Waters™

Gas Chromatography Atmospheric Pressure Chemical Ionization (GC-APCI) GC/MS/MS of Semivolatiles

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THE NELAC INSTITUTE

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Overview

- Semivolatiles Background
- Source Description and Ionization
- Semivolatiles Performance Data
  - Sensitivity
  - Linearity
  - Reproducibility
- Adapting to Nitrogen Carrier Gas
- Conclusions

Semivolatile Organic Compounds (SVOCs)

- Volatile compound categories
  - SVOC, VOC, VVOC (gases)
- GC/MS amenable
- SVOC = higher bp (100 - 600°C)
- Broad characterization of samples
- Long analyte lists with multiple compound classes
- Common, high volume analysis

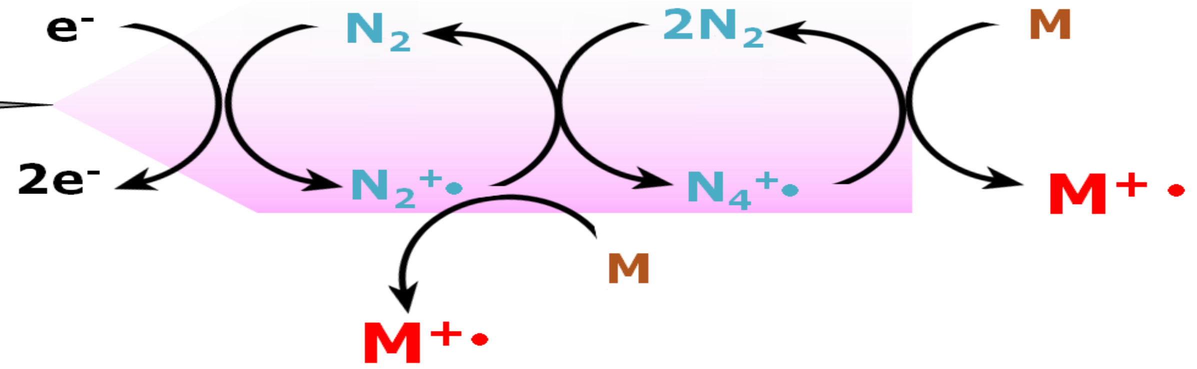
GC-APCI MS/MS Conditions

TQ MS	
Source Type	**GC-APCI, dual CI mode**
Source Temp	150°C
Transfer Line Temp	320°C
Corona Current	2.0 µA
Auxiliary Gas	200 L/hr
Cone Gas	240 L/hr
Make Up Gas	350 mL/min
Detector Gain	0.10

GC	
Column	5% phenyl 30 x 0.25 x 0.25
Column Outlet	14 psi
Injection	SSL at 300°C, **Split 100:1** 4 mm id pkd liner
Carrier Gas	Helium 2.0 mL/min
Temperature Program	40°C 1min, to 120°C at 10°C/min, to 320°C at 25°C/min hold 3 min. 20min run time

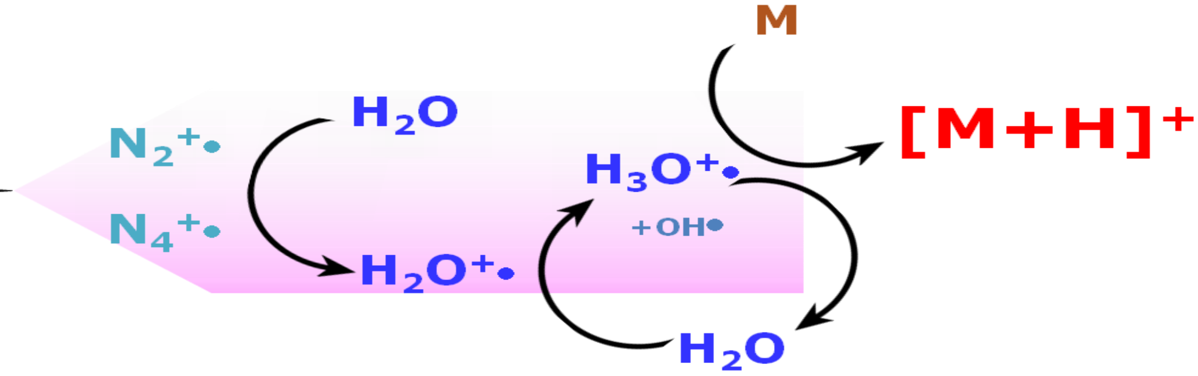
Chemical Ionization Types

Charge Transfer



- N_2 = reagent
- IE = 15.6 eV

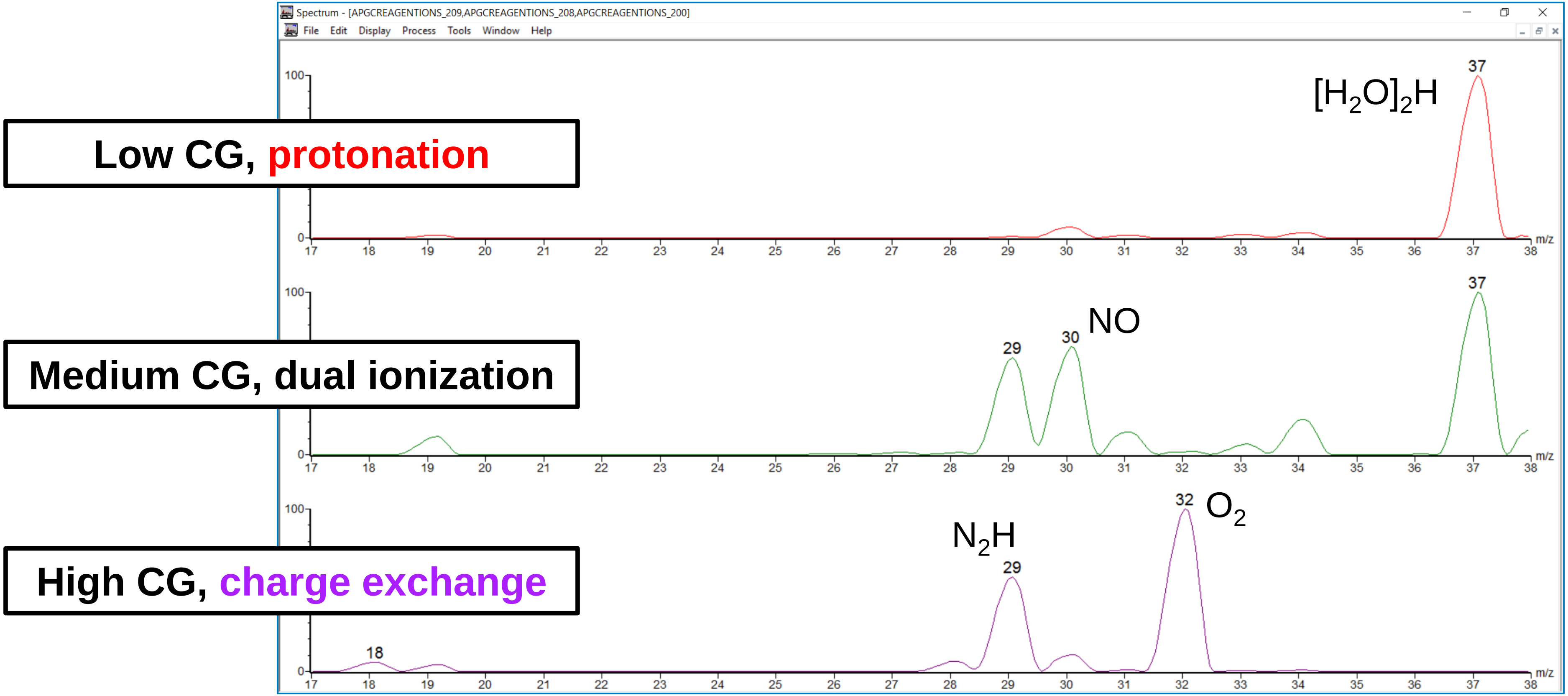
Protonation



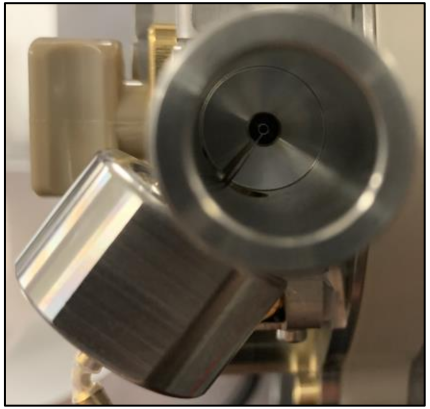
- H_2O = reagent
- PA = 691 kJ/mol

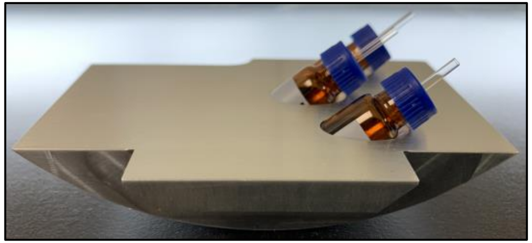
Munson. “CIMS: ten years later." *Anal Chem* (1977) Gross. *Mass spectrometry.* Springer (2006)

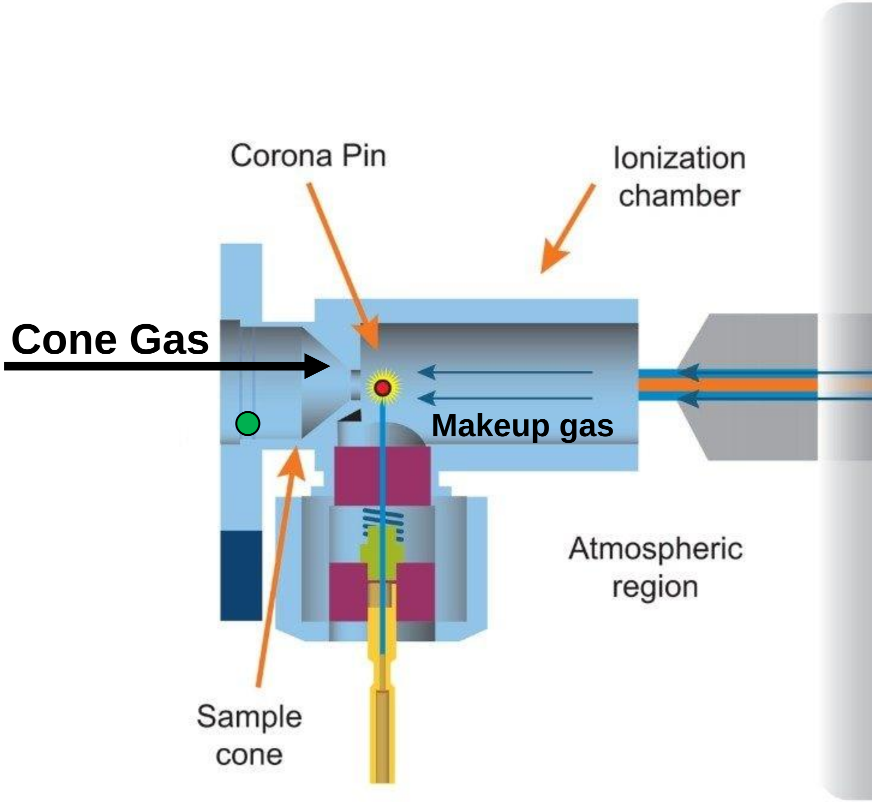
Reagent Ions, Varied Cone Gas



GC-APCI Source: Cone Gas

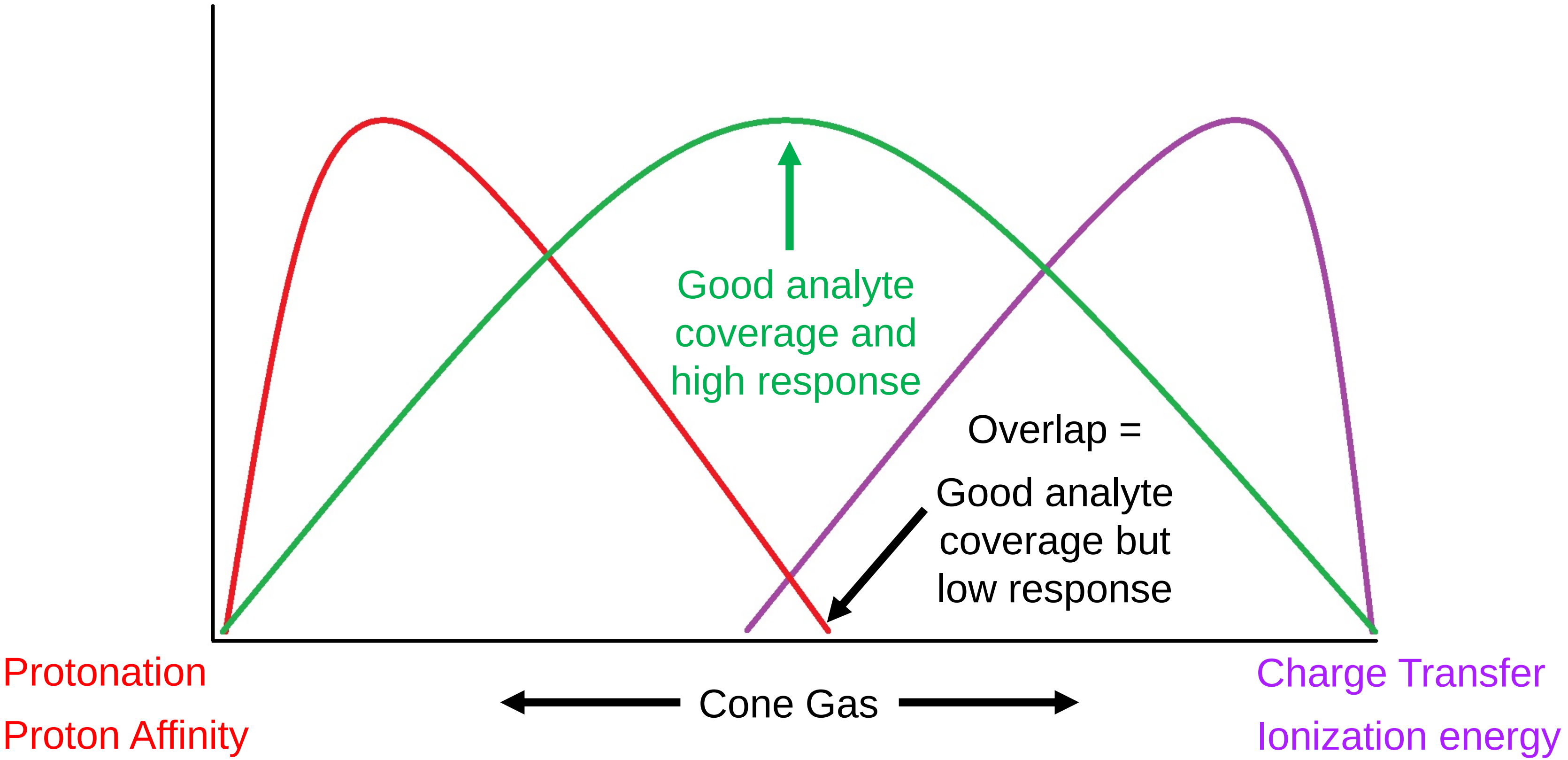




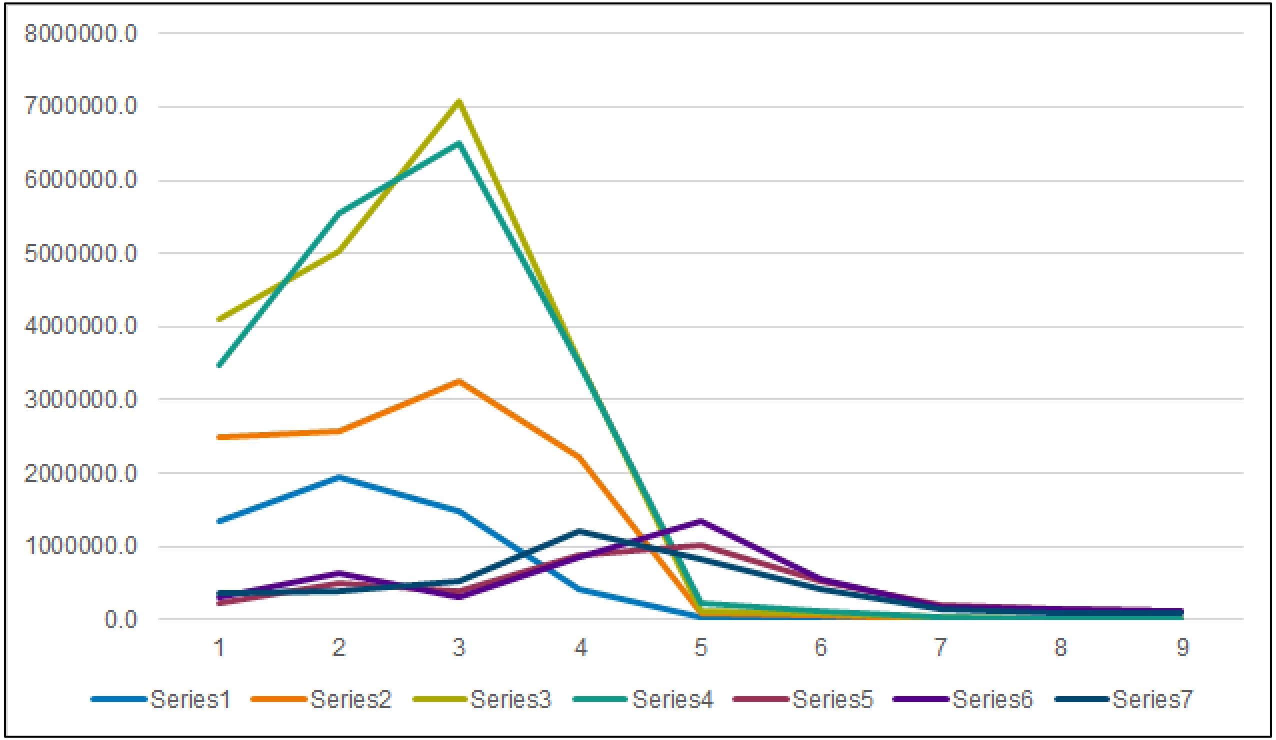


Horning, Analytical Chemistry 45.6 (1973)
McEwen, https://doi.org/10.1016/j.jasms.2005.07.005

Response Characteristics



Response Characteristics



Protonation

Proton Affinity

Cone Gas

Charge Transfer

Ionization energy

MRM Transition Database

Quanpedia - SVOC

Compound:

Compound	CAS	Mass	Formula
1,2 dinitrobenzene	528-29-0	168.0171	C6H4N2O4
1,2,4 trichlorobenzene	120-82-1	179.9300	C6H3Cl3
1,2-dichlorobenzene	95-50-1	145.9690	C6H4Cl2
1,3 dinitrobenzene	99-65-0	168.0171	C6H4N2O4
1,3-dichlorobenzene	541-73-1	145.9690	C6H4Cl2
1,4 DCB-d4	3855-82-1	149.9941	C6D4Cl2
1,4 dintrobenzene	100-25-4	168.0171	C6H4N2O4
1,4-dichlorobenzene	106-46-7	145.9690	C6H4Cl2
1-methylnaphthalene	90-12-0	142.0783	C11H10
2 chloronaphthalene	91-58-7	162.0236	C10H7Cl
2 methylphenol	95-48-7	108.0575	C7H8O

Quanpedia - SVOC

Ion Information

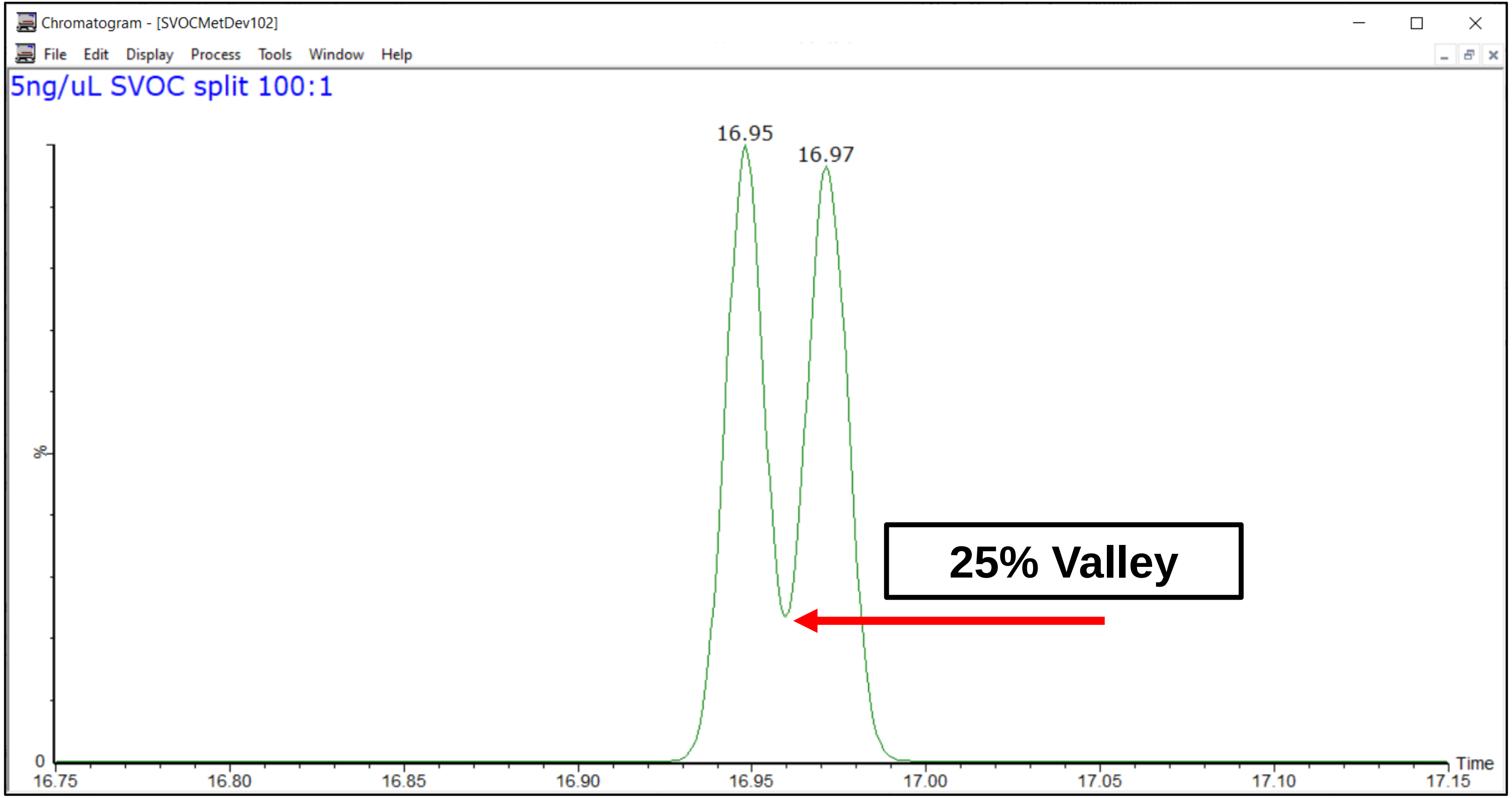
Enter the MS acquisition information for this compound.
Spectra and ion details can be entered for different ion modes.

Ion mode: API+ Compound name: 1,2 dinitrobenzene

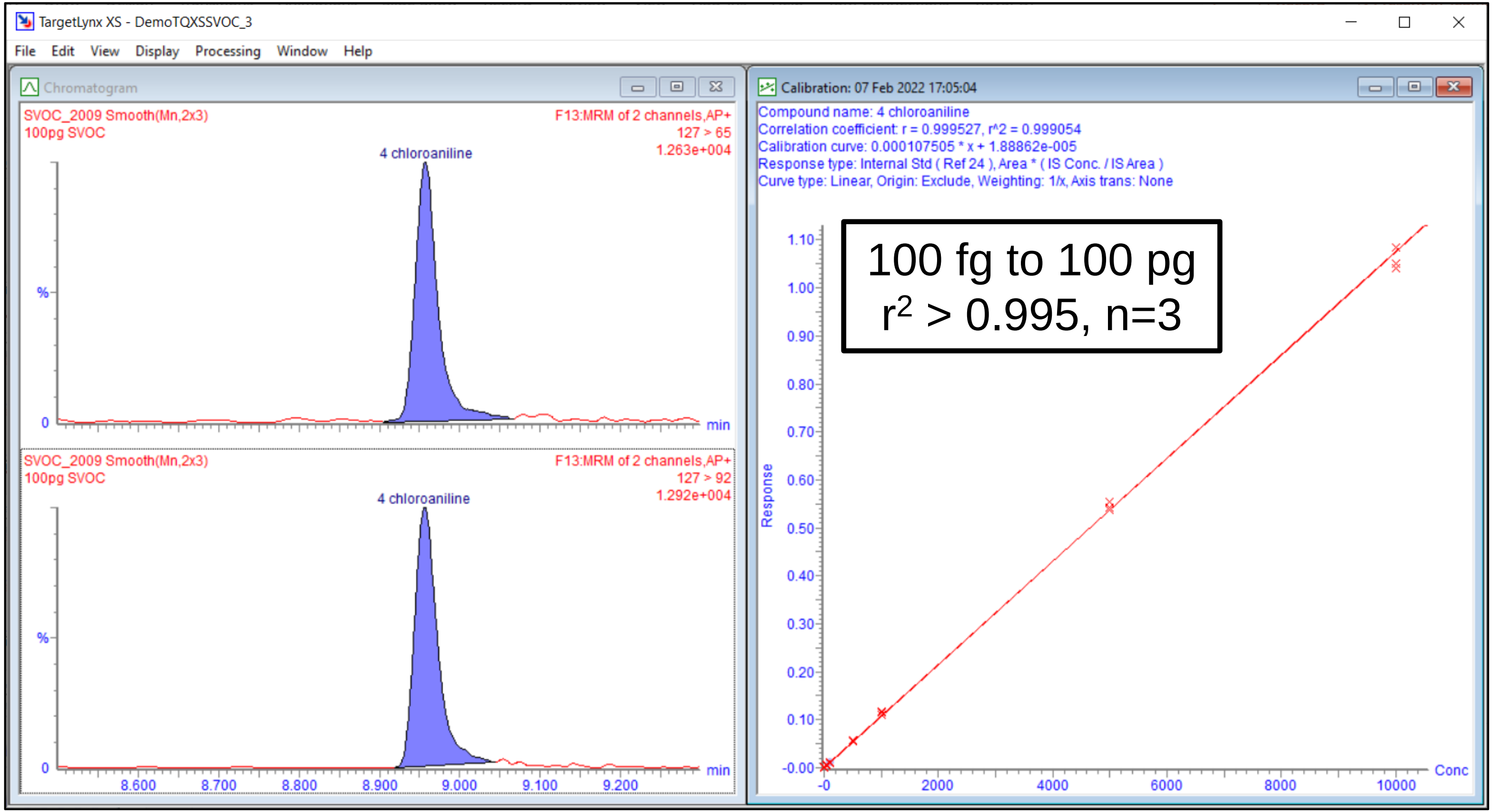
	Precursor Mass (Da)	Product mass (Da)	Cone voltage (V)	Collision energy (V)	Spectrum
First ion:	169.05	75.05	30	20	
Second ion:	169.05	92.05	30	17	
Third ion:	169.05	152.05	30	12	
Fourth ion:					
Fifth ion:					

☐ Use Soft Transmissio

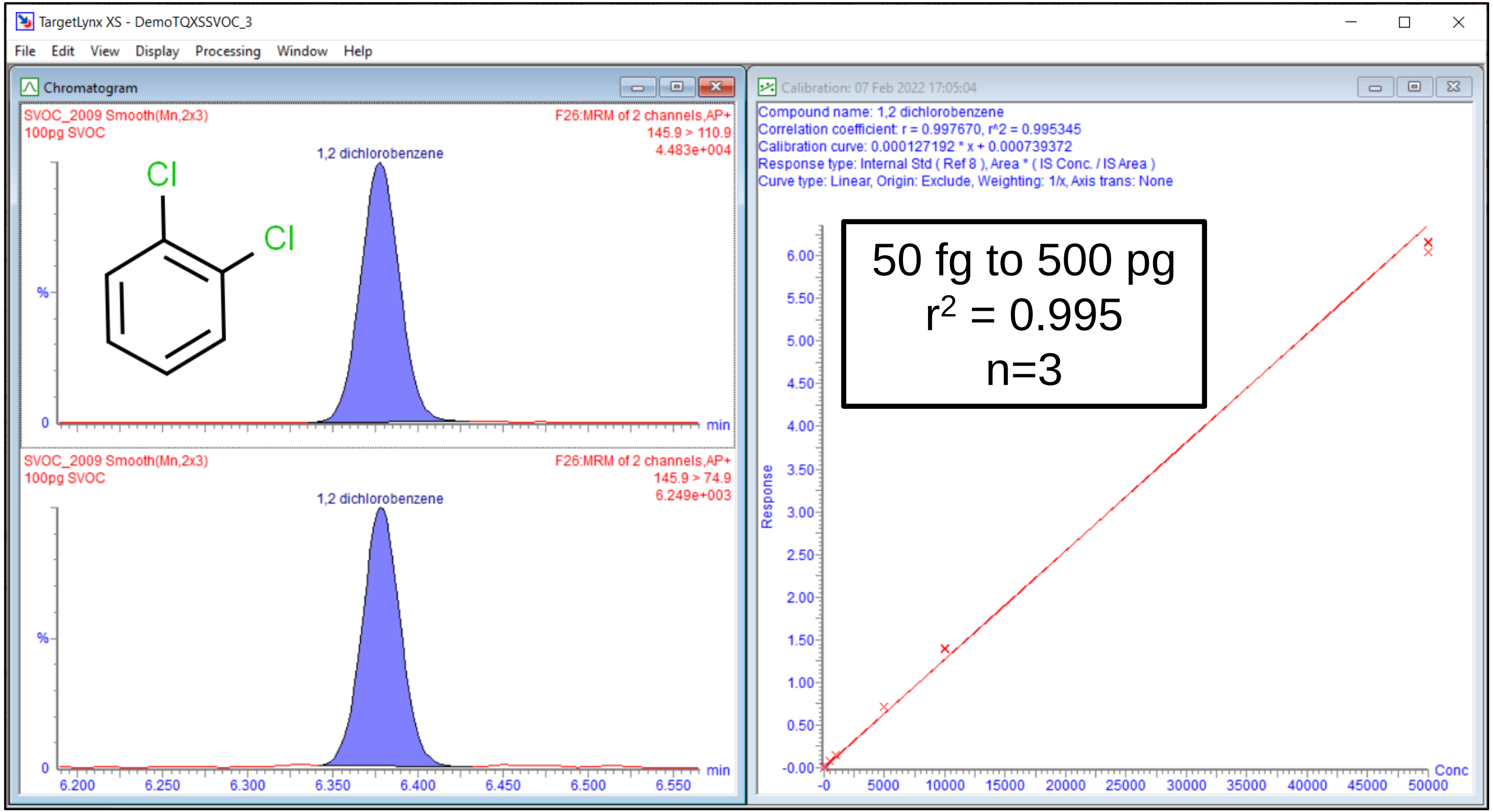
Separation of Isomers
PAHS: benzo[b]fluoranthene and benzo[k]fluoranthene



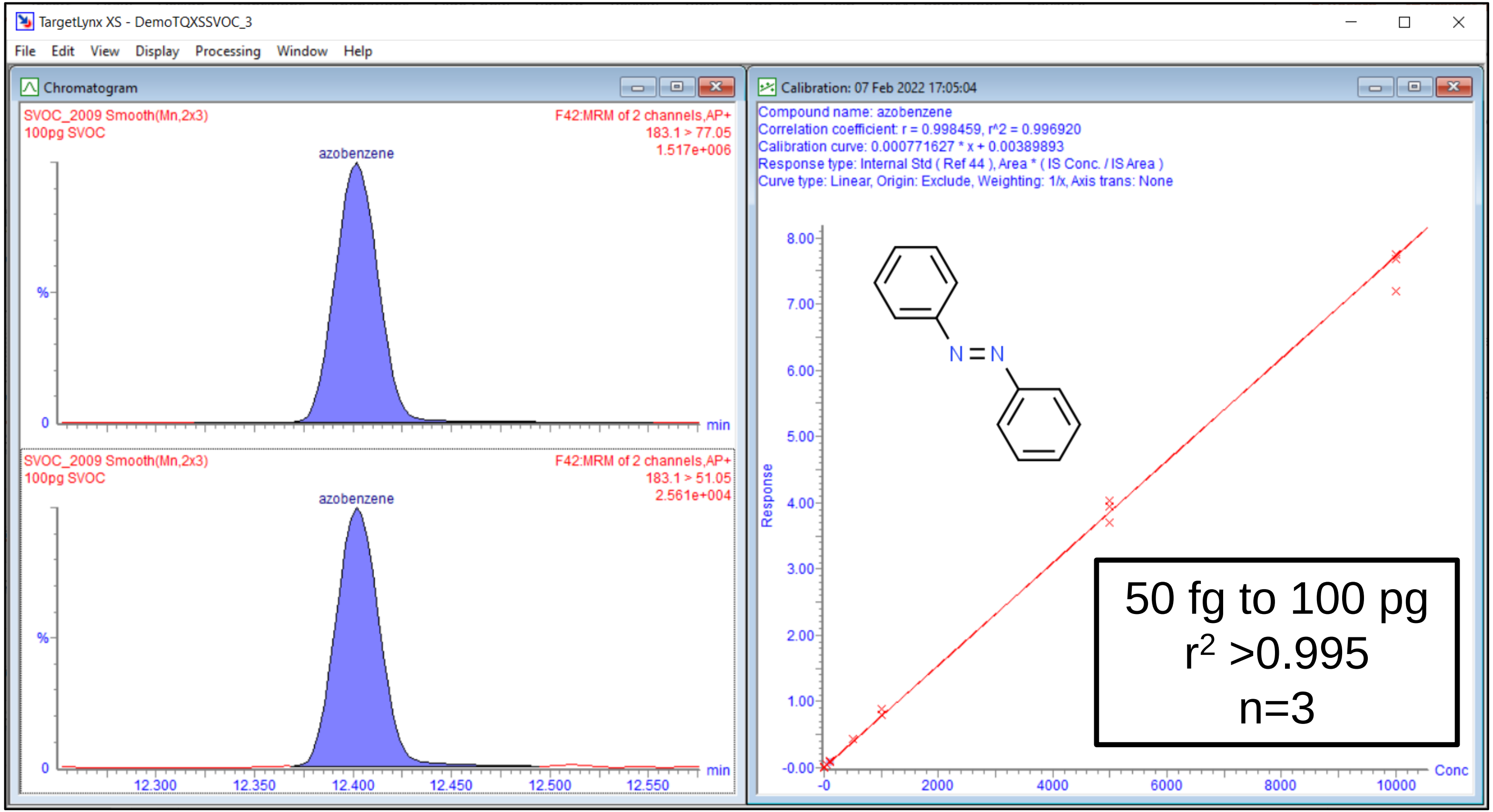
4-Chloroaniline, Charge Transfer Example



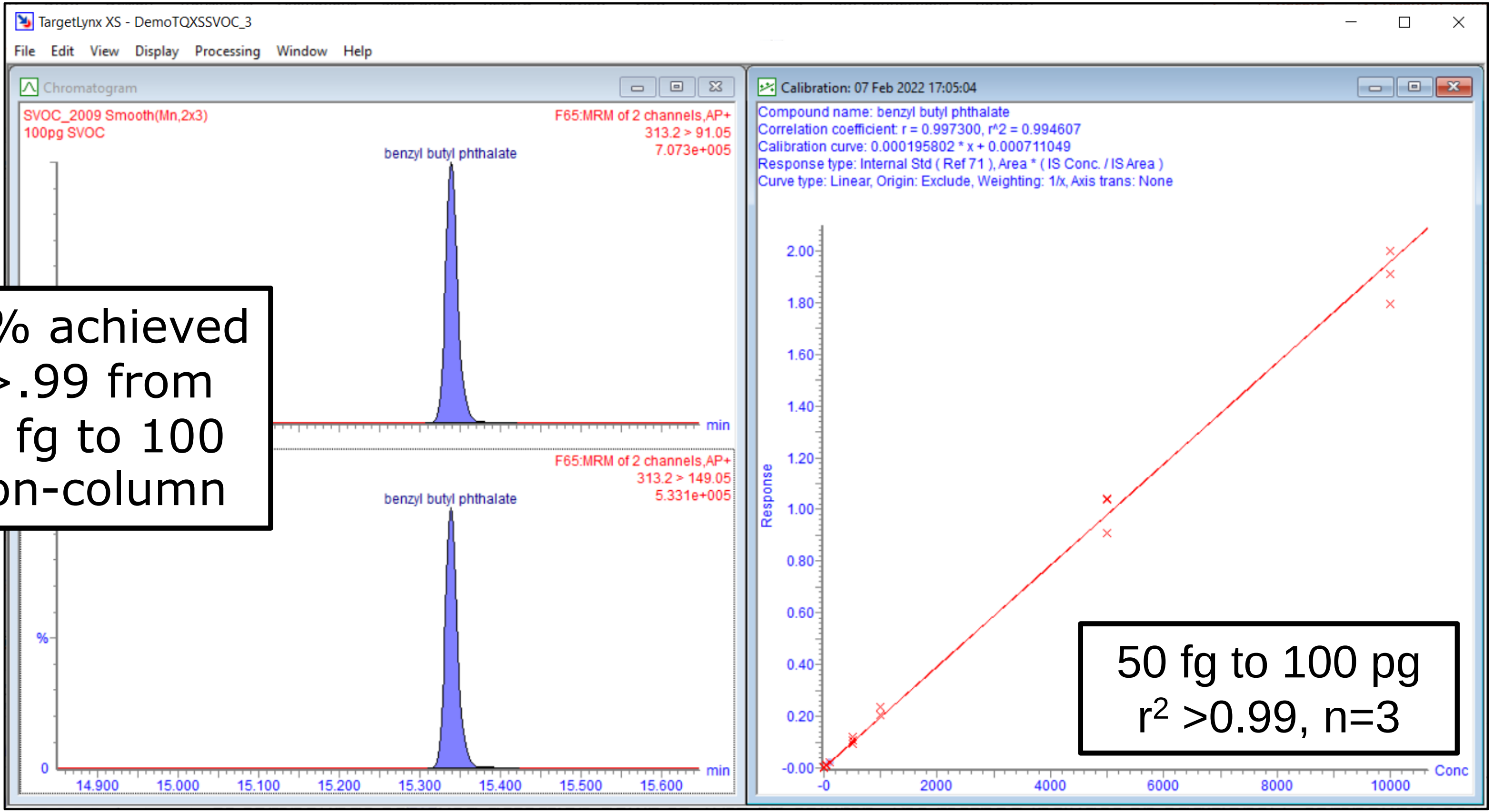
1,2 Dichlorobenzene, Charge Transfer Example



Azobenzene, Protonation Example



Benzyl Butyl Phthalate, Protonation Example

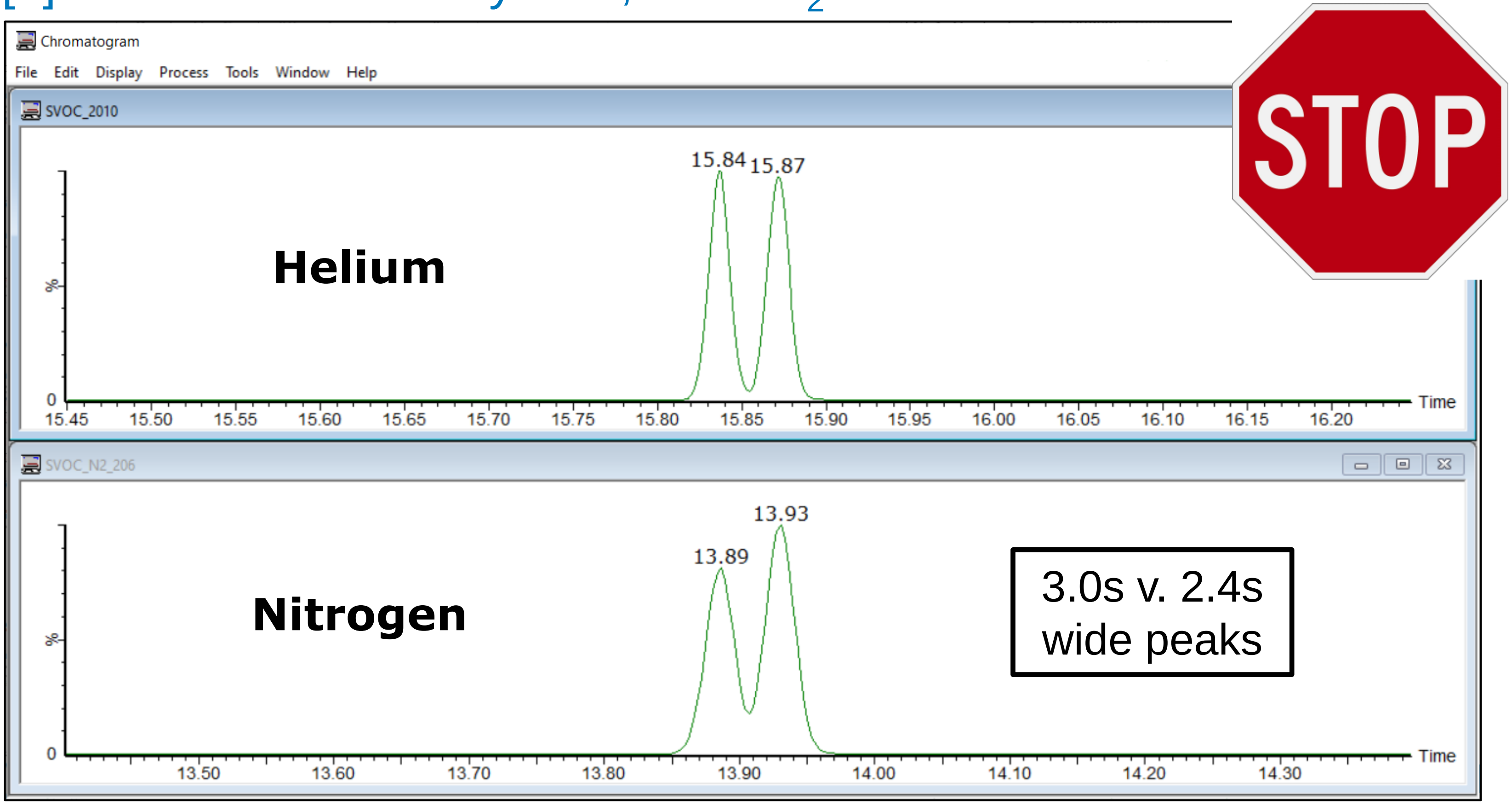


>85% achieved r^2 >.99 from 100 fg to 100 pg on-column

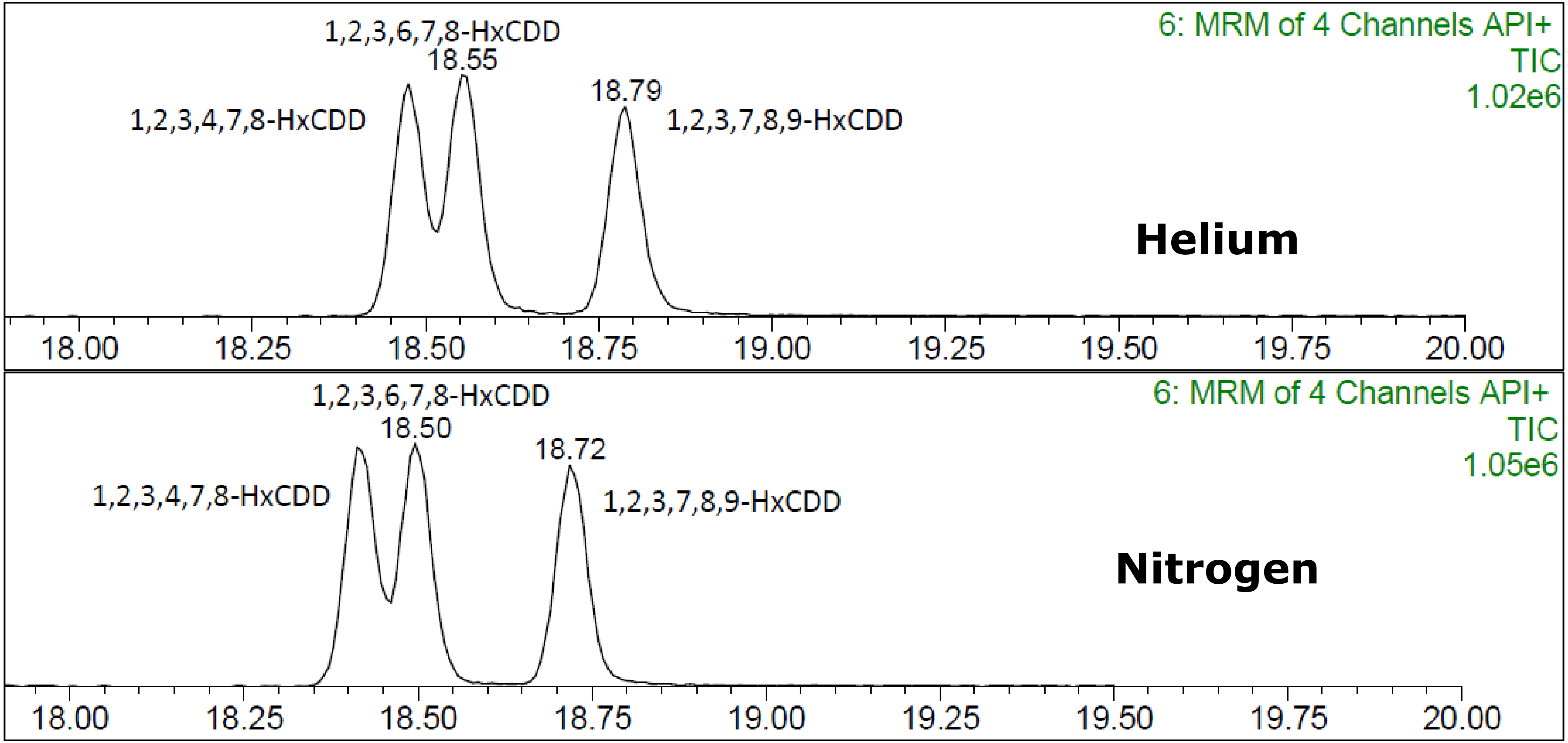
50 fg to 100 pg r^2 >0.99, n=3

Perylene-d12 Ionization Stability Monitoring

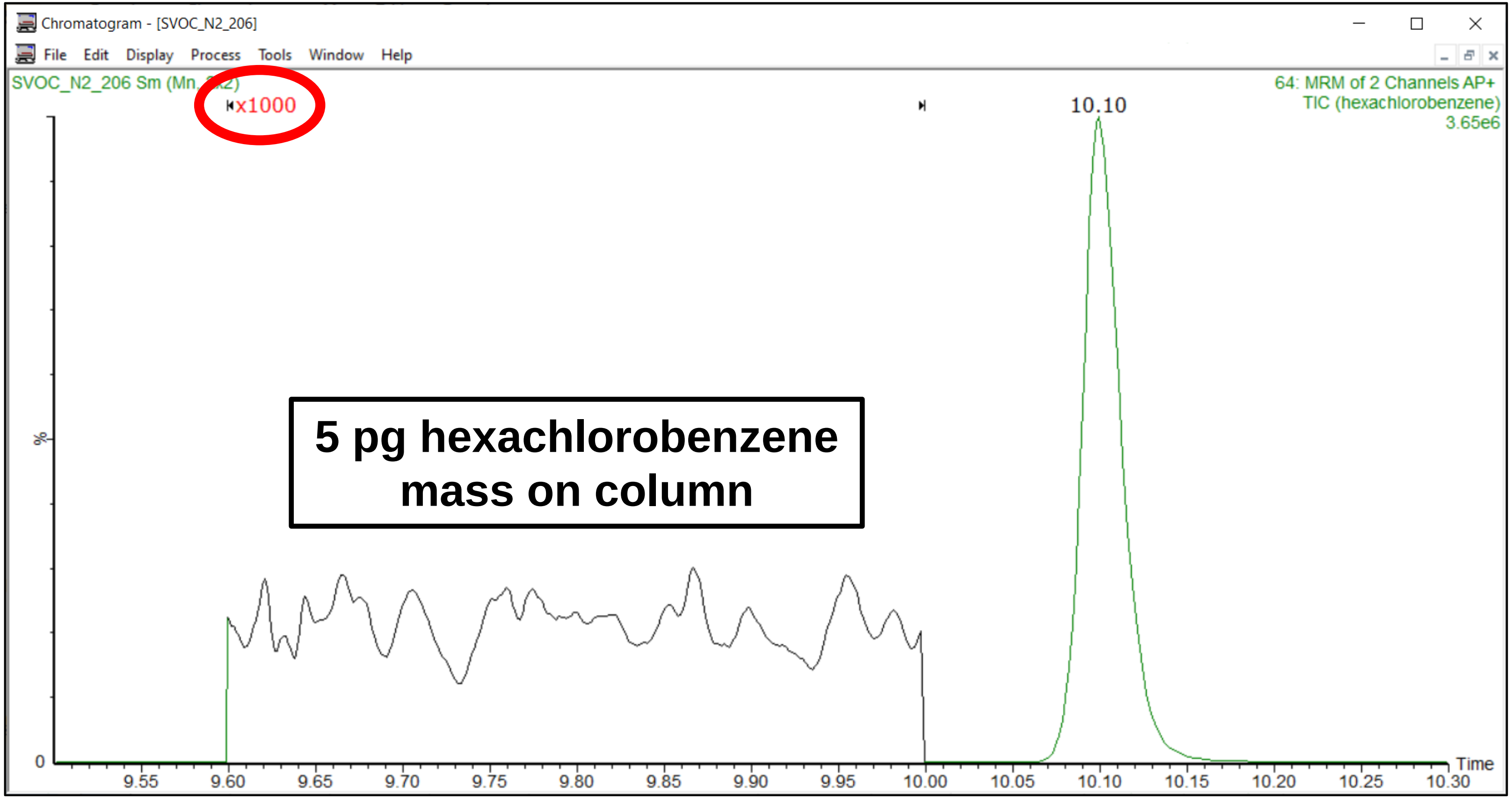
Separation of Isomers
Benz[a]anthracene and Chrysene, He v. N_2 Carrier



Scaled Columns Dioxins



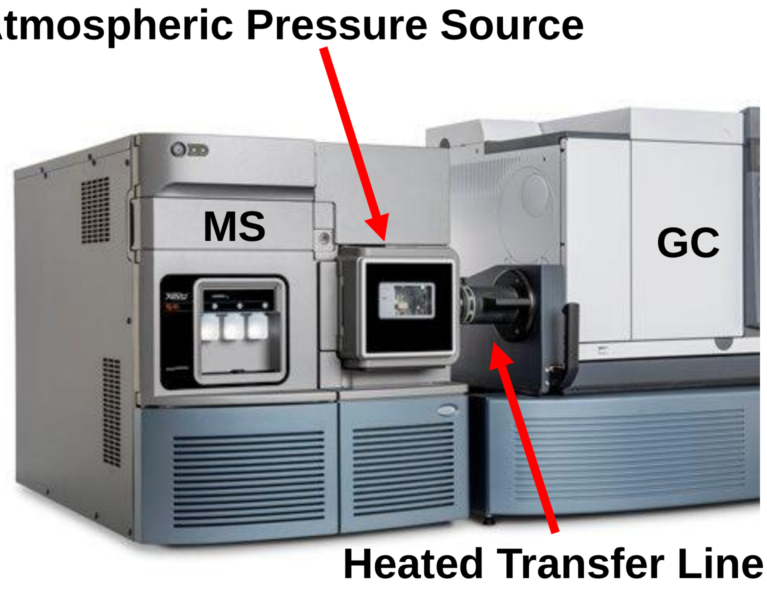
Sensitivity Assessment N2 Carrier Gas, Pesticide



Conclusions

- Analytes compatible with both charge exchange and protonation exhibit good sensitivity, linearity and reproducibility using dual chemical ionization mode
- The two ionization modes maintain a broad and stable fixed performance ratio for extended periods allowing concurrent analysis of multiple classes of SVOCs in a single injection
- The method is adaptable to nitrogen carrier gas without loss of sensitivity
- **Future work:** extracted samples; N2 carrier with scaled column

GC-APCI MS/MS System
APGC Xevo TQ-XS Tandem Quadrupole



MS	Xevo™ TQ-XS
Source Type	**APGC™, dual CI mode**
Source Temp	150°C
Transfer Line Temp	320°C
Corona Current	2.0 µA
Auxiliary Gas	200 L/hr
Cone Gas	240 L/hr
Make Up Gas	350 mL/min
Detector Gain	0.10

GC	Agilent 7890
Column	Rxi®-5Sil MS 30 x 0.25 x 0.25
Column Outlet	14 psi
Injection	SSL at 300°C, **Split 100:1** 4 mm id pkd liner
Carrier Gas	Helium 20 mL/min
Temperature Program	40°C 1min, to 120°C at 10°C/min, to 320°C at 25°C/min hold 3 min. 20min run time

Acknowledgements

- Rhys Jones
- Sarah Dowd
- Peter Hancock
- Janitha De-Alwis

O'Hair, Richard AJ. "**Chemical ionization** mass spectrometry: **50 Years** on." *Journal of The American Society for Mass Spectrometry* 27.11 (2016): 1787-1788

"And the end of all our exploring
Will be to arrive where we started
And know the place for the first time." T.S. Eliot