Helium Shortage: Agilent solutions

Exploiting Hydrogen with a Novel EI Source
Determination of Pesticides by GC/MS/MS

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13th October 2022

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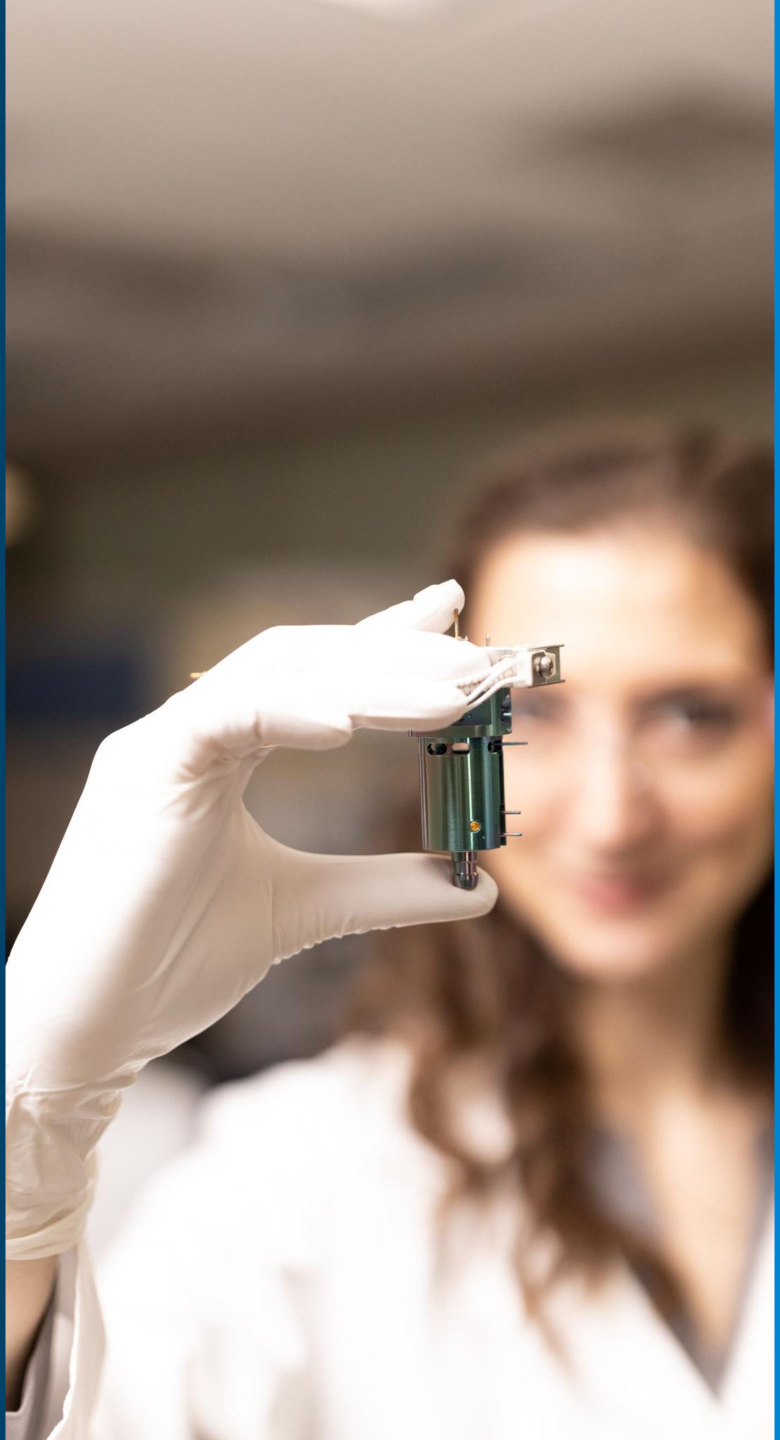
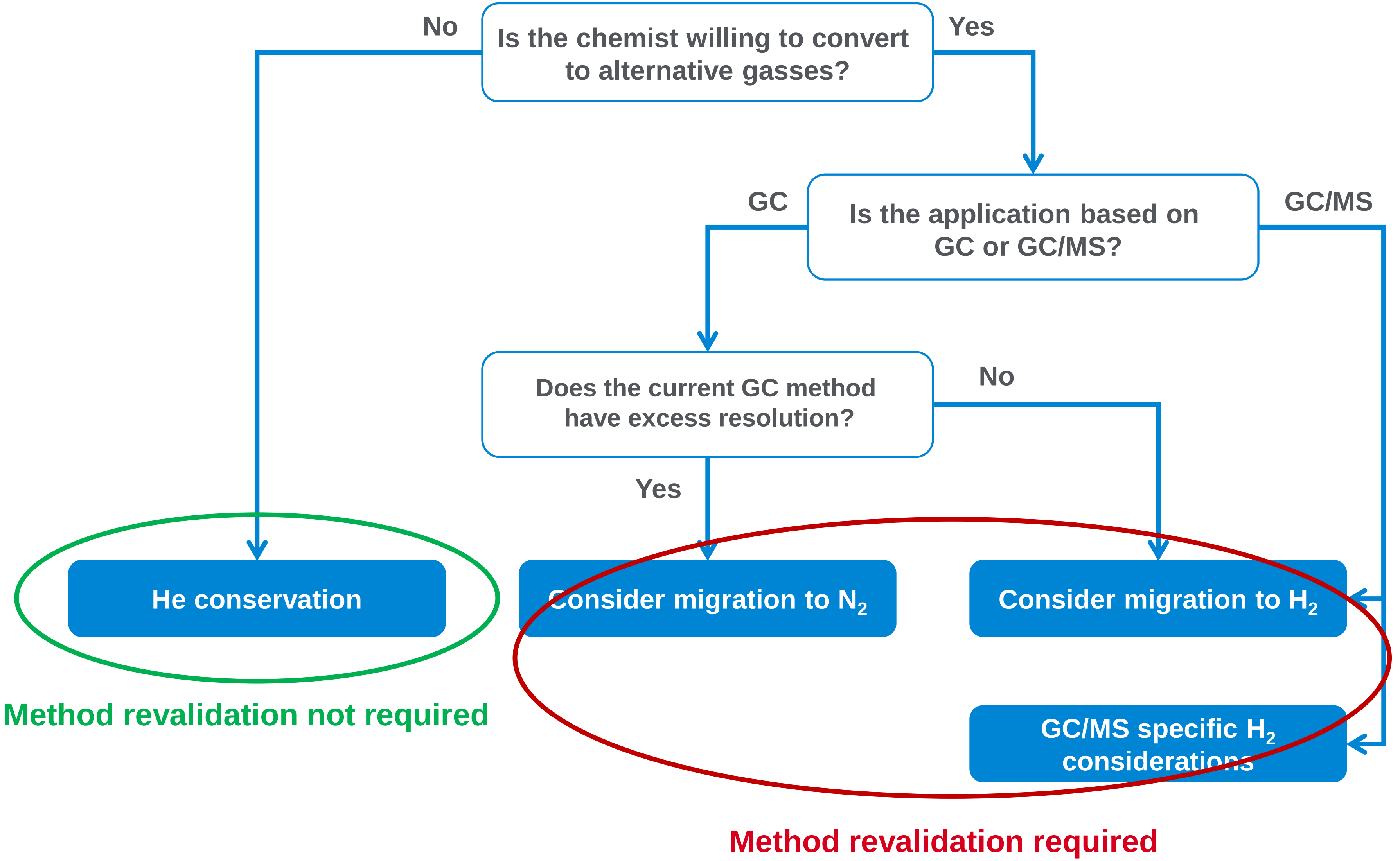


Carrier Gas Decision Tree

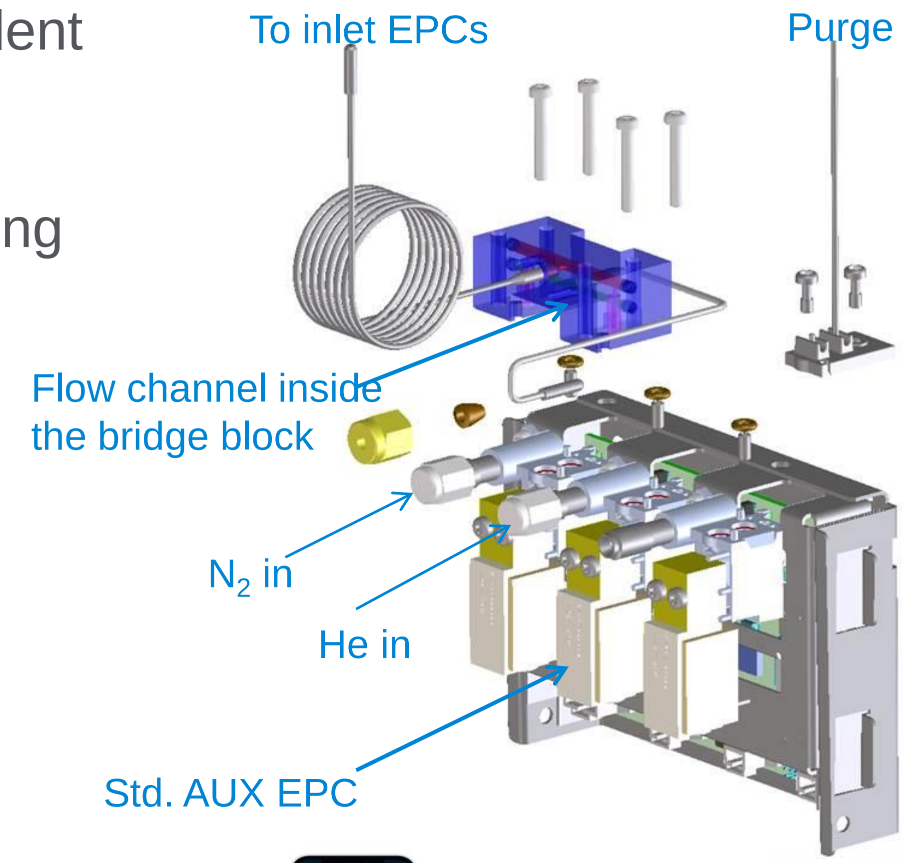
Continue using helium, but in a smarter way



Reducing Helium Use With Conservation

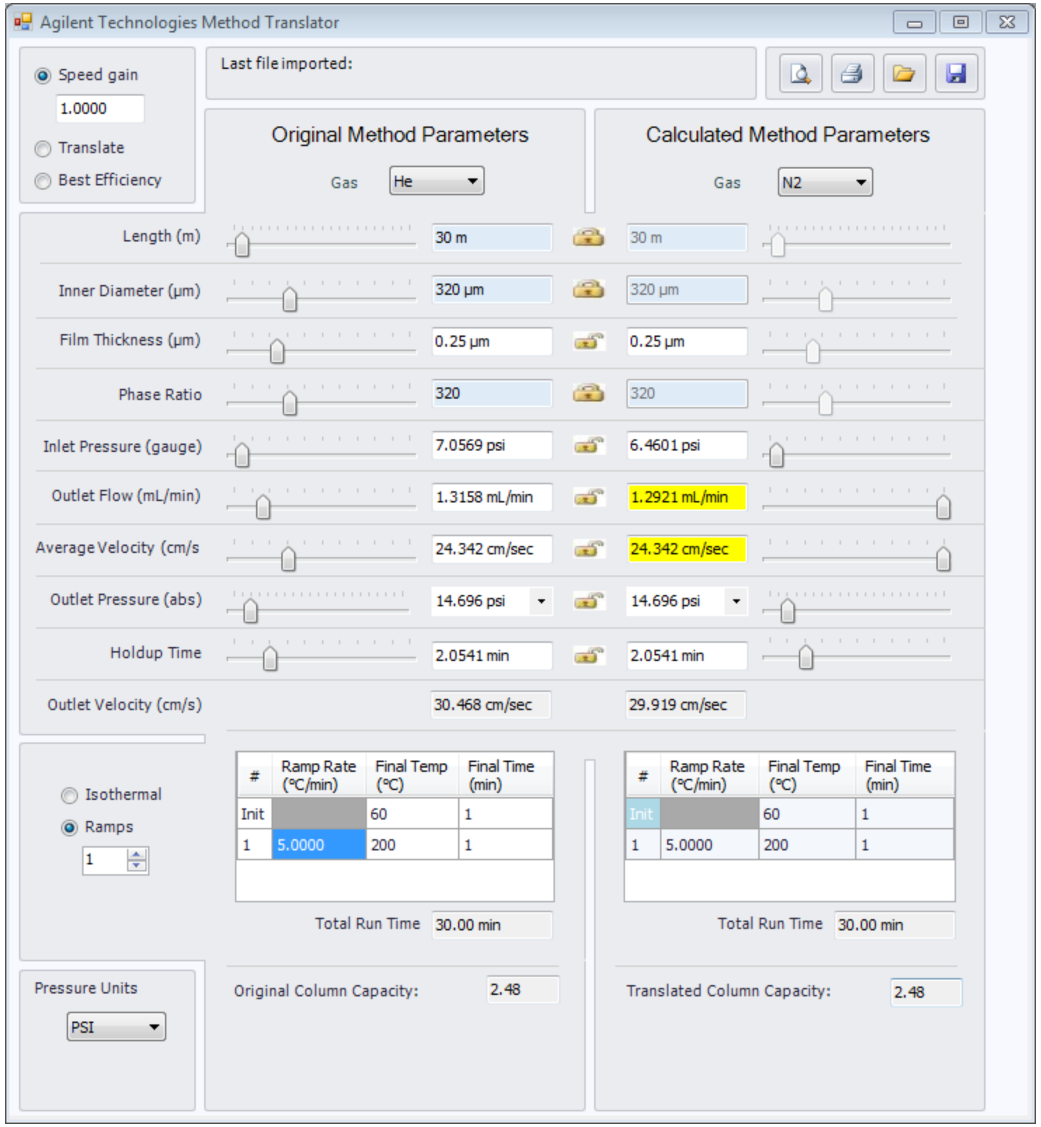
Programmable helium conservation module (available for Agilent 7890B, 8860, 8890 GC systems including MSD)

- Automatically switches carrier gas supply to N_2 standby during idle time
- Integrates into the Sleep and Wake function of the GC
- Combined with Helium Gas Saver to **greatly** reduce helium consumption
- Better alternative to just “shutting off the GC”
  - No system contamination with ambient air exposure
  - Faster restart of heated zones
- **The tune recover in just 15 minutes**

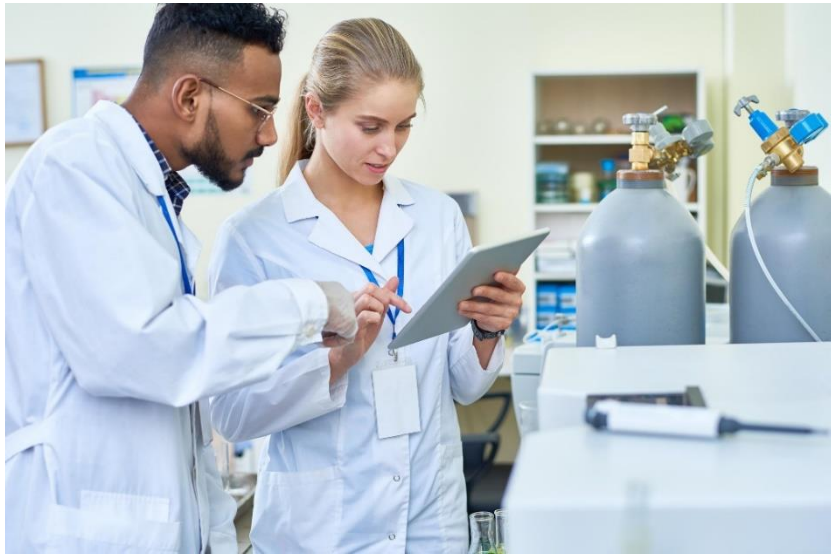


Method Translation Calculator

Another useful tool for carrier gas calculations



- Flexible tool helps convert existing helium methods to alternative carrier
- Built into the new OpenLab CDS software
- Can also run as Windows 7 program
- Download from here: https://www.agilent.com/en/support/gas-chromatography/gccalculators



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Introduction: Converting from He to H_2 Carrier Gas

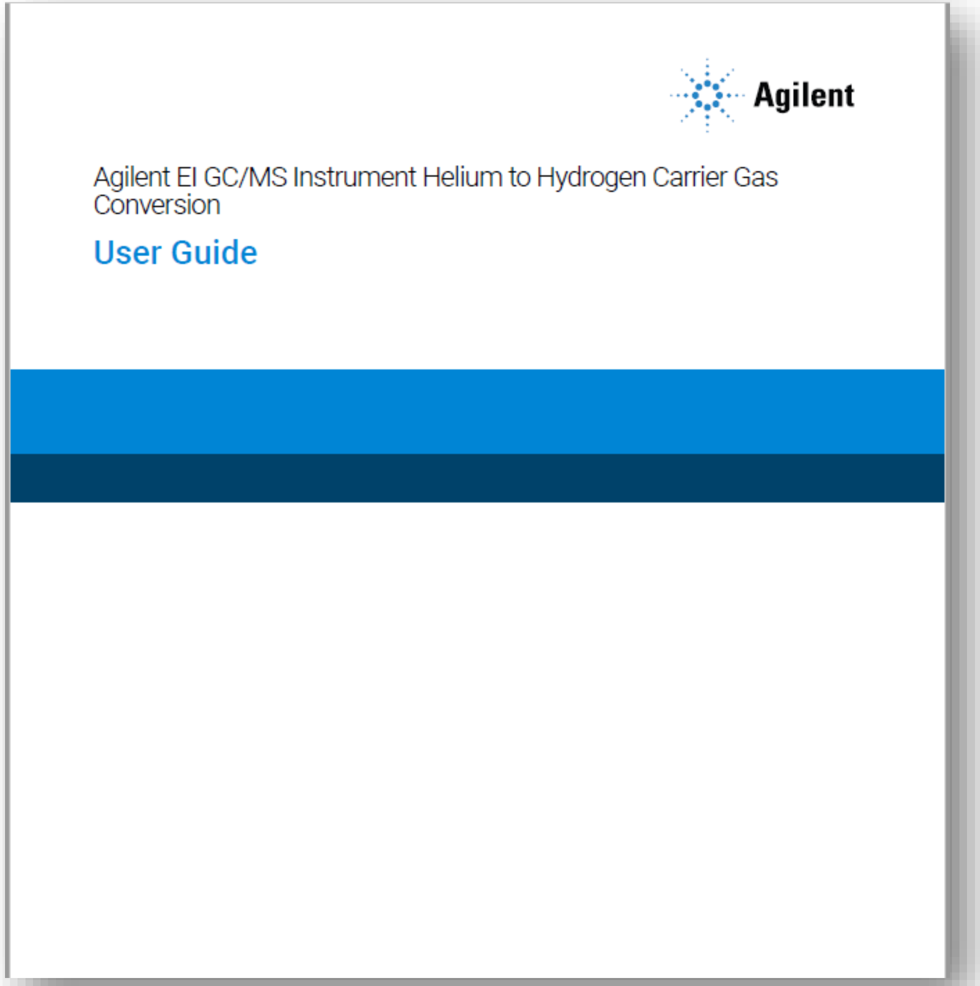
It is important to recognize the differences with using hydrogen carrier. Time should be allotted for adapting the method, optimization, and resolving potential problems.

Areas that will need attention include:

- Choice of supply of H2 (cylinders or generator)
- GC/MS hardware changes (EI source)
- choosing new chromatographic conditions (usually with a smaller bore column)
- potential reduction in signal-to-noise ratio due to higher noise
- changes in spectra and abundance ratios for some compounds
- activity and reactivity with some analytes

Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion

5994-2312EN


Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion

User Guide

Contains detailed instructions for method conversion from He to H_2 carrier.

Read this before beginning the conversion.

https://www.agilent.com/cs/library/usermanuals/public/user-guide-coverting-ei-gcms-instruments-5994-2312en-agilent.pdf

GC/MS/MS Analysis of Pesticides with HydroInert Source

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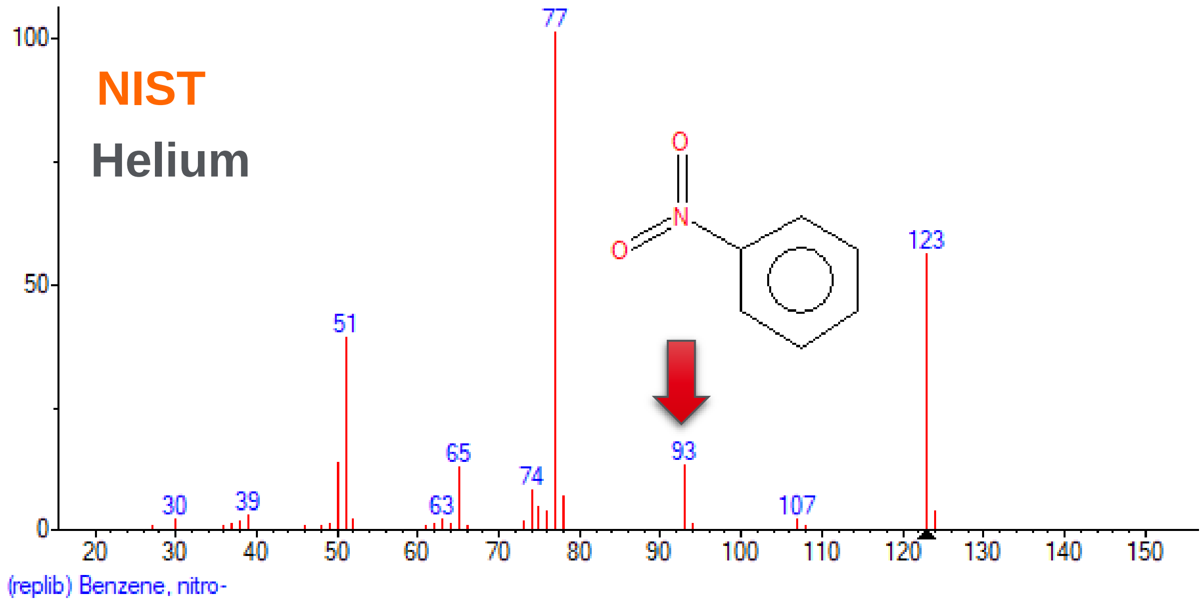
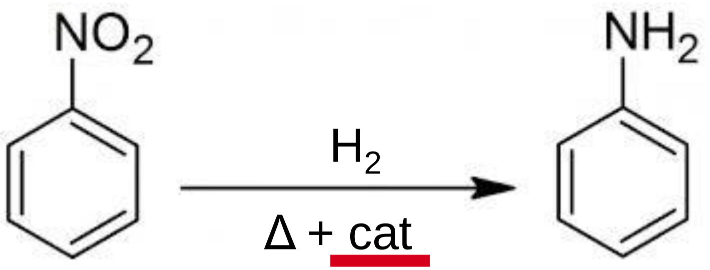
Trusted Answers

Source-Induced Problems with Hydrogen Carrier: Nitrobenzene Conversion



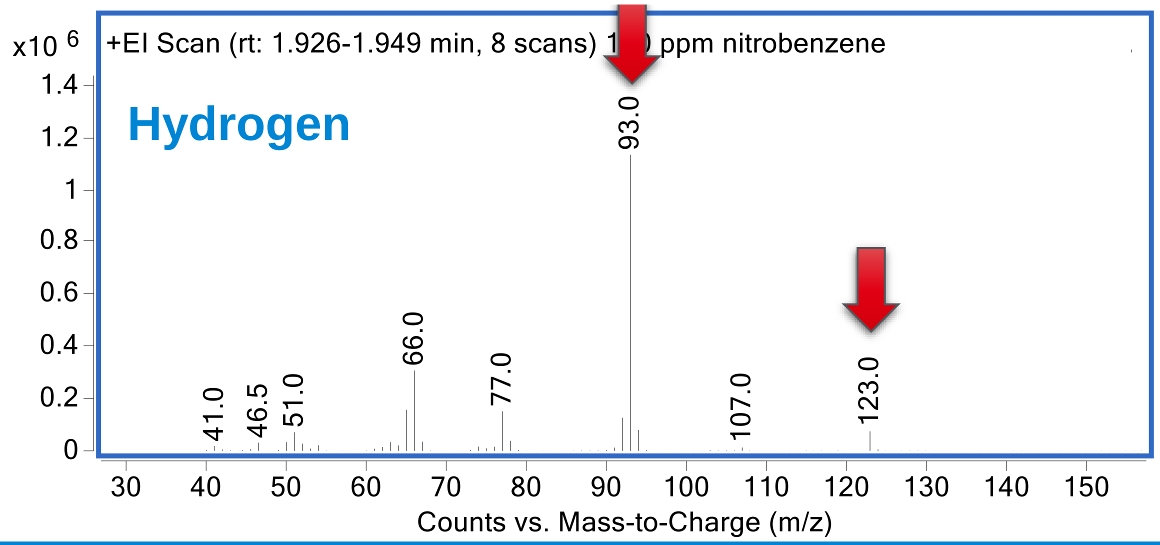


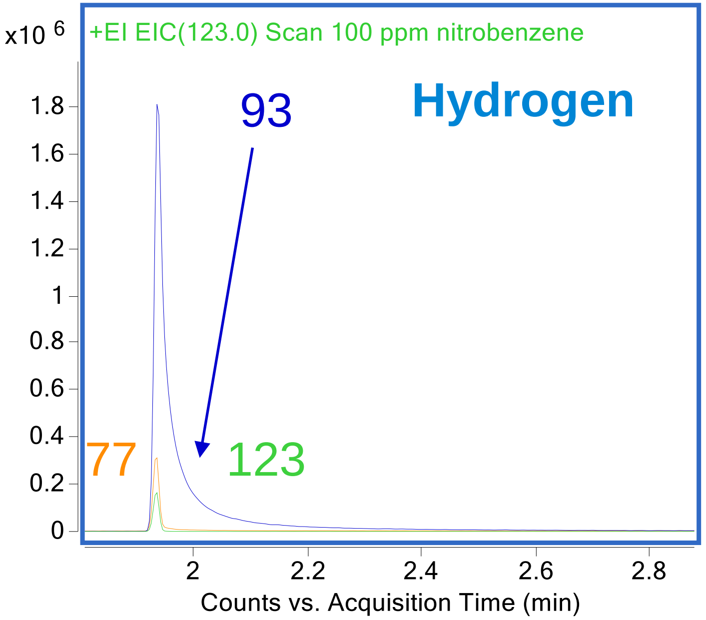
MW 123
Nitrobenzene

MW 93
Aniline

Inert Extractor source,
3 mm drawout, H_2 carrier

"the worst case"





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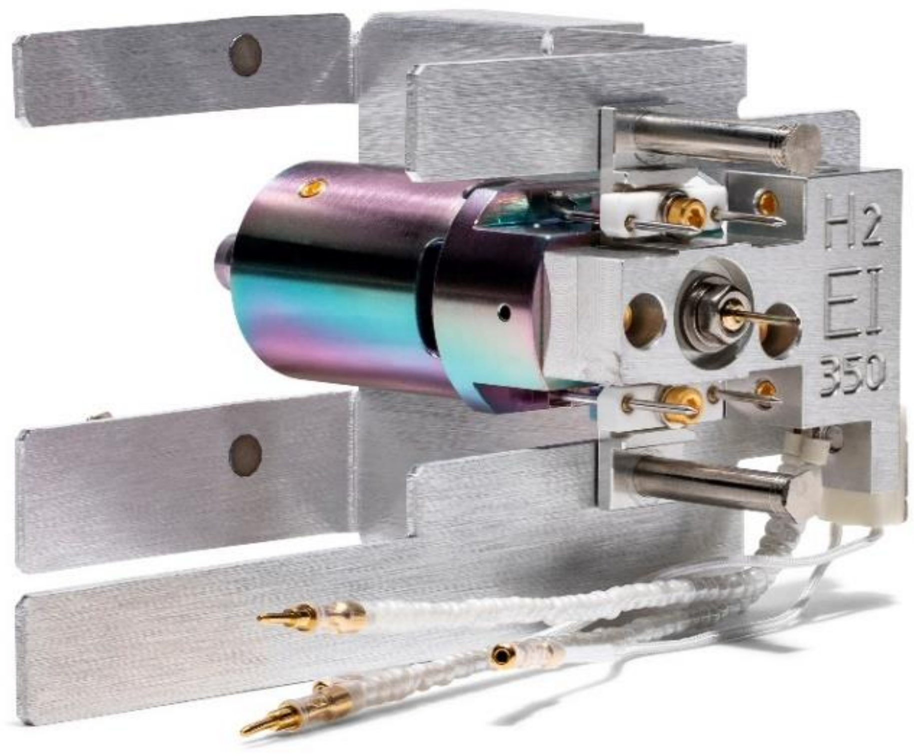
Agilent HydroInert Source for Hydrogen Carrier Gas on GC/MS



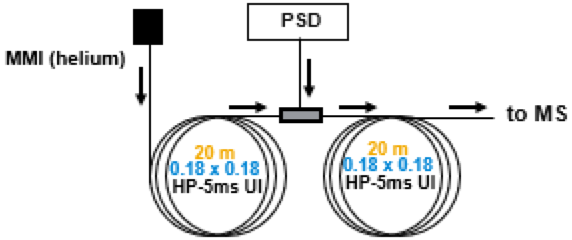
- Allows for the use of Hydrogen Carrier Gas with better supply and reduced cost
- Faster, shorter Separations
- Reduces loss of sensitivity and spectral anomalies
- Reduced source cleanings and maintenance

Analysis Time: 20 or 10 min
with Excellent Chromatographic Resolution

203 pesticides

20x20m
(0.18mm x 0.18µm)

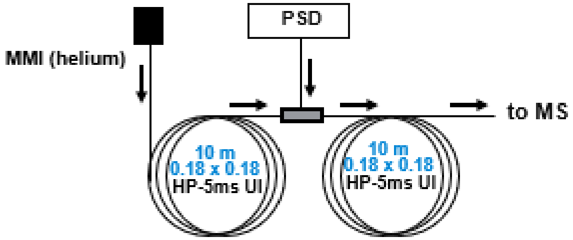
Compatible with H_2 carrier gas



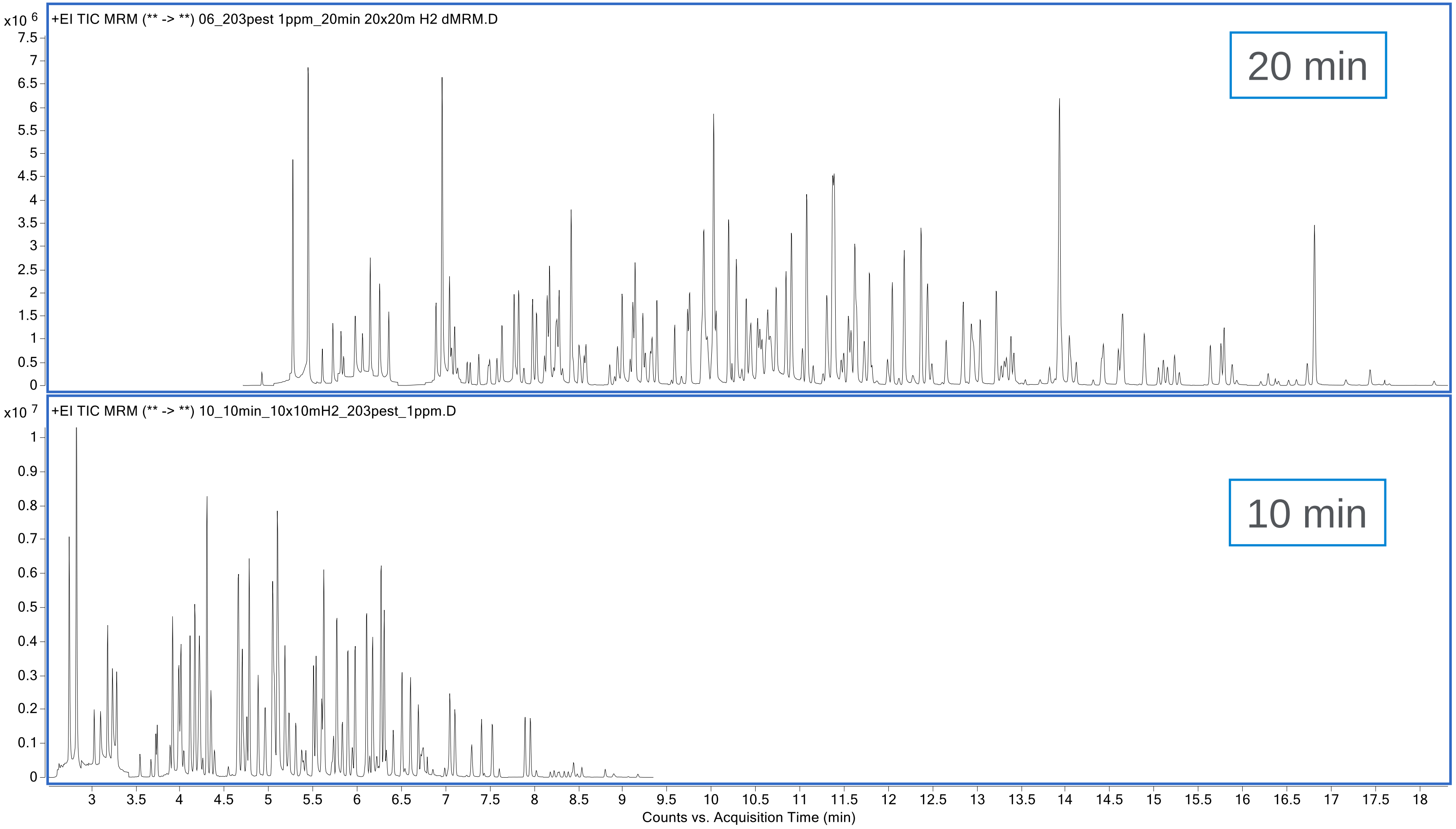
Analysis time 20 min
+ backflush (1-1.5 min)

Narrow Bore 10x10m
(0.18mm x 0.18µm)

Compatible with H_2 carrier gas



Analysis time 8 or 10 min
+ backflush (1-1.5 min)

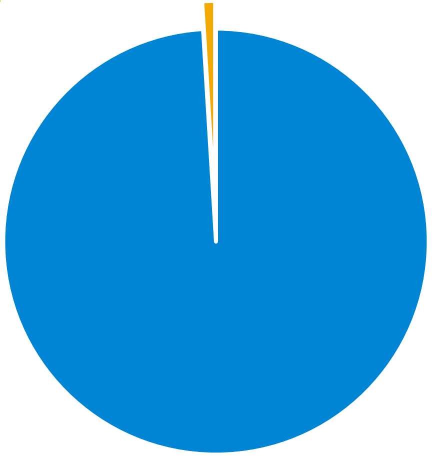


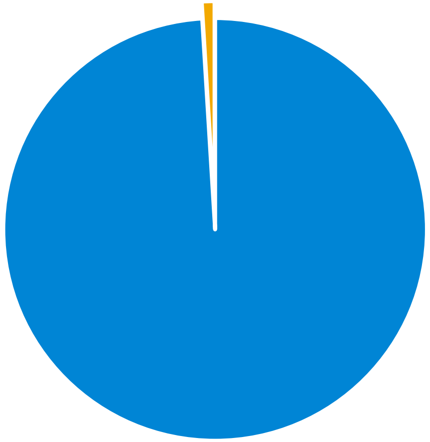
Calibration in Cayenne Pepper with H_2 (20x20 m, 20 min)

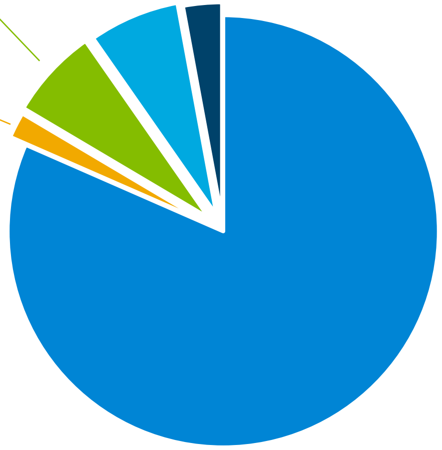
Using the HydroInert Source Equipped with a 9 mm Extractor Lens

103 analytes (many GC-only)

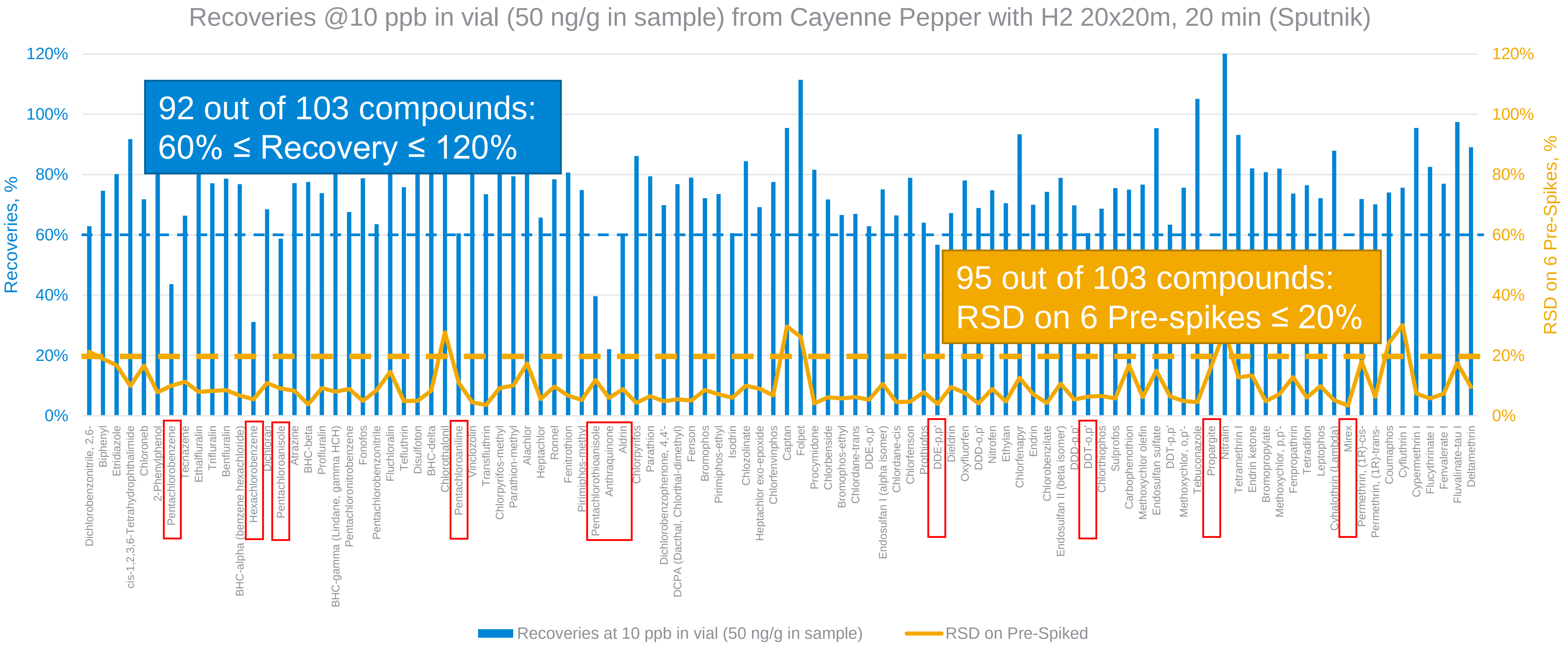
Calibration over 1-500 ppb in vial (5-2,500 ng/g in sample)
R^2 > 0.99
Average RSE 10.1







Extraction Recoveries at 10 ppb in Vial (50 ng/g in sample) from
Cayenne Pepper with 20x20m, 20 min H_2, HydroInert Source 9mm



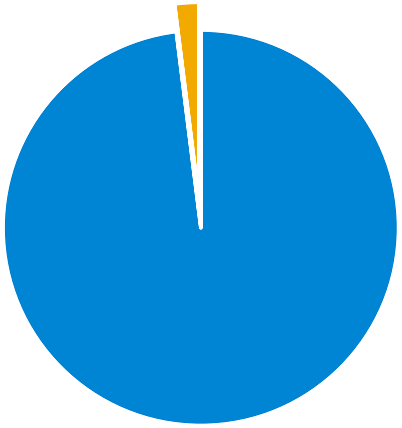
Calibration in Cayenne Pepper with H_2 **(10x10 m, 10 min)**

Using the HydroInert Source 9mm

101 analytes (many GC-only)

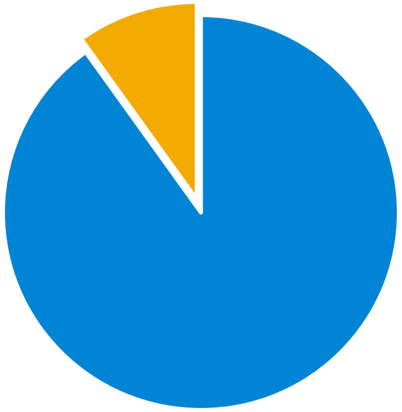
Calibration over 1-500 ppb in vial (5-2,500 ng/g in sample)
R^2 > 0.99
Average RSE 14.4

2 quadratic calibration curve (2x)



99 linear calibration fit

10 (10x)
Relative Standard Error (RSE) > 20

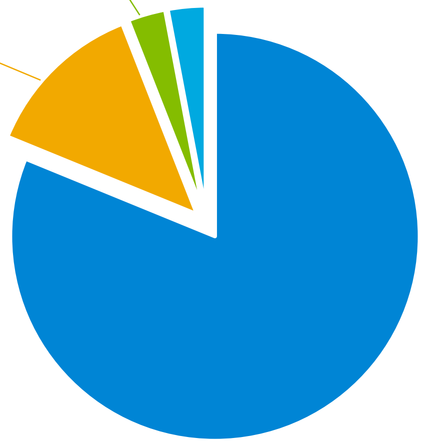


91
RSE < 20

3 (1:2)
5-500 ppb

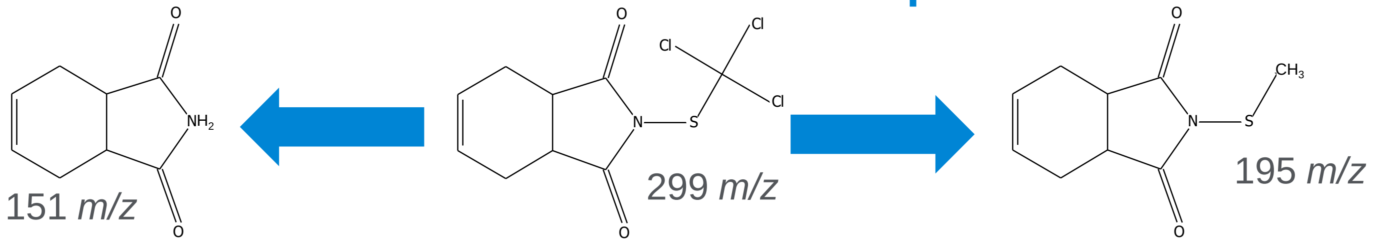
3 (--)
10-500 ppb

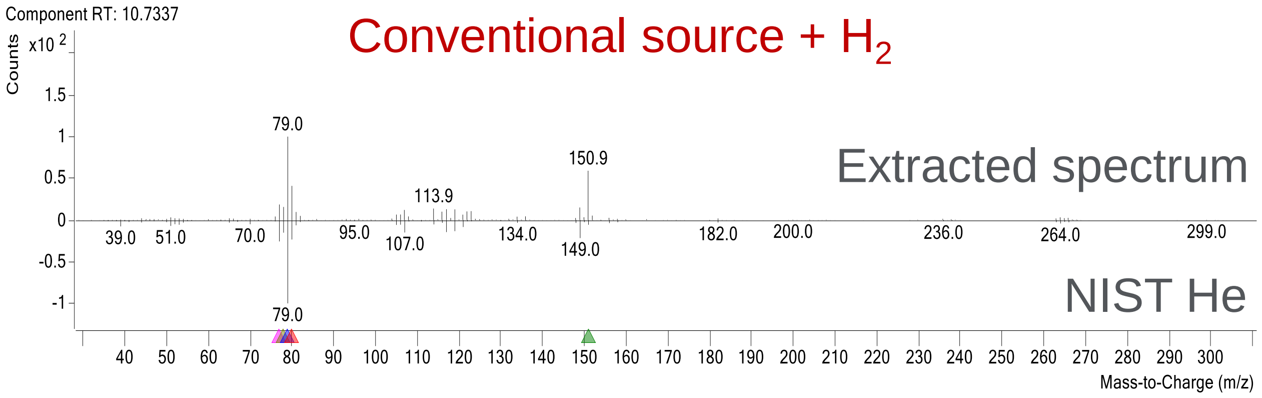
13 (2x)
2.5-500 ppb

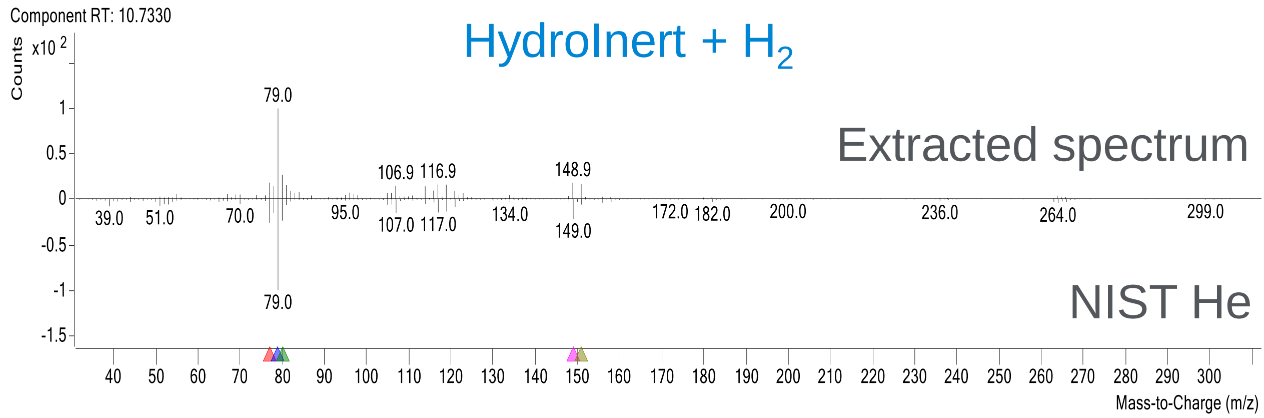


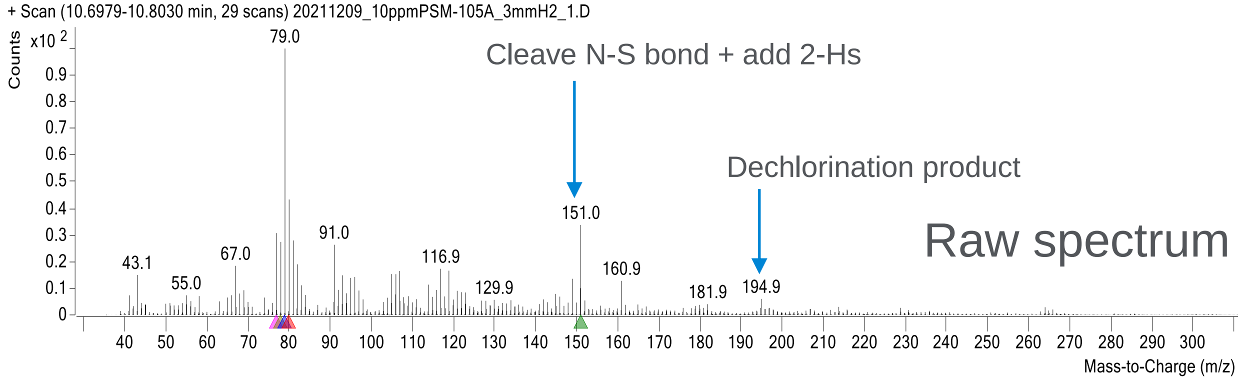
82 (--)
1-500 ppb

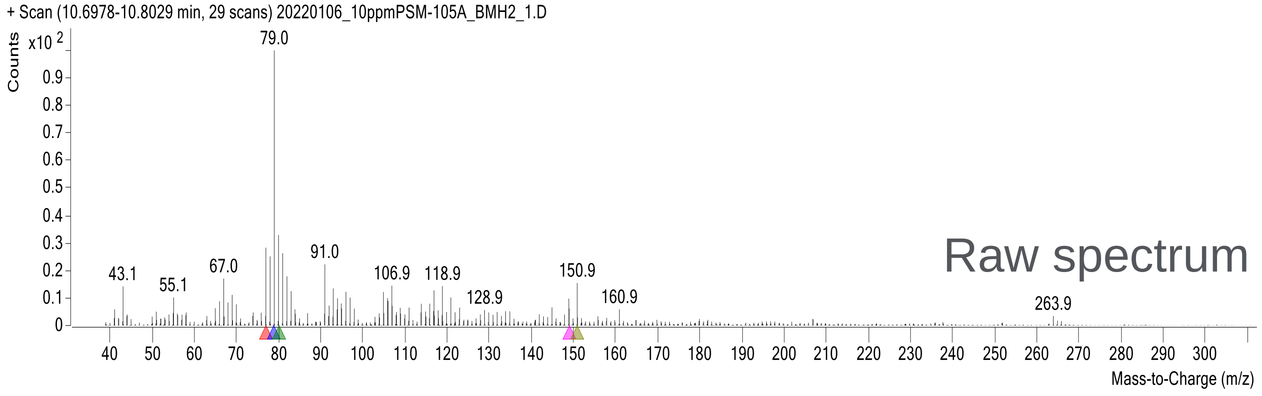
H_2 Cleavage Reactions in the Source: Captan





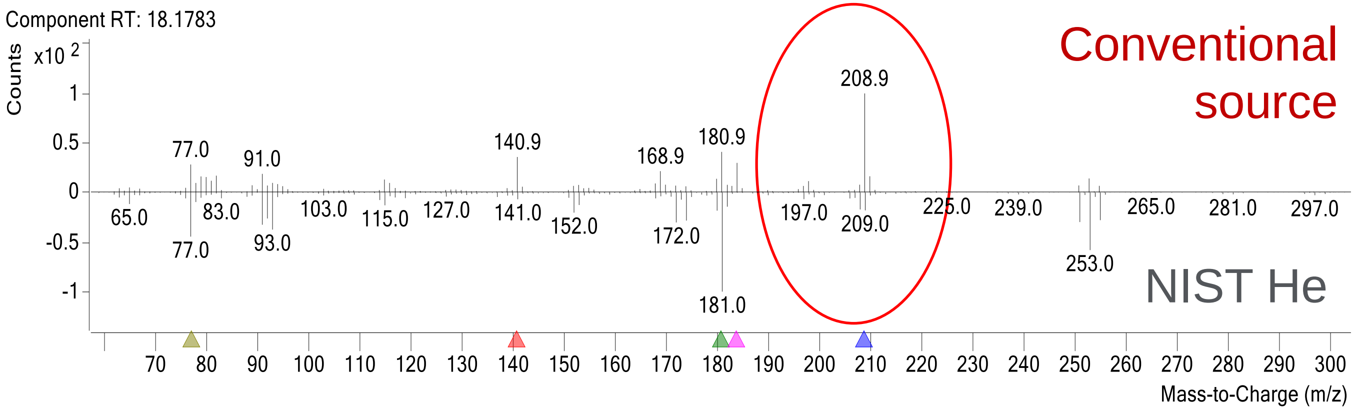




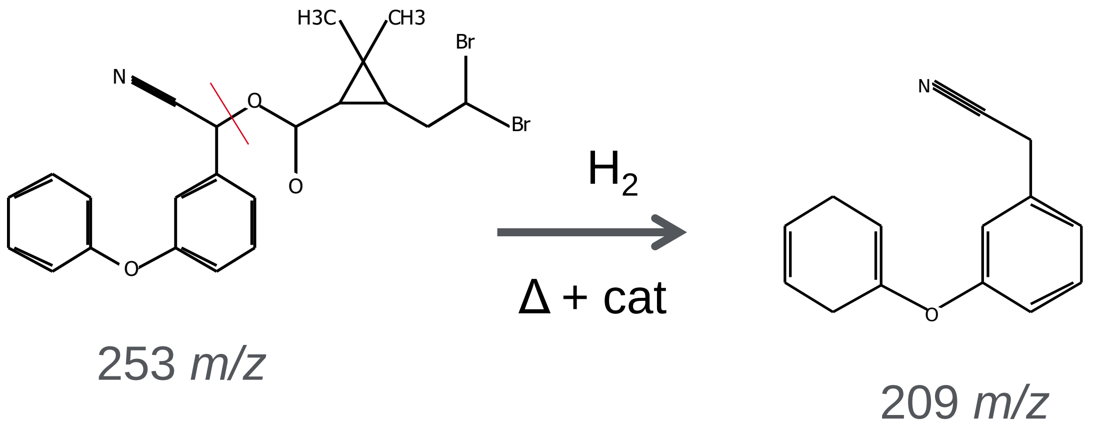


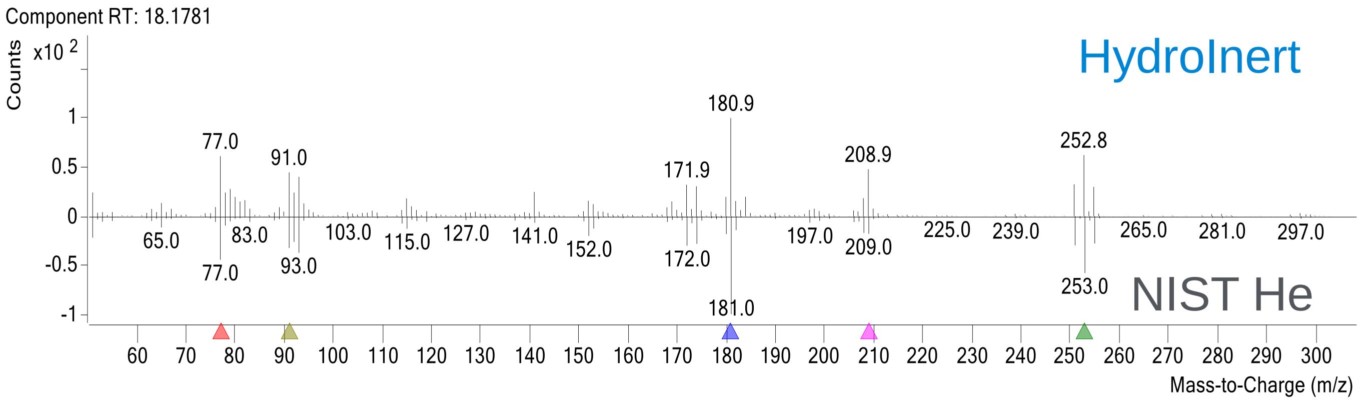
Less hydrogenation in HydroInert source and better NIST match scores

H_2 Cleavage Reactions in the Source: Deltamethrin



- (m-phenoxyphenyl)-acetonitrile identified in some runs with LMS 74.4
- Deltamethrin identified in most runs with LMS range of 70-77





Deltamethrin identified in ALL runs with HydroInert (LMS 90+)

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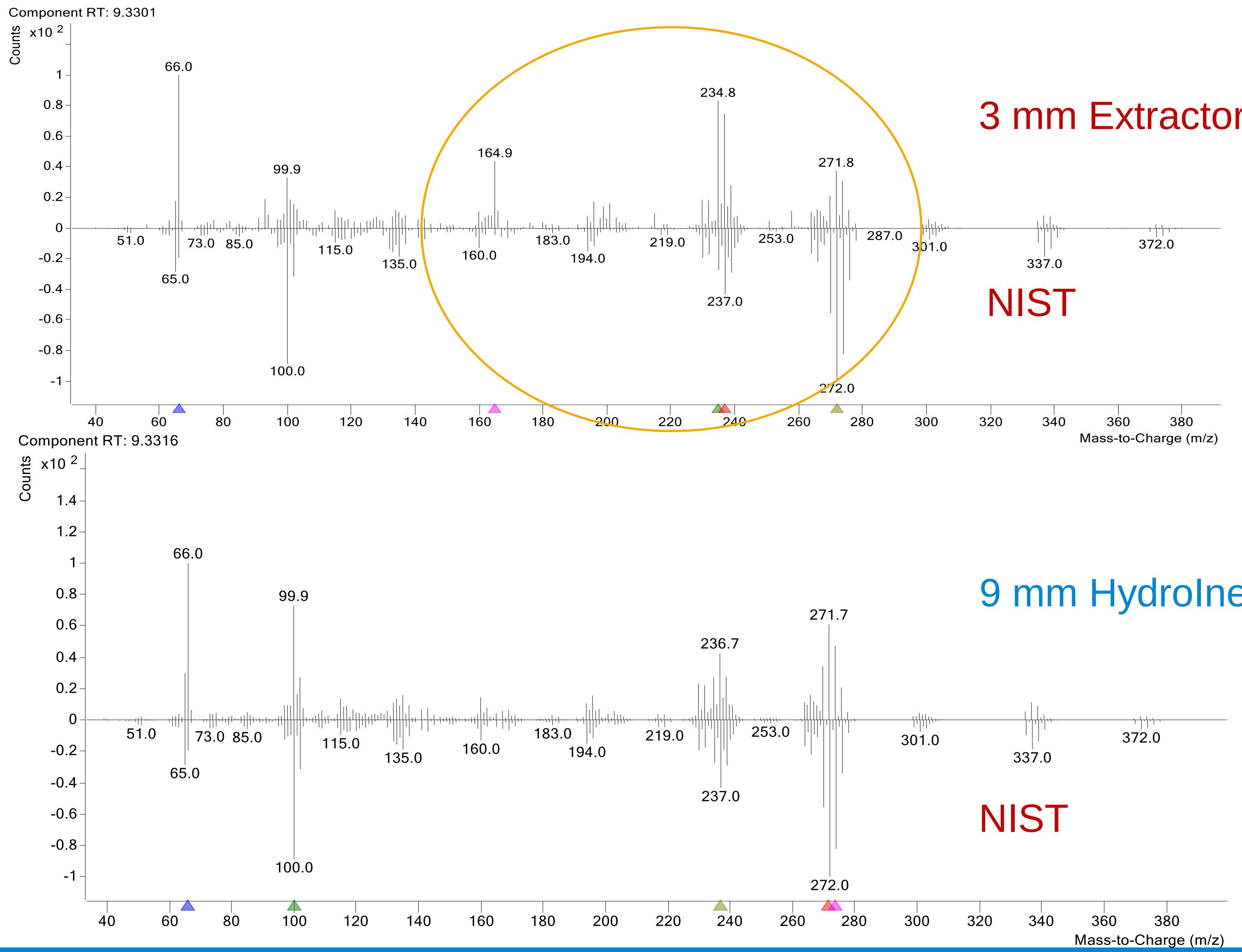
H_2 Cleavage Reactions in the Source: Heptachlor



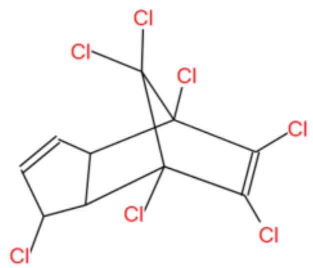
3 mm Extractor

NIST

9 mm HydroInert

NIST

De-chlorination causes disturbed ion ratios



Maintained ion ratios with HydroInert

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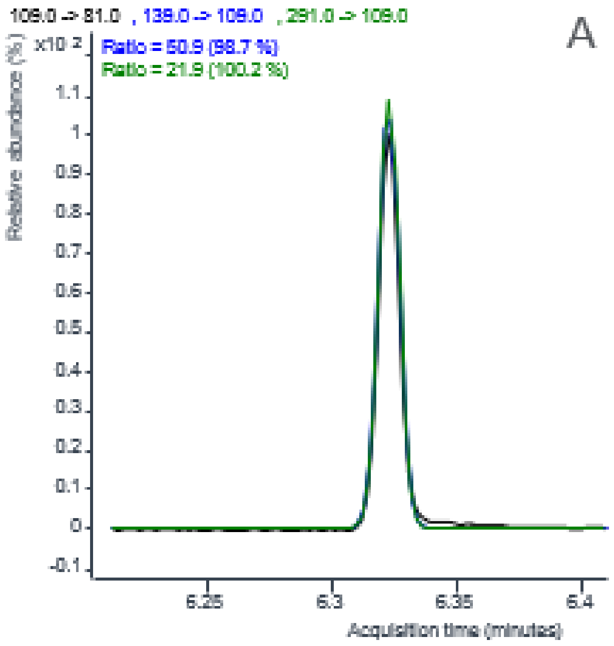
HydroInert Source Allows to Maintain Ion Ratios with H_2 Carrier

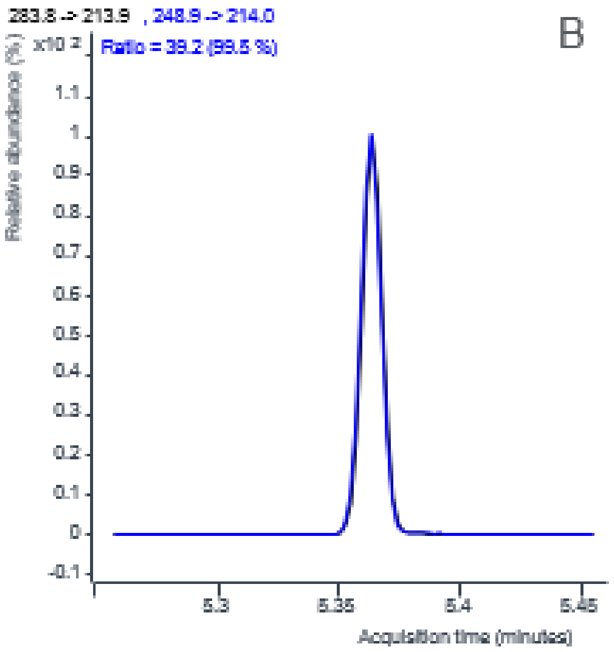
- The same MRM transitions can be used with H_2 carrier gas
- Comparable MRM ratios are expected with H_2 when compared to He
- Collision energies can be re-evaluated using the fully automated process with the Optimizer for GC/TQ

MRM transitions are from helium generated data!

Parathion



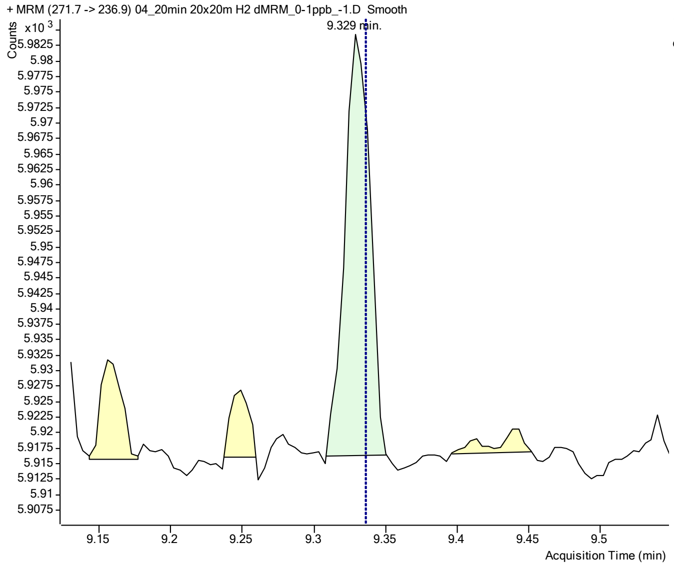
Hexachlorobenzene



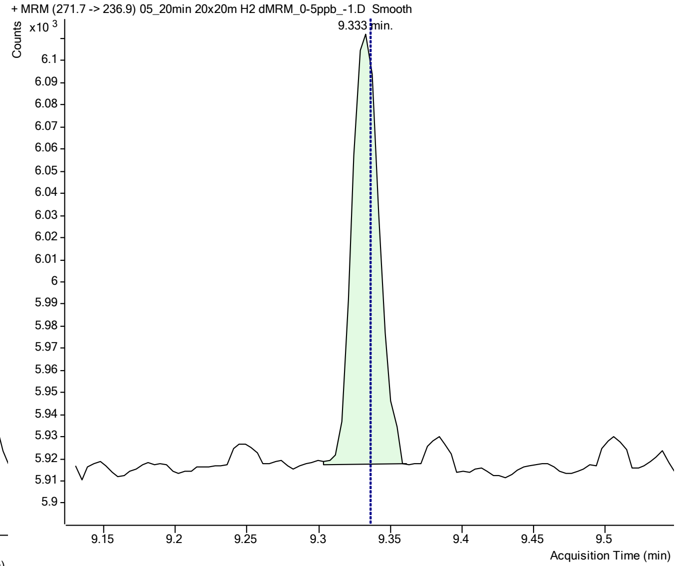
Heptachlor with H_2 Carrier with GC/TQ in Spinach QuEChERS Extract

Same MRMs were used with H_2 as with He

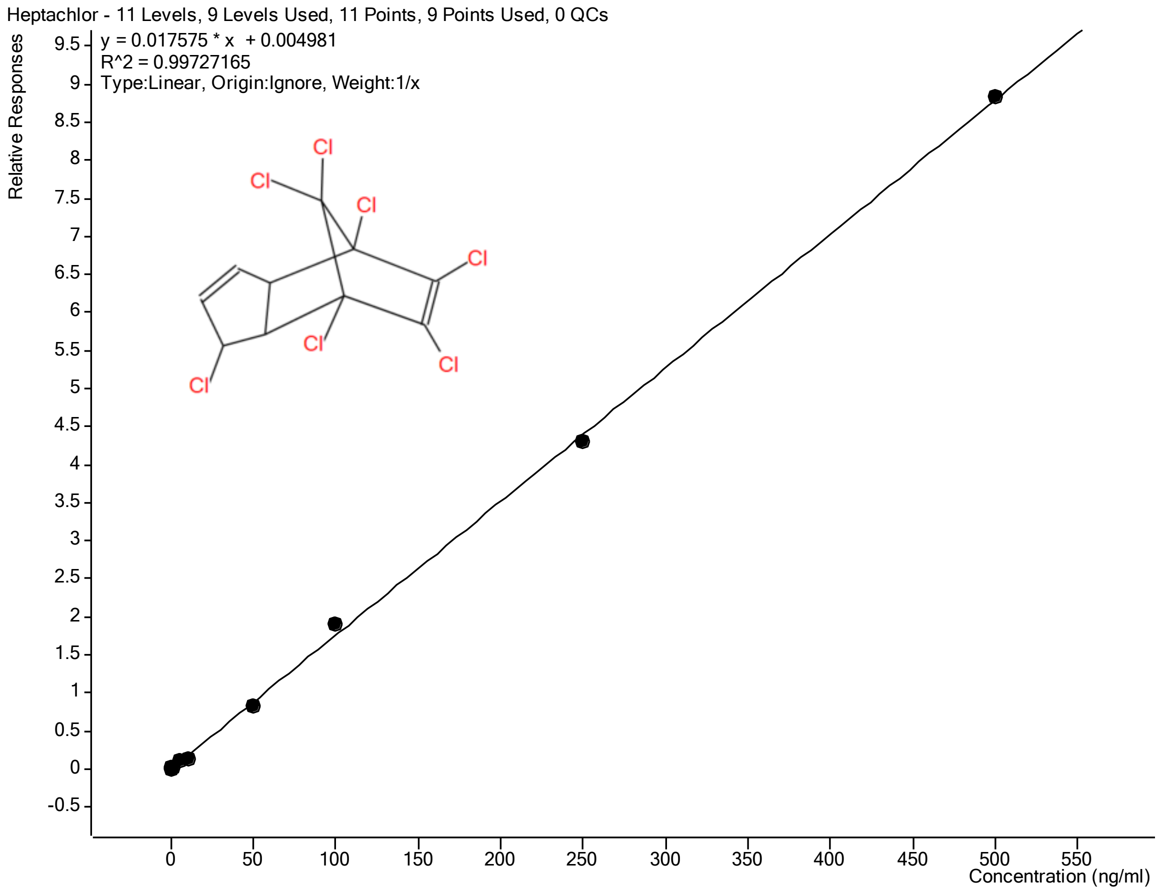
0.1 ppb with H_2 in spinach



0.5 ppb with H_2 in spinach

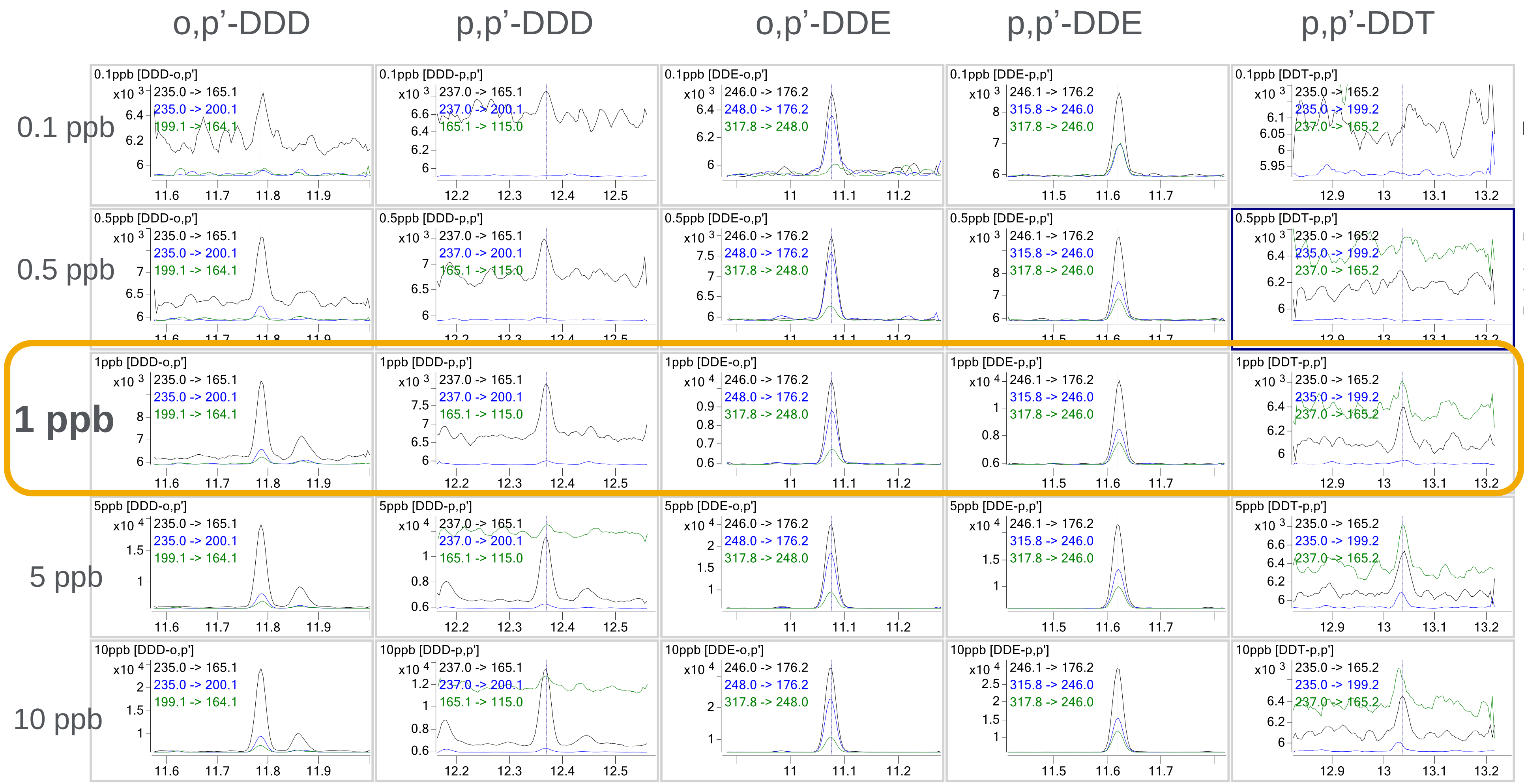


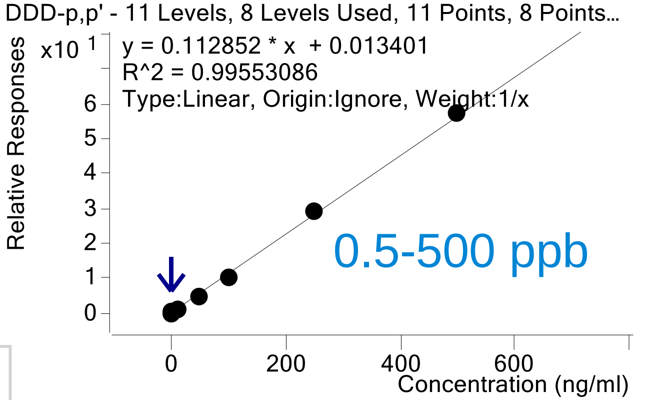
0.1-500 ppb with H_2 with 20mx20m
$R^2 = 0.997$

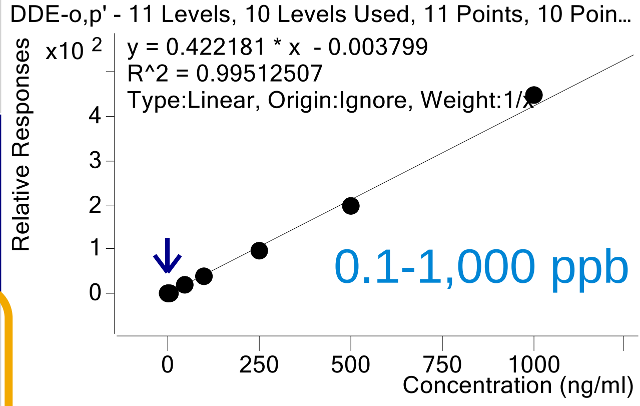


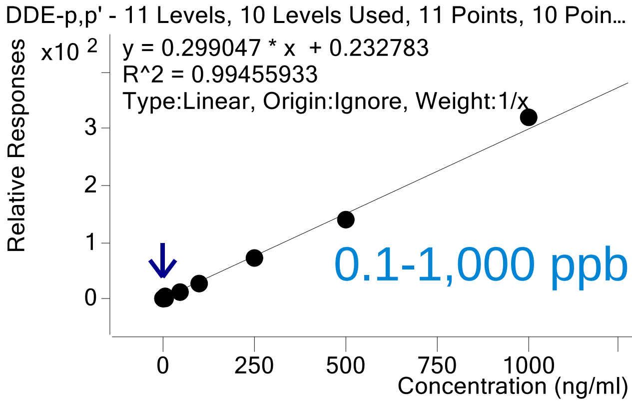
The RTs precisely matched the 20 min He method (P&EP database) for all compounds

Sensitivity and Calibration for Organochlorine Pesticides with H_2 Carrier with GC/TQ in Spinach QuEChERS Extract

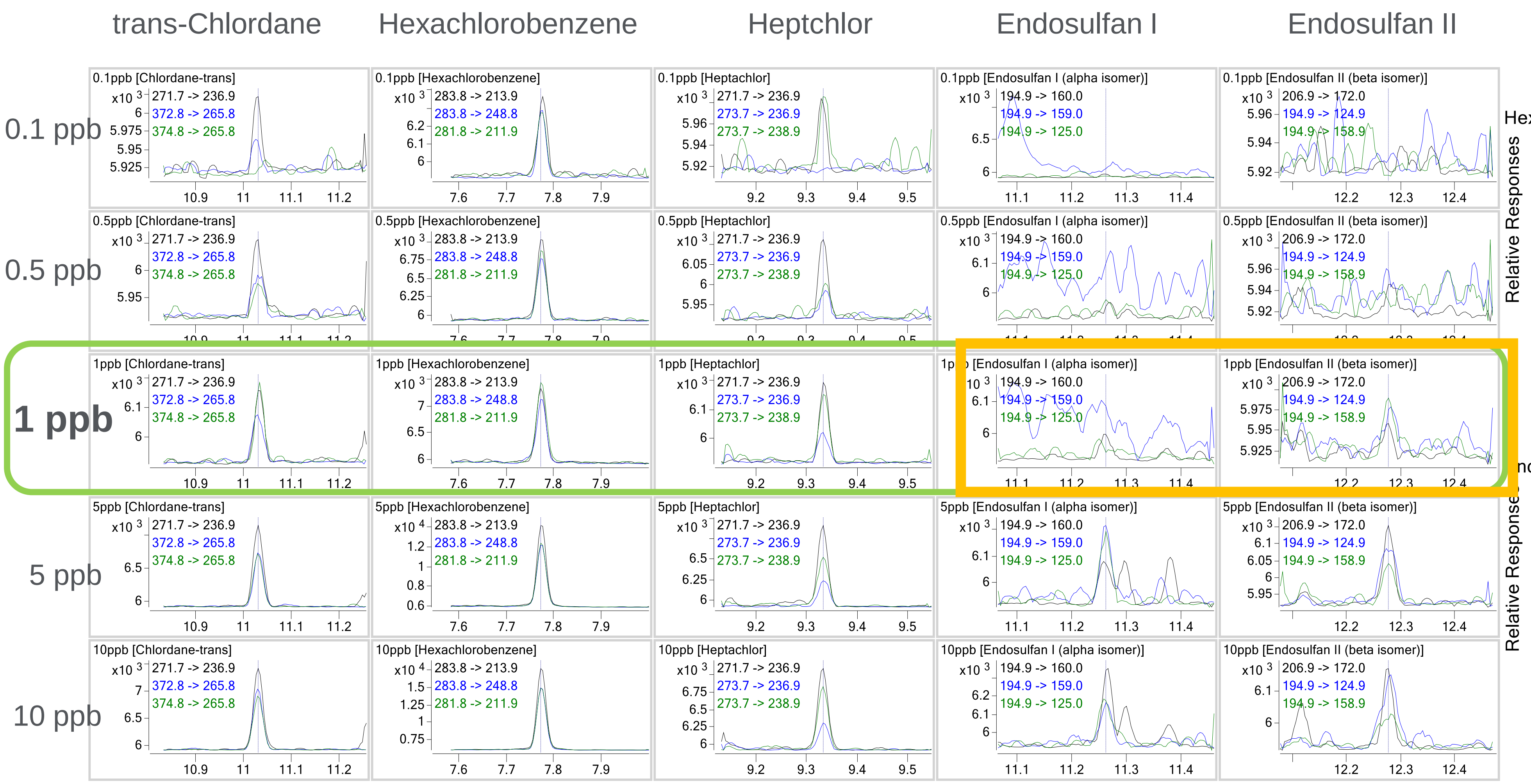


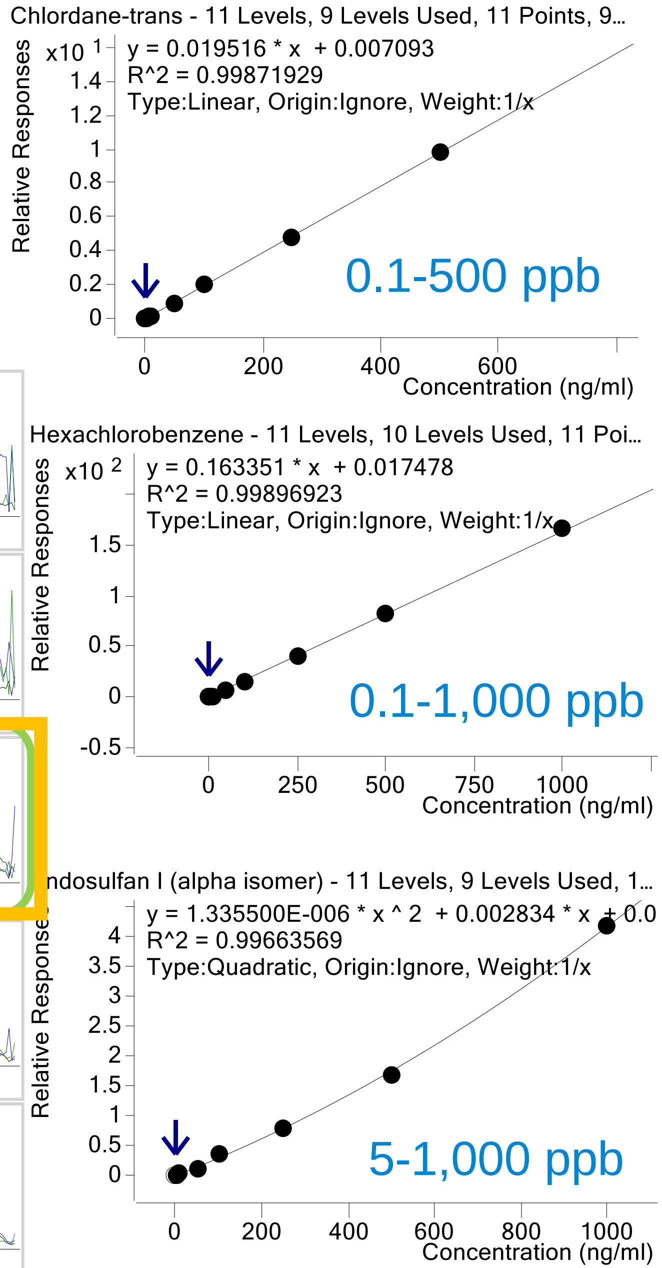






Sensitivity and Calibration for Organochlorine Pesticides with H_2 Carrier with GC/TQ in Spinach QuEChERS Extract





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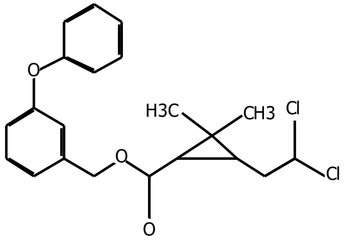
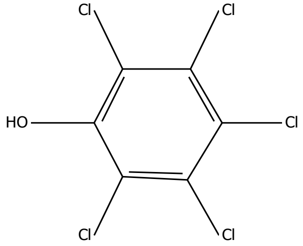
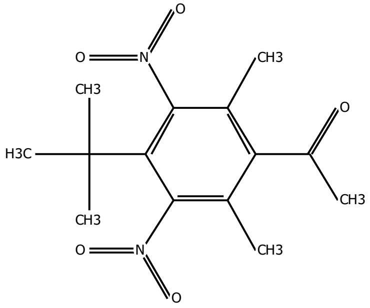
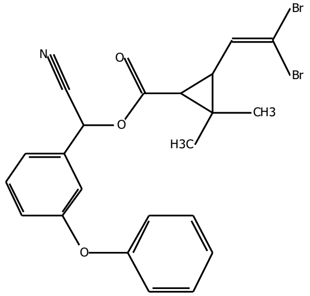
What compound classes can benefit from HydroInert source ?

Compound class	Example compound(s)	H_2 Carrier Gas + Standard GC/MS source	H_2 Carrier Gas + HydroInert source
Nitro-compounds	Nitrobenzene, fenitrothion, ethalfluralin	Unacceptable	Differentiating
Heavily chlorinated compounds	DDT, Endrin, heptachlor, BHC compounds, pentachlorophenol	Unacceptable	Differentiating
Polycyclic aromatic hydrocarbons (PAHs)	Benzo(b)fluoranthene, benzo[g,h,i]perylene,	Neutral	Neutral
Alkanes >C24	Tetratriacontane, hexadecane, tetracontane	Neutral	Neutral
Pesticides	Deltamethrin, fipronil, permethrin, captan	Unacceptable	Differentiating
Fragrance/flavor compounds	Musk ketone, musk ambrette, linalool	Unacceptable	Differentiating
Volatile Organic compounds	1,4-dioxane, tichloromethane, bromodichloromethane	Neutral	Differentiating



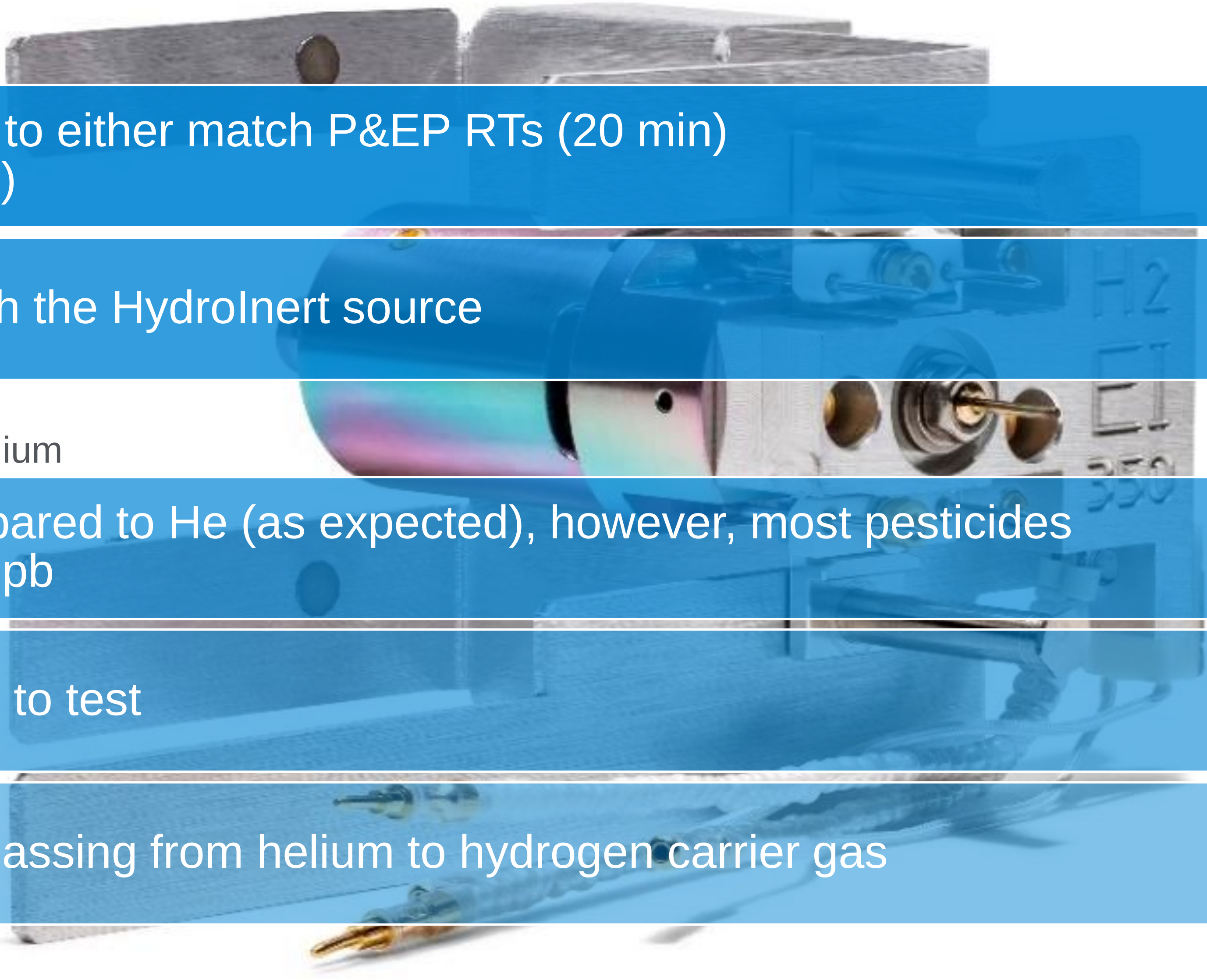






Summary on H_2 for Pesticides Analysis with Hydroinert source

- Two column configurations allow to either match P&EP RTs (20 min) or accurately predict RTs (10 min)
- Spectral fidelity is maintained with the HydroInert source
  - Can retain existing MRM transitions
  - Can use standard Library used in helium
- Sensitivity is reduced when compared to He (as expected), however, most pesticides can be detected starting from 1 ppb
- Work continue with new matrices to test
- Hydroinert good solution when passing from helium to hydrogen carrier gas



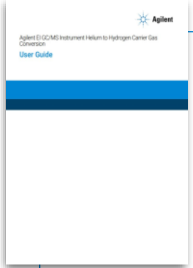
Resources and Application Notes

SVOCs 8270 with 5977B GC/MSD with H2 and HydroInert (includes DFTPP): [5994-4890EN]

SVOCs 8270 with 7000E GC/TQ, H2, and HydroInert: [5994-4891EN]

VOCs with Headspace and 5977C GC/MSD with H_2 and HydroInert: [5994-4963EN]

HydroInert tech overview: [5994-4889EN]



He to H_2 conversion guide: [5994-2312EN]

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