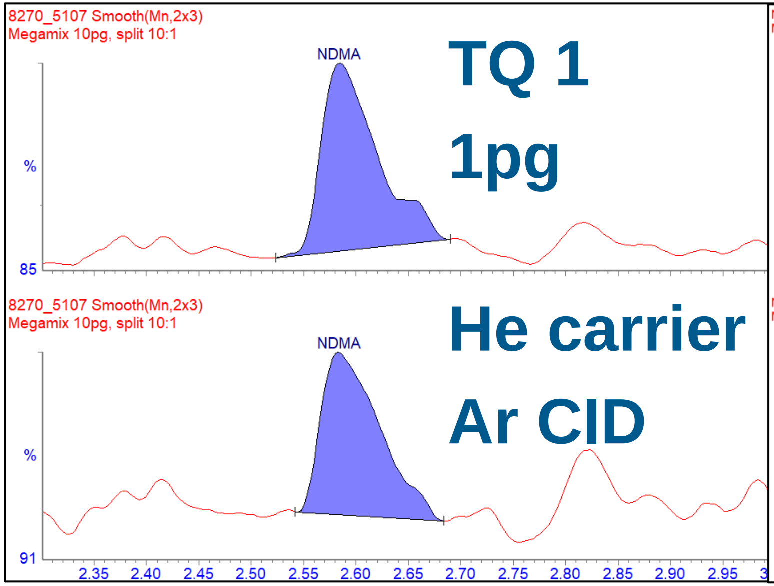


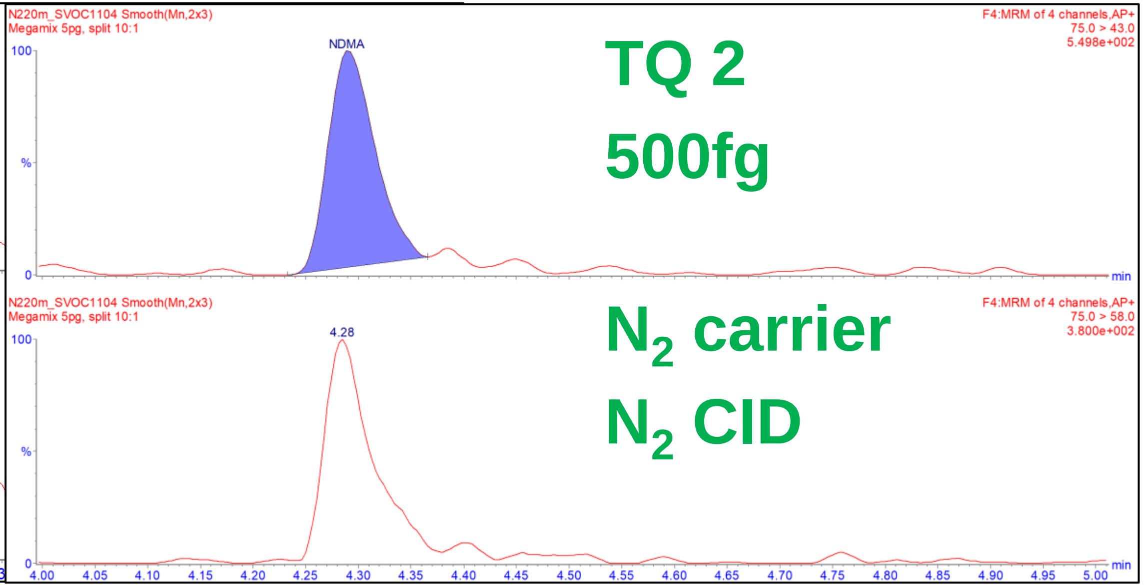
6 IStds

<10% RSD

All N2 System, TQ2 v. He/Ar System TQ1

- Coefficient of determination > 0.992 v. 0.994
- %RSD IStds <10% v < 7%
- 65 of 67 analytes gave same LOQ on both





Conclusions

- GC-APCI enables translation of SVOC methods to N_2 carrier gas without loss of separation or sensitivity
- N_2 CID gas, in place of Ar, allows a GC/MS/MS system to be operated using a single gas supply
- Dry source (charge exchange) ionization mode demonstrated compatibility with multi-class SVOCs

- However…
- N_2 carrier gas not allowed for EPA SVOC methods (8270, 525, 1625)
- Ability to meet long term stability requirements CCV of some methods requires further evaluation

Acknowledgements

- Quebec Laboratory for Environmental Testing (QLET)
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Thank You for Your Attention. Questions?

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