Unlocking Pesticide Analysis Excellence: Proven Tactics for Optimal Results with GC/MS/MS Using Helium and Hydrogen

Becoming a Better Chromatographer
Educational Webinar Series
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Agilent
Trusted Answers

Pesticides in Food

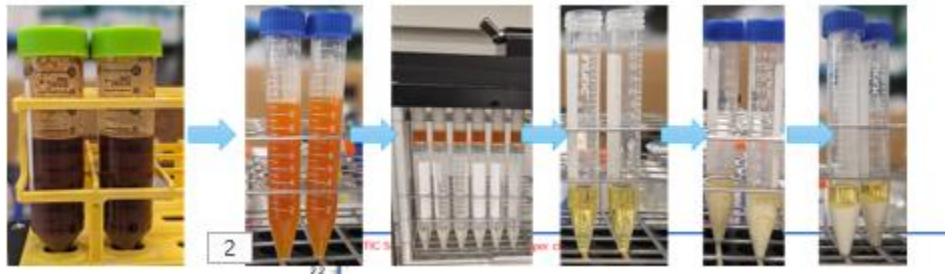
- 5.6 billion pounds of pesticides are used worldwide annually
- 1 billion pounds in the US annually
- The global market for agricultural pesticides was estimated at $106,530 million in the year 2022
- Projected to reach $144,820 million by 2028
- Government agencies determine *safe* levels of pesticide in food

Rev Environ Health. 2009 Oct–Dec; 24(4): 303–309.

Pesticide Testing

- Consumer safety: ensure compliance within maximum residue limits (MRLs)
- Product confidence and quality control

Pesticide Analysis Workflow



Sample preparation

GC/MS analysis

Sample

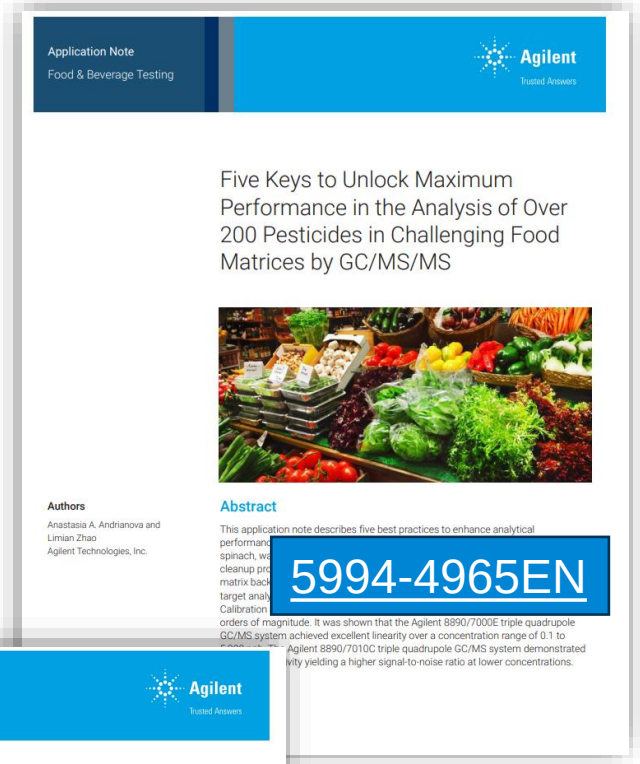
GC/MS & LC/MS Analysis

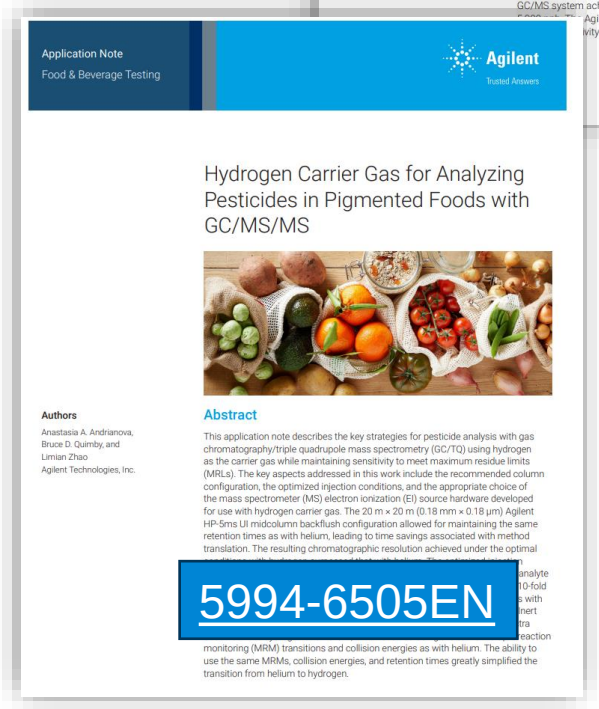
Data Analysis & Reporting

In Today's Presentation…

I. Five key components of successful pesticide analysis with GC/TQ

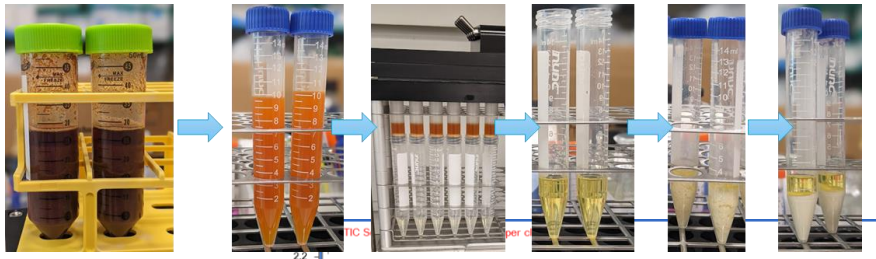
II. Hydrogen as a carrier gas for GC/TQ analysis of pesticides

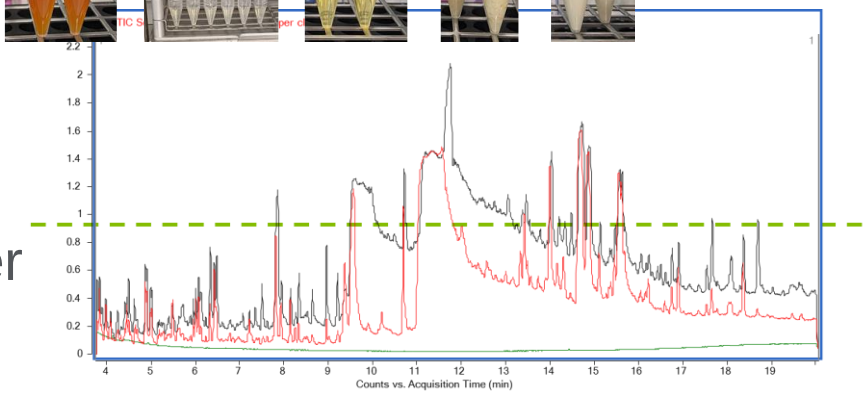


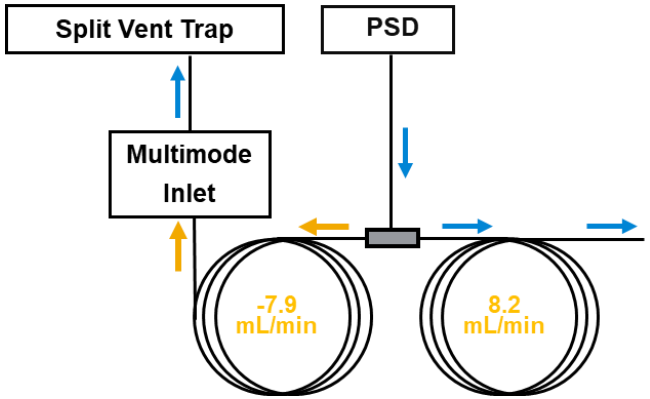


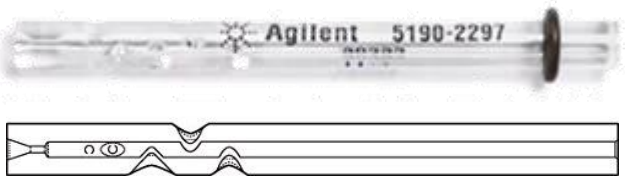
Five Key Components of Successful Pesticide Analysis

1. Effective sample extraction and matrix cleanup
2. Evaluation of the matrix in full scan
3. Midcolumn backflushing
4. A leak-free GC/TQ
5. Temperature-programmed MMI inlet with a 2 mm dimpled liner





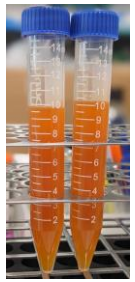


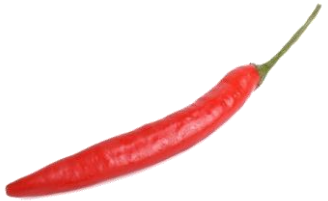


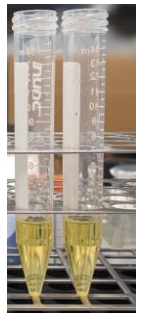
1. Effective Sample Extraction and Matrix Cleanup

Adequate sample preparation (especially with the GC/TQ 7010C)
Sometimes dilution may yield better sensitivity and enhance robustness

For walnut and spinach extract comparison, check the app note







The Enhanced Matrix Removal (EMR) with Carbon S Passthrough Cleanup for Pigmented Food Matrices

- **Novel** Captiva EMR with Carbon S cartridges
  - Carbon S is an advanced hybrid carbon material
  - **Simplified** passthrough **cleanup** after QuEChERS extraction
  - Optimized formula based on different matrix complexities and pigment level
  - **Improved method performance**

- Compared to the traditional GCB included products
  - Efficient pigment removal with the compromise of sensitive analytes loss
  - Poor matrix cleanup for complex pigmented dry matrices

Captiva EMR Passthrough Selection Guide

Captiva EMR-HCF

High Chlorophyll Fresh
- Spinach, arugula, chard

Captiva EMR-GPF

General Pigmented Fresh
- Berries, peppers, broccoli

Captiva EMR-GPD

General Pigmented Dry
- Spices, seasoning, herbal medicine

Captiva EMR-LPD

Low Pigmented Dry
- Nuts, tobacco, light pigmented spices

Simplified Passthrough Workflow

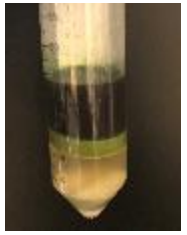
Baby spinach

Blackberry

Almond flour

Cinnamon powder

Standard QuEChERS extraction

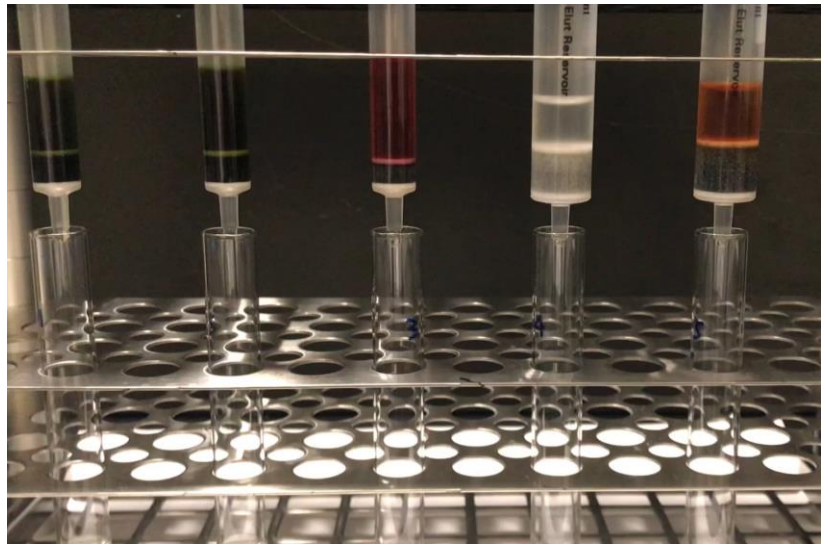


Crude ext. loading

Gravity elution or w/ low level external force

Captiva EMR cartridges

HCF1-NH_2 HCF1-PSA GPF LPD GPD



Collected eluent

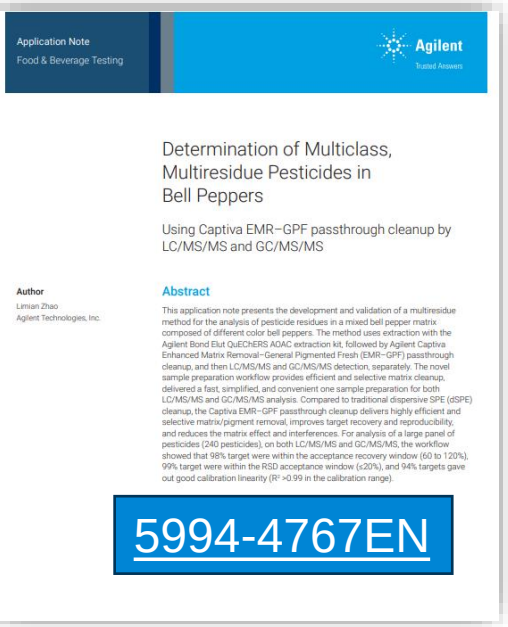
Post-treatment before instrument analysis

Conclusions – Value of Captiva EMR with Carbon S

Data quality

Improved quantitation results quality

- Improved sensitive pesticides recovery and reproducibility
- Reduced matrix interferences and matrix effect on targets, and thus improved method sensitivity and selectivity.
- Overall higher pass rate for multiclass multiresidue pesticides analysis, plus improved detection method robustness



Ease of use/ throughput

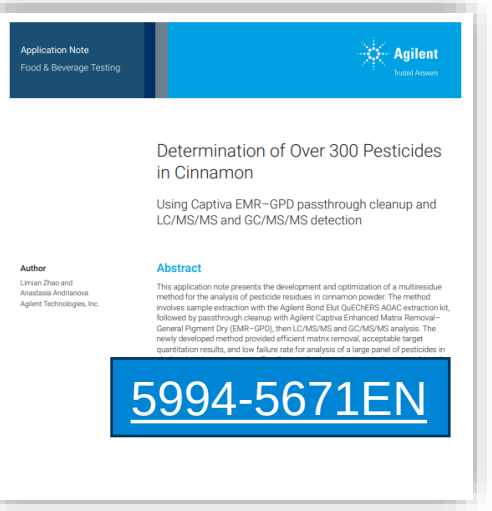
Simplified preparation procedure

- One sample preparation method can serve both GC and LC applications
- Simplified passthrough cleanup provides easier and faster workflow – saving 15 to 30% sample preparation processing time

Five new part numbers

Simple and easy selection

- Three for fresh pigmented matrices, Captiva EMR-HCF 1 and 2, Captiva EMR-GPF
- Two for dry complex matrices, Captiva EMR-GPD, Captiva EMR-LPD



2. Evaluation of the Matrix in Full Scan

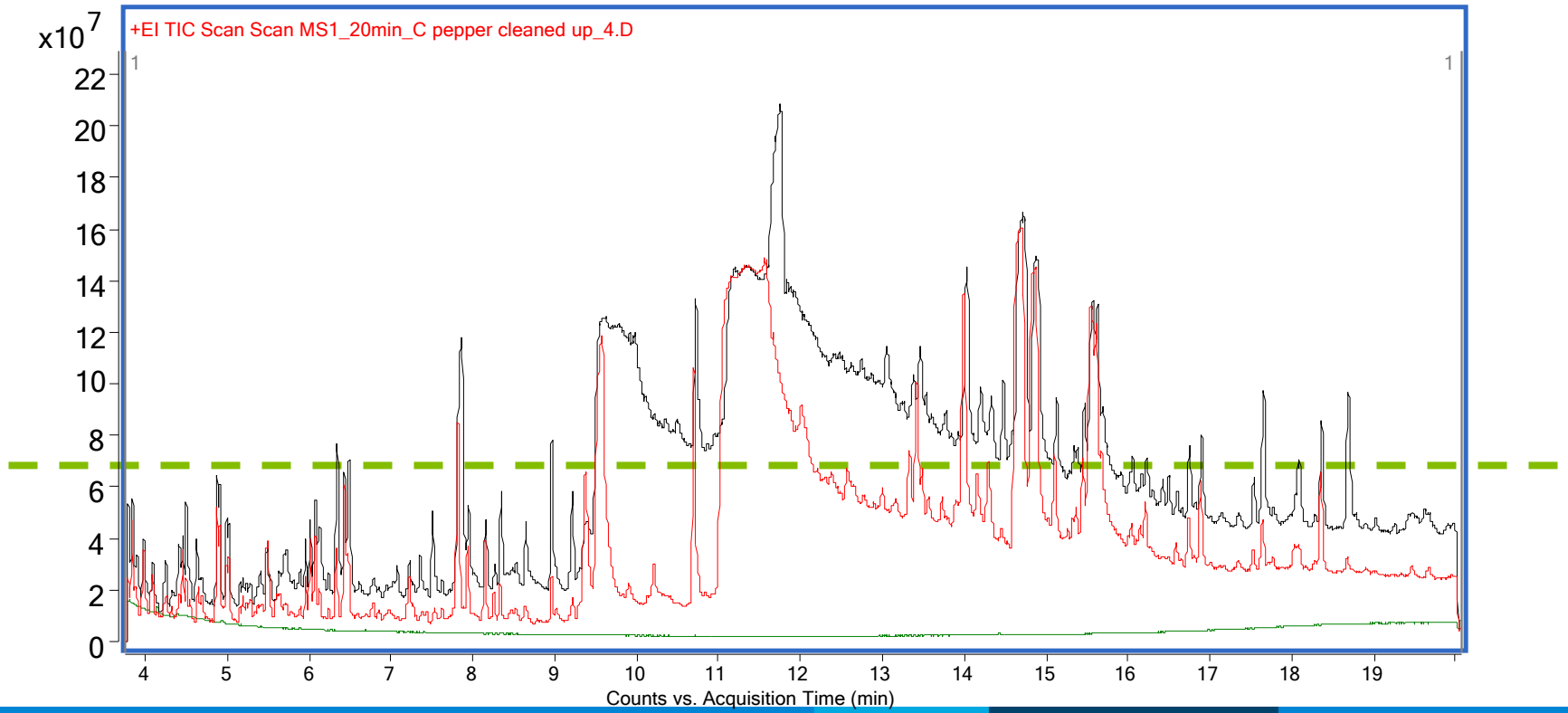
1

Adequate sample preparation (especially with the 7010C)
Sometimes dilution may yield better sensitivity and enhance robustness

2

Evaluation of in-source loading of the matrix in full scan:
Sometimes less is more

If TIC > $7x10^7$
in Scan mode
with gain 1 - dilute



3. Midcolumn Backflushing

Adequate sample preparation (especially with the 7010C)
Sometimes dilution may yield better sensitivity and enhance robustness

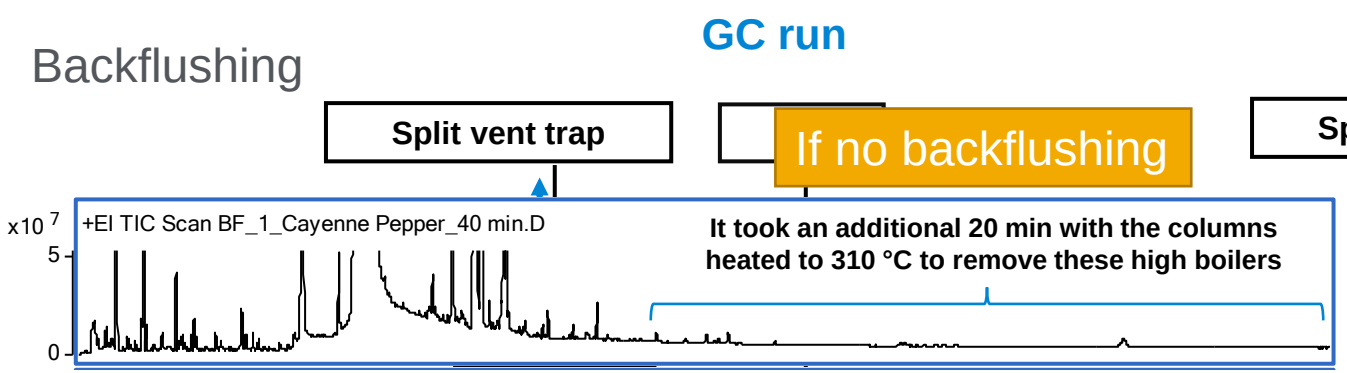
Evaluation of in-source loading of the matrix in full scan:
Sometimes less is more

Backflushing

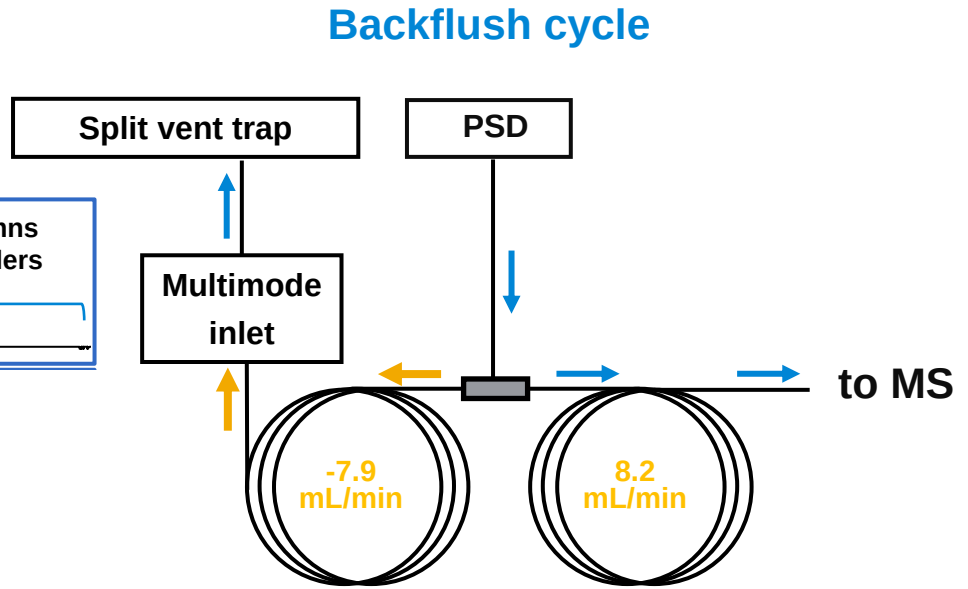
3. Midcolumn Backflushing

3

Backflushing



With backflushing



If no backflushing

3. Midcolumn Backflushing

3

Backflushing eliminates the need for bakeout:

- No deposition of high-boilers and GC column stationary phase into the EI source
- Increases GC column lifetime
- Significantly reduces the need for column trimming

Self Tightening Column Nut Installation – Inlet and Detectors https://www.agilent.com/en/video/stcn-inlet-detector
Self Tightening Column Nut Installation – MS Interface https://www.agilent.com/en/video/stcn-mass-spec
Gold-plated Flexible Metal Ferrules for GC – p/n G2855-28501

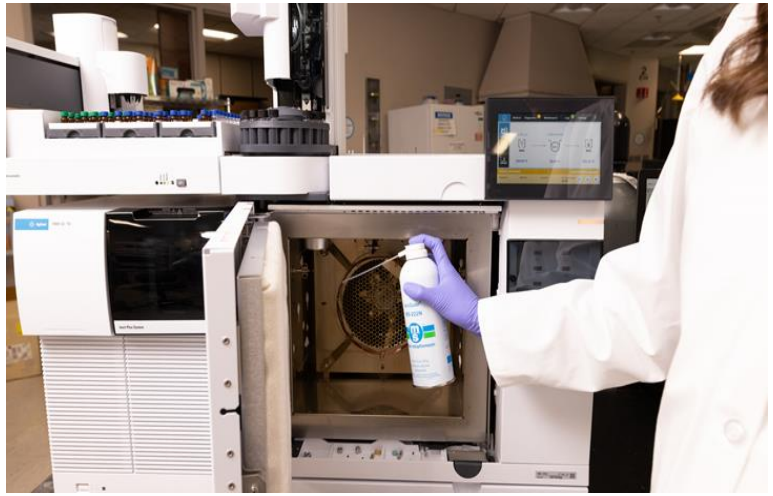
Keys to Unlocking Excellent Performance in Pesticides Analysis with GC/TQ

1. Evaluation of in-source loading of the matrix in full scan:
   Sometimes less is more

2. Adequate sample preparation (especially with the 7010C)
   Sometimes dilution may yield better sensitivity and enhance robustness

3. Backflushing

4. Keep the leaks out



Keys to Unlocking Excellent Performance in Pesticides Analysis with GC/TQ

1. Evaluation of in-source loading of the matrix in full scan:
   Sometimes less is more
2. Adequate sample preparation (especially with the 7010C)
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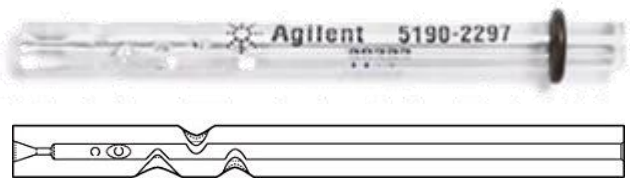
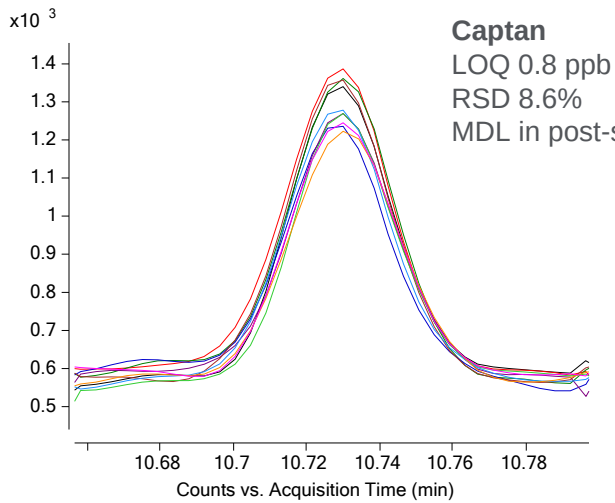
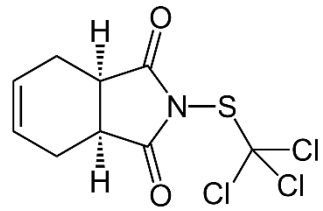
3. Backflushing
4. Keep the leaks out
5. Use of the temperature-programmed MMI with a 2 mm dimpled liner





Captan
LOQ 0.8 ppb in vial (100 ppb in dried cannabis)
RSD 8.6%
MDL in post-spiked matrix 584 fg on-column



https://www.agilent.com/cs/library/applications/application-sensitive-and-robust-detection-of-pesticides-in-dried-cannabis-8890-7010b-triple-quadrupole-gc-ms-5994-0568en-agilent.pdf

Results

App note 5994-4965EN

Application Note

Food & Beverage Testing

Agilent

Trusted Answers

5994-4965EN

Five Keys to Unlock Maximum Performance in the Analysis of Over 200 Pesticides in Challenging Food Matrices by GC/MS/MS

Authors

Anastasia A. Andrianova and Limian Zhao

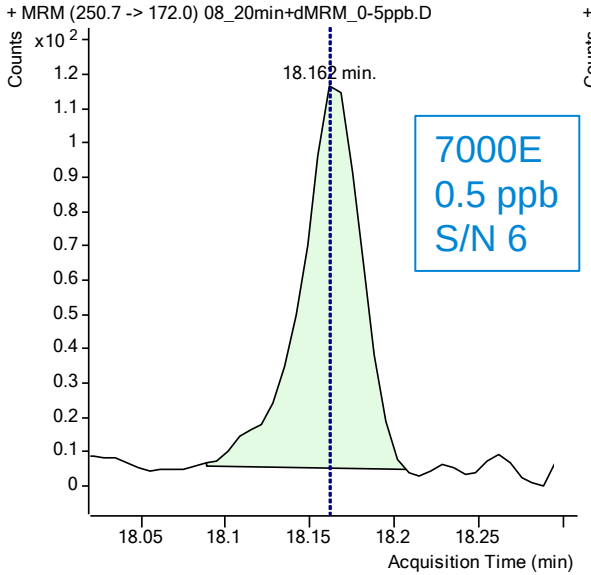
Agilent Technologies, Inc.

Abstract

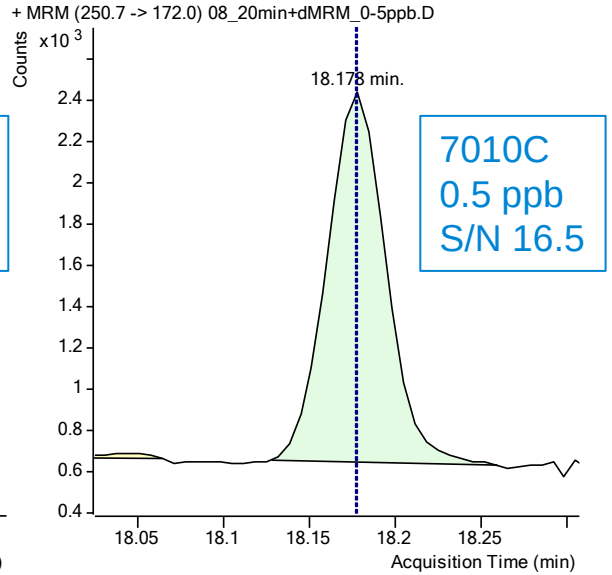
This application note describes five best practices to enhance analytical performance in the analysis of over 200 pesticides in challenging matrices including spinach, walnut, and cayenne pepper. The novel Agilent Captiva EMR passthrough cleanup procedure following the Agilent QuEChERS extraction enabled a cleaner matrix background. The cleanup and extraction reduced matrix interferences with target analytes and extended the maintenance-free operation time of the instrument. Calibration performance was demonstrated over a wide dynamic range to over four orders of magnitude. It was shown that the Agilent 8890/7000E triple quadrupole GC/MS system achieved excellent linearity over a concentration range of 0.1 to 5,000 ppb. The Agilent 8890/7010C triple quadrupole GC/MS system demonstrated superior sensitivity yielding a higher signal-to-noise ratio at lower concentrations.

High Sensitivity for Deltamethrin and Pentachloronitrobenzene in Walnut

Deltamethrin: MRL in walnut 100 ppb

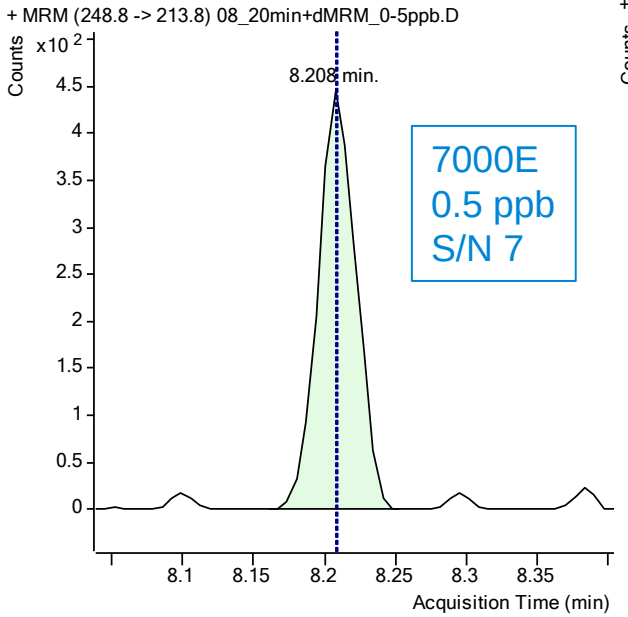


7000E
0.5 ppb
S/N 6

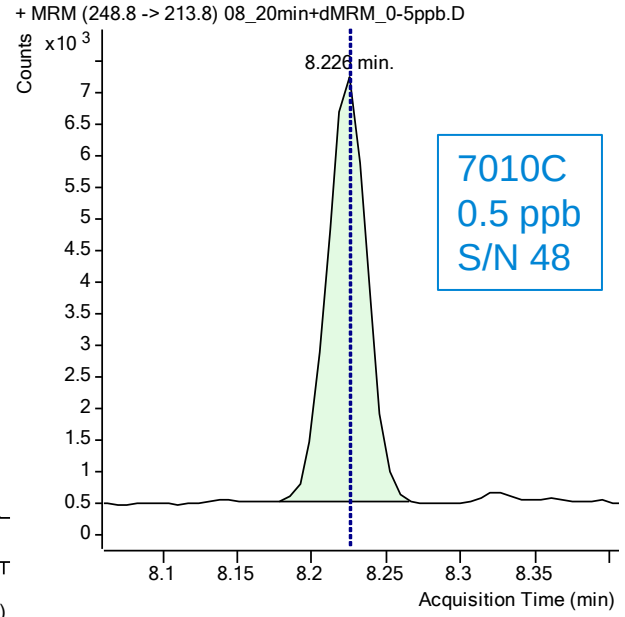


7010C
0.5 ppb
S/N 16.5

Pentachloronitrobenzene: No MRL in walnut
But regulated in many vegetables and fruits (20 ppb – 1 ppm)
Cannot be done with LC/MS



7000E
0.5 ppb
S/N 7

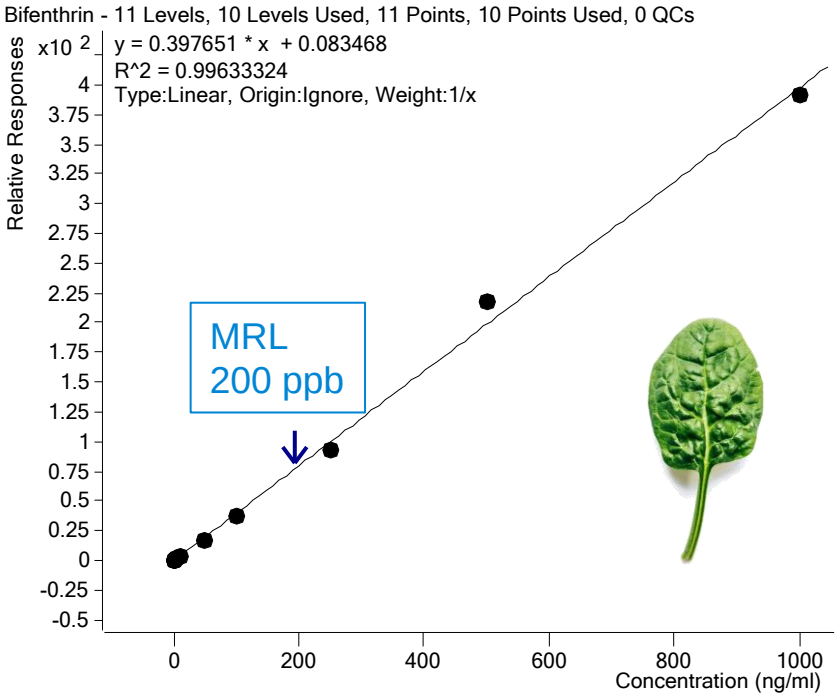


7010C
0.5 ppb
S/N 48

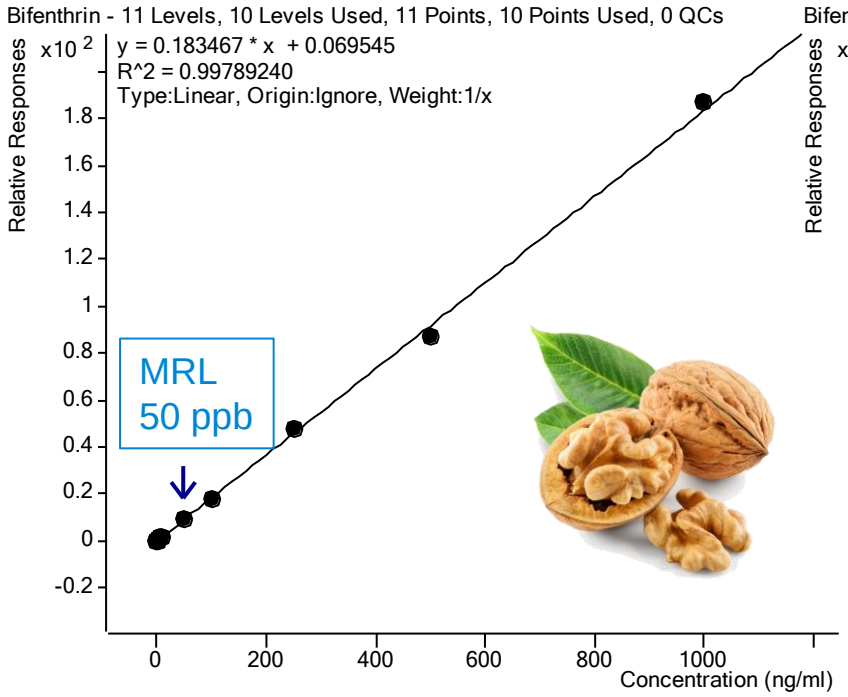
Calibration Performance Over a Wide Dynamic Range with the 7000E GC/TQ

Bifenthrin: encompassing varying MRLs in different commodities

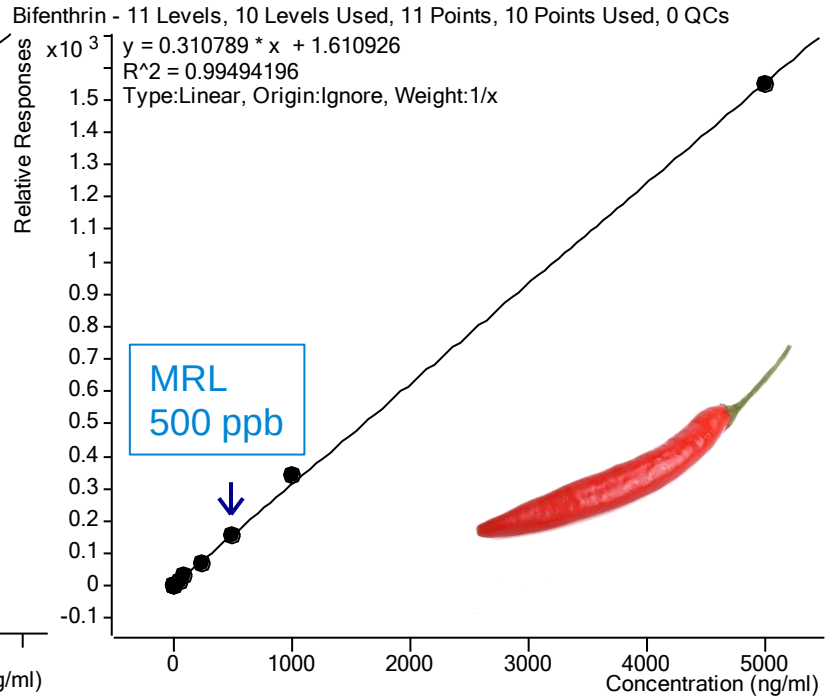
Spinach



Walnut



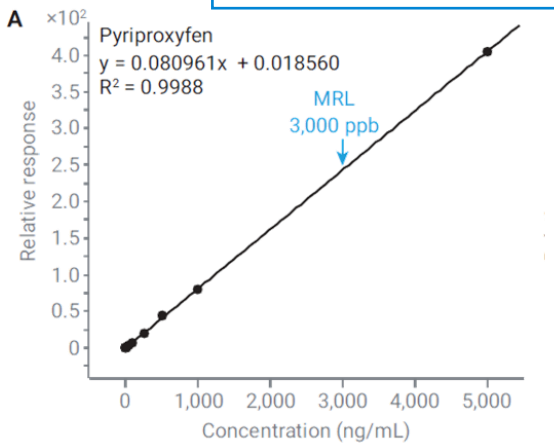
Cayenne pepper



Calibration Over a Wide Dynamic Range with the 7000E and 7010C GC/TQ

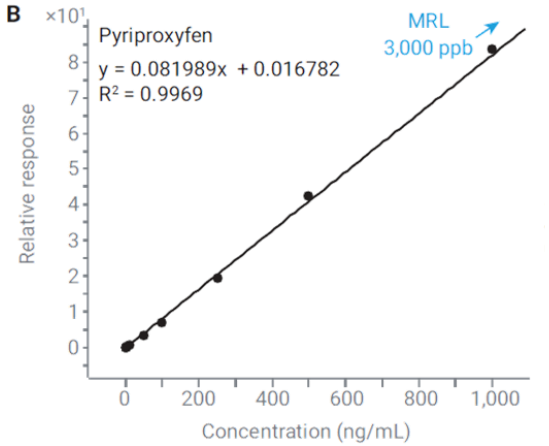
Pyriproxyfen and fludioxonil: widely different MRLs in spinach (3,000 and 10 ppb)

7000E: 0.1-5,000 ppb



Pyriproxifen:
MRL in spinach 3,000 ppb

7010C: 0.1-1,000 ppb



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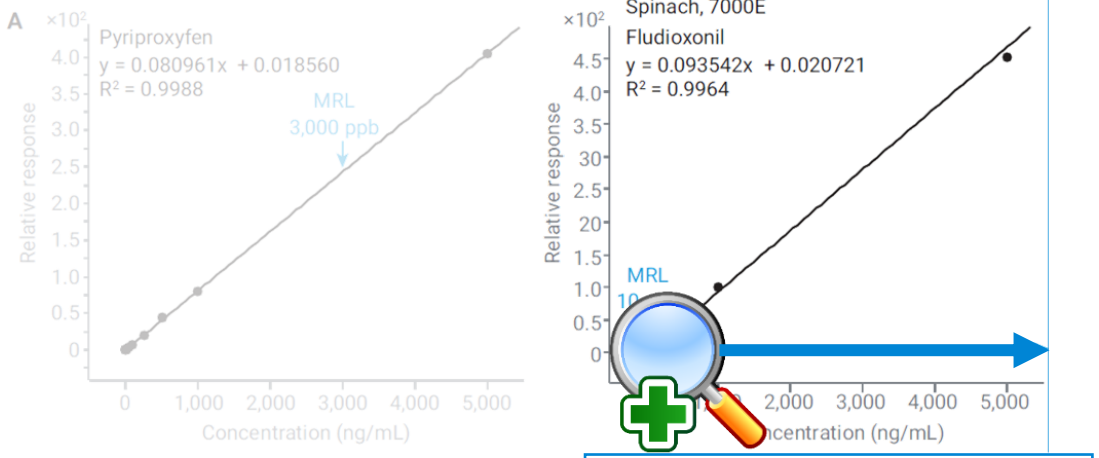
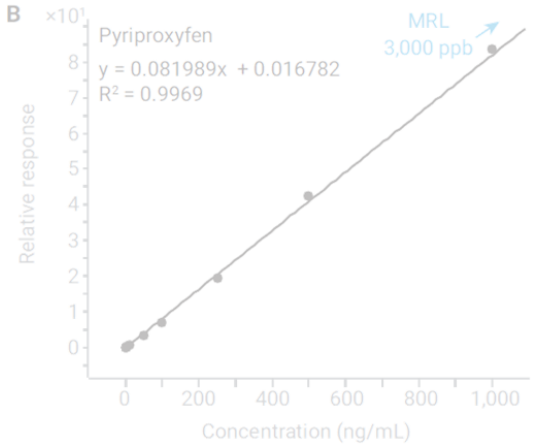
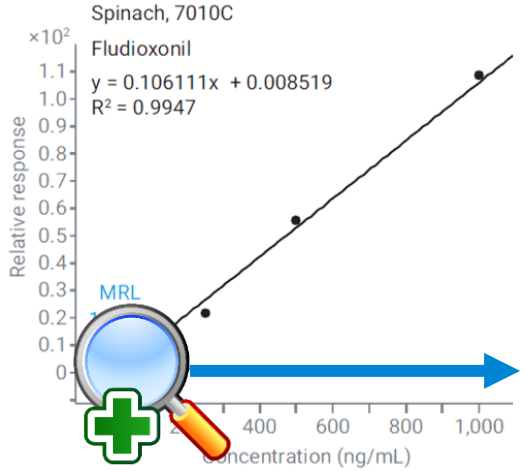


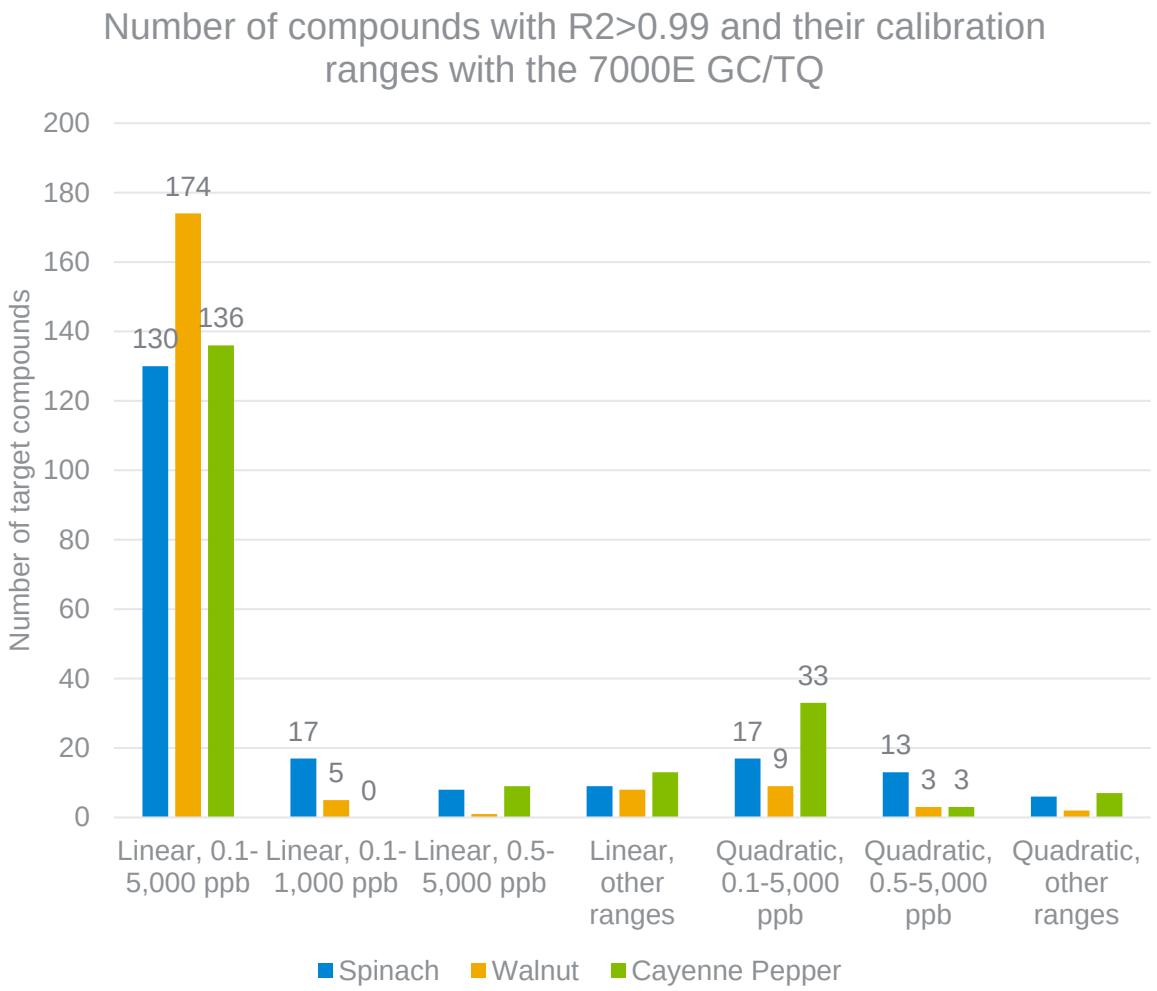
7010C: 0.1-1,000 ppb

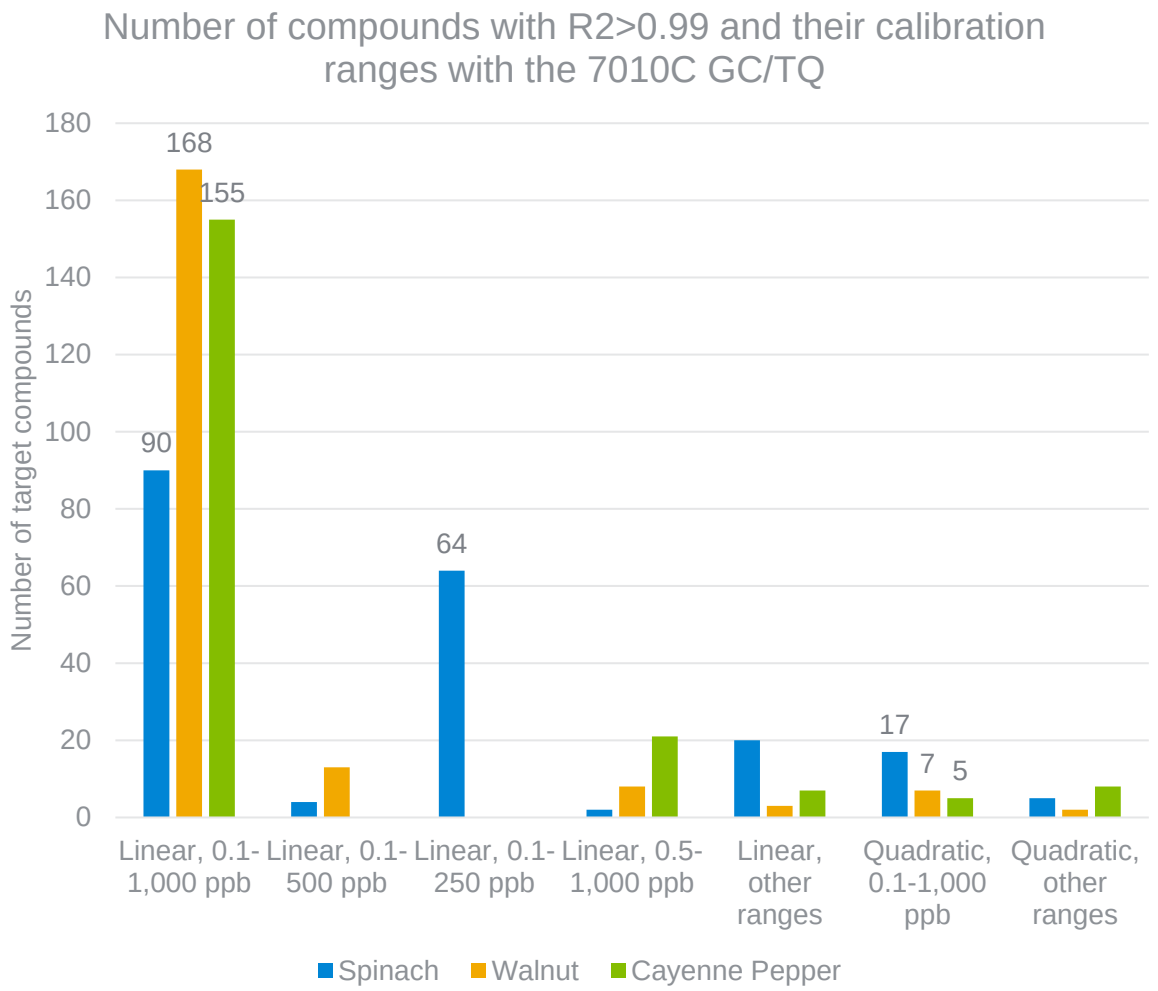




Fludioxonil:
MRL in spinach 10 ppb

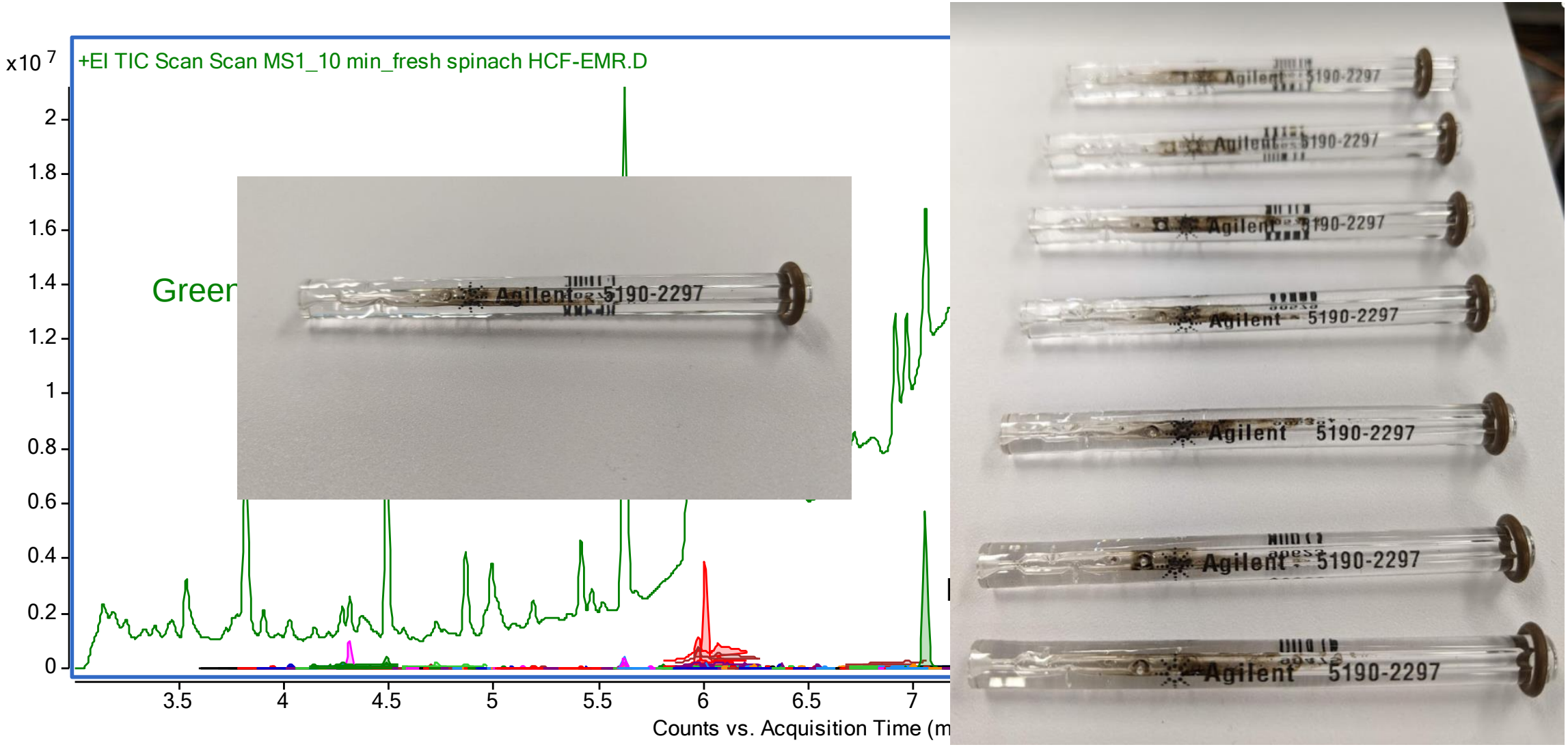
Calibration Performance for the 203 Pesticides with the 7000E and 7010C GC/TQ in Spinach, Walnut, and Cayenne Pepper





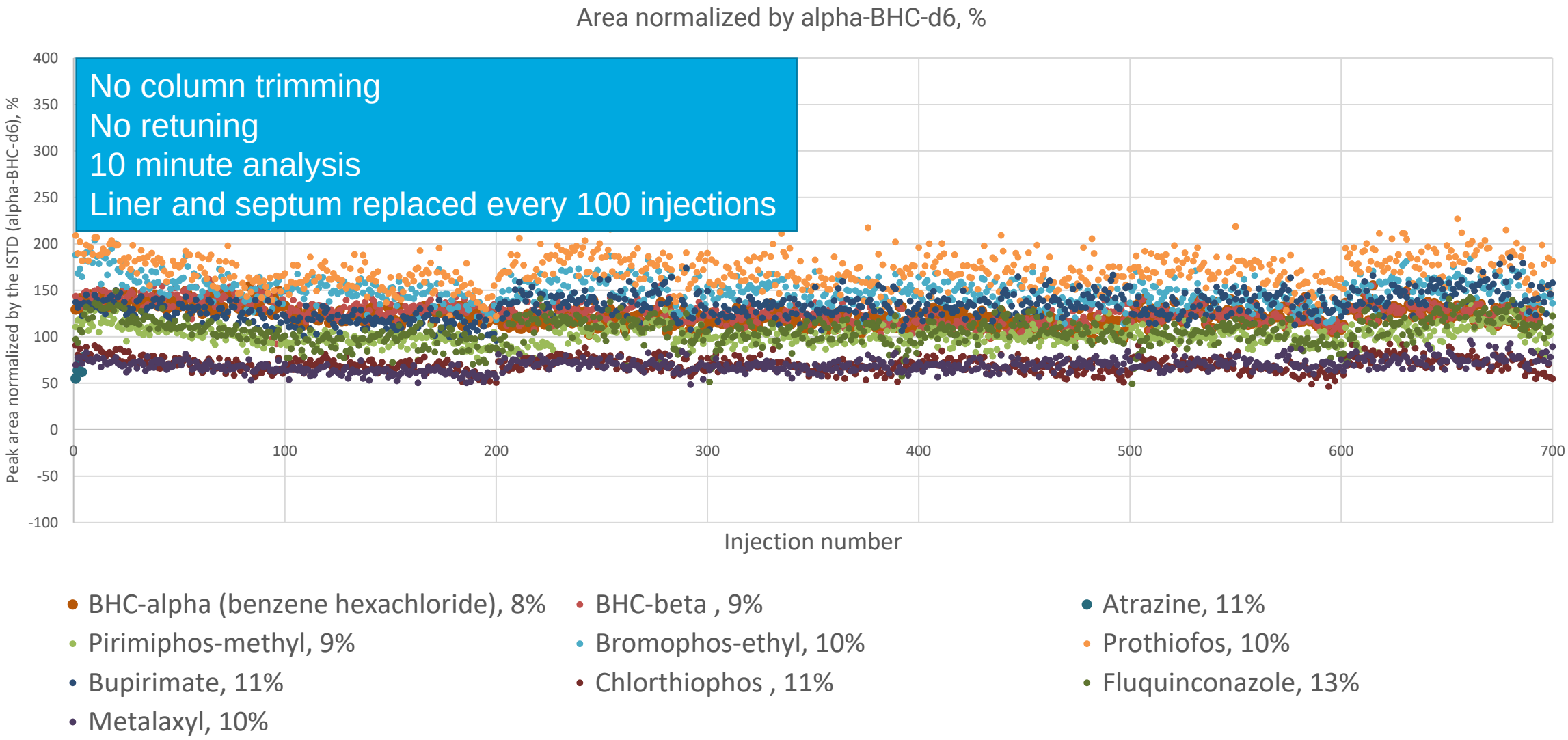
Spinach QuEChERS Extract – for Longevity Study

7000E (pesticides spiked at 20 ppb), 10 minute analysis



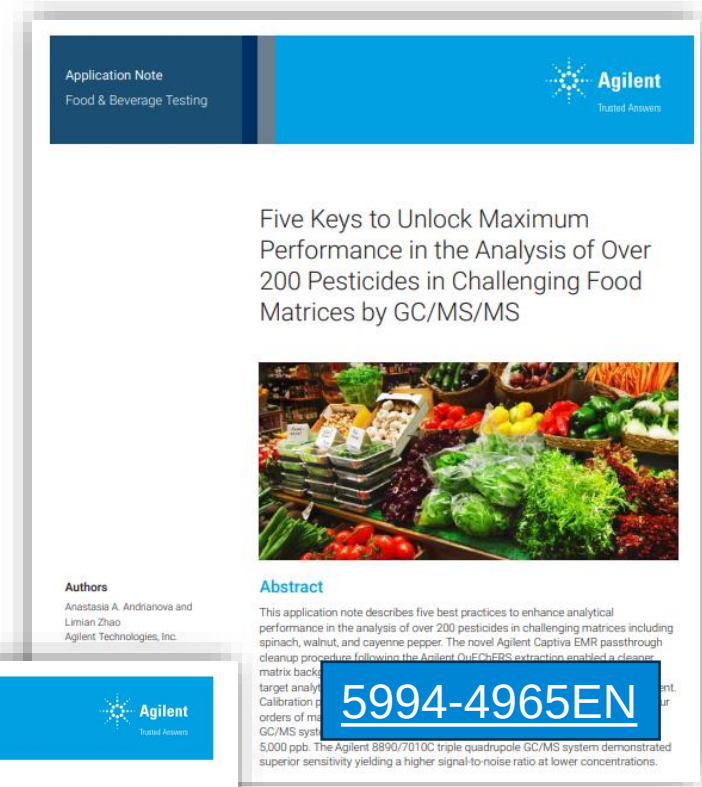
Longevity: Area Normalized by the ISTD, 20 ppb in Spinach with 7000E (10 min)

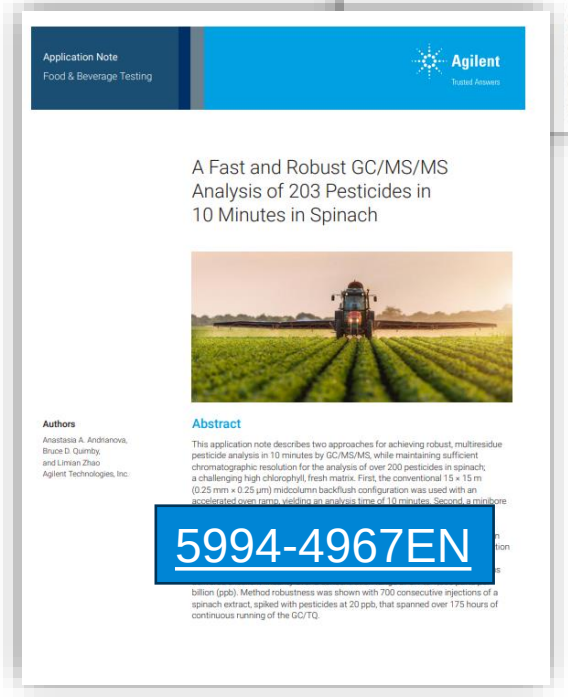
Normalized response of pesticides at 20 ppb spiked into QuEChERS EMR-HCF spinach



Five Best Practices in Sample Preparation and GC/MS/MS Analysis

- Simplified and improved sample preparation
  achieved with the novel and improved Agilent Captiva EMR pass-through cleanup, following traditional Agilent QuEChERS extraction
- Evaluation of in-source loading of the matrix in full scan data acquisition mode
- Midcolumn backflushing
- Leak-free GC/triple quadrupole system
  enabled with Self Tightening collared column nuts and CFT gold-plated flexible metal ferrules
- Use of temperature-programmed multimode inlet with a 2 mm dimpled liner (no glass wool)
- Robustness over 700 injections

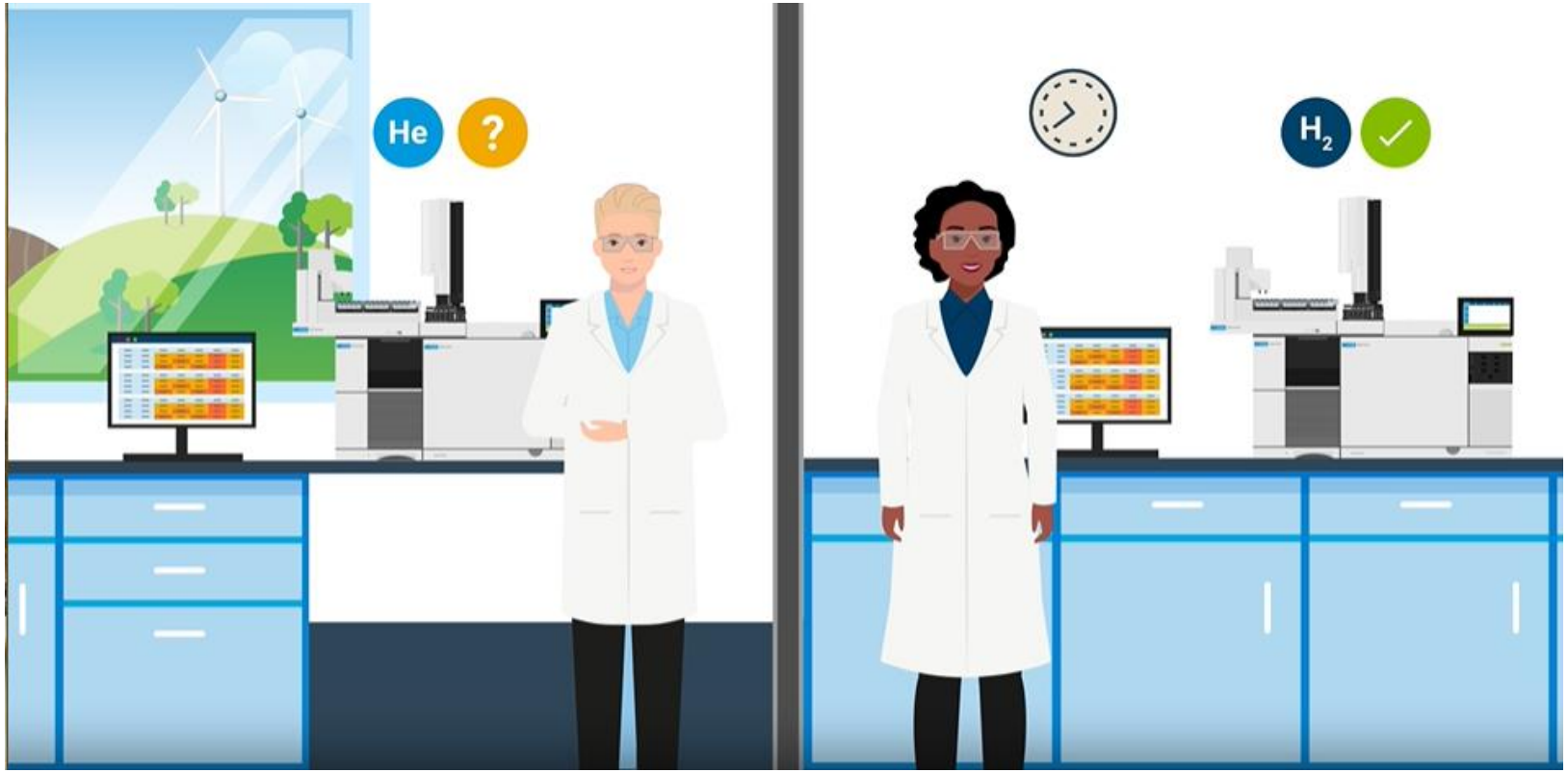




How About Hydrogen Carrier Gas?

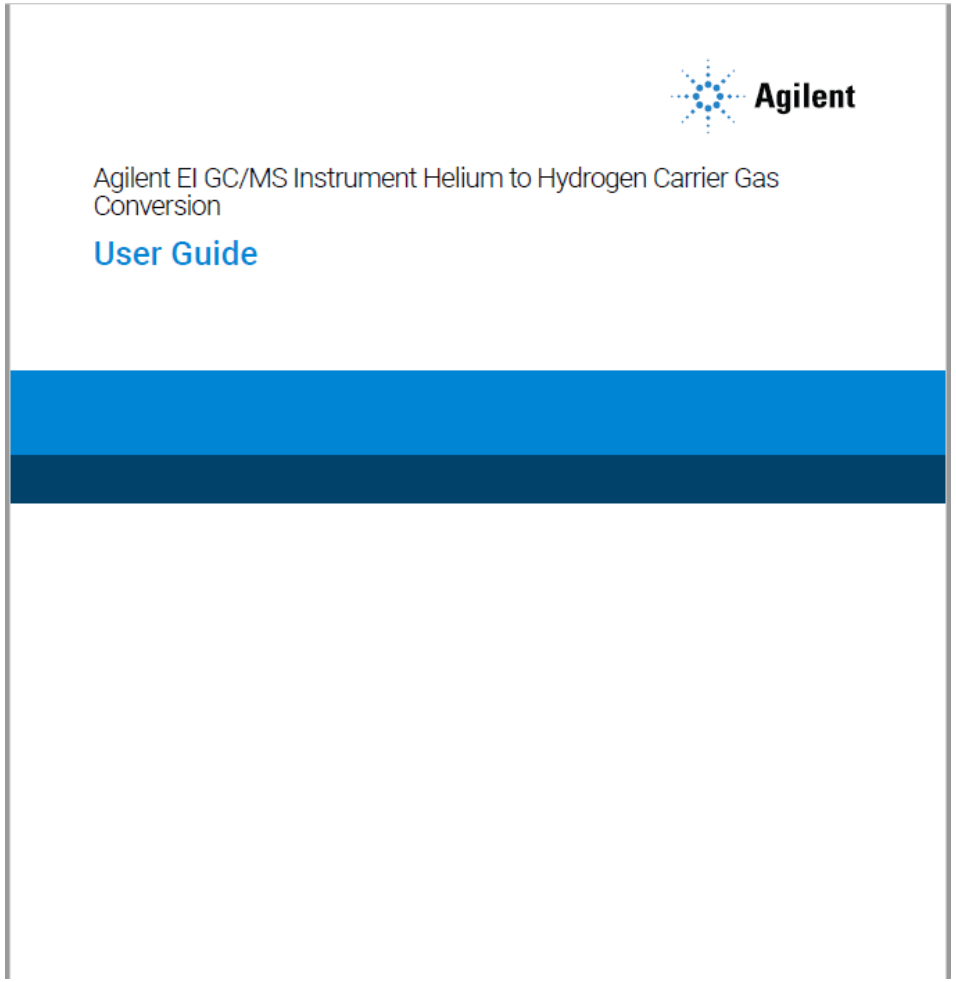
Hydrogen As a Carrier Gas in GC/MS/MS

- Hydrogen is the preferred carrier gas for GC/MS
- Ongoing shortages and increased prices cause unpredictability



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

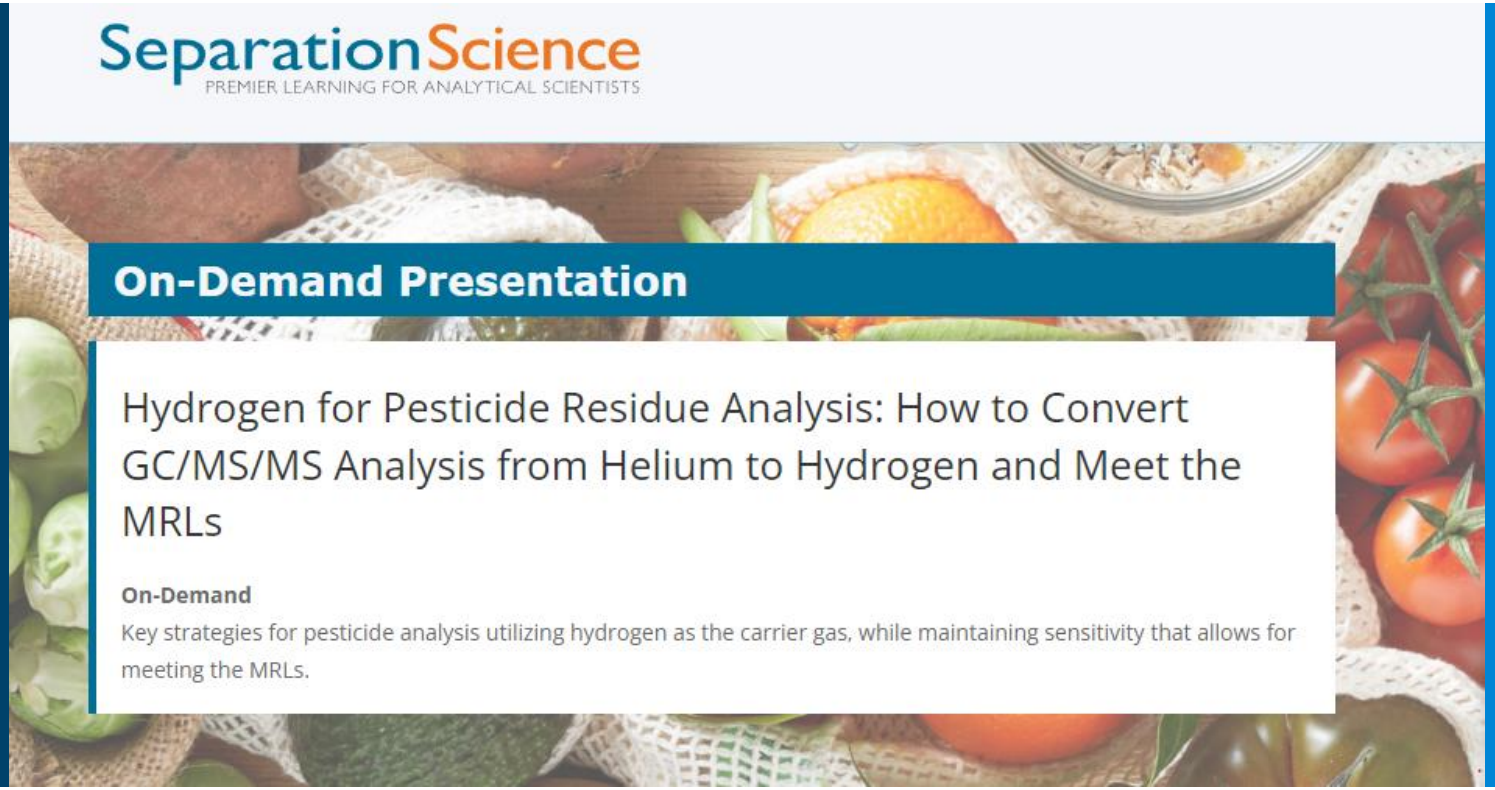
5994-2312EN



- Contains detailed instructions for method conversion from He to H_2 carrier.
- **Essential read** before converting to H_2.

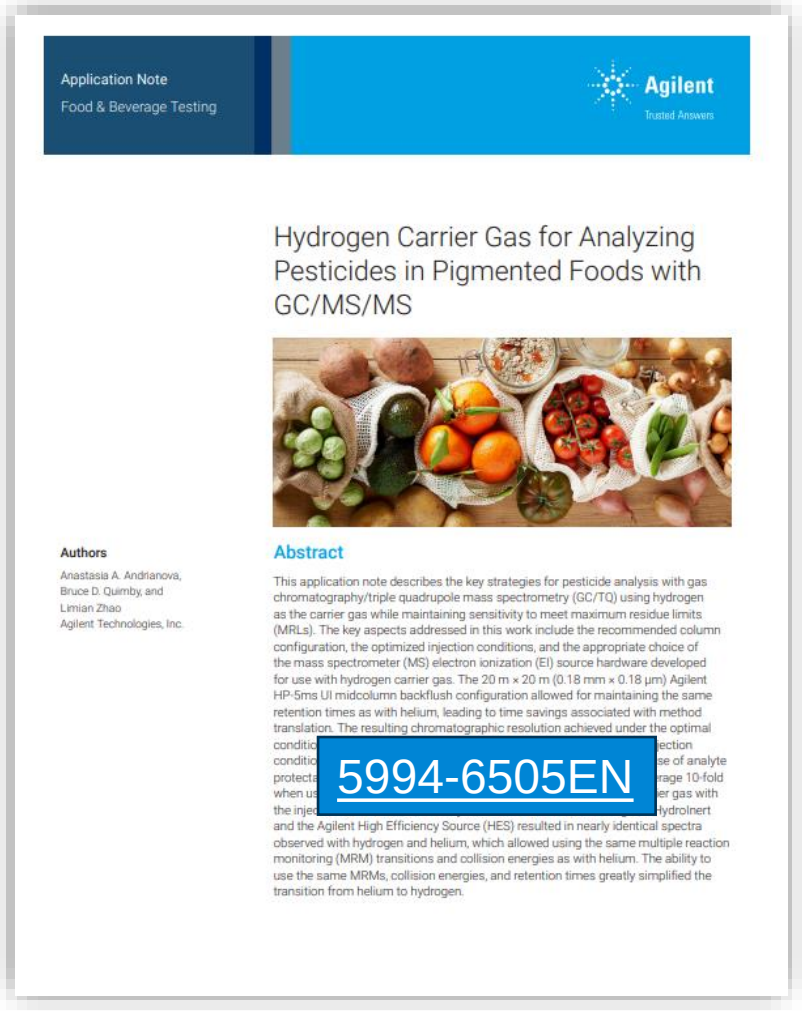
Hydrogen for Pesticide Residue Analysis: How to Convert GC/MS/MS Analysis from Helium to Hydrogen and Meet the MRLs

Webinar available ondemand:
Link to watch



GC/MS Recipe for Success with Hydrogen

- H_2 carrier gas
- HydroInert Source optimized for use with hydrogen
- 20 × 20 m (0.18 mm × 0.18 µm) HP-5ms UI
- Starting column flows: 0.9 and 1.1 mL/min
- Retention time lock to chlorpyrifos methyl (9.143 min)
- **Same retention times** with H_2 as with the conventional He method (20 minutes)
- Ability to perform 10 minute analysis with excellent resolution


Application Note
Food & Beverage Testing

Agilent
Trusted Answers

Hydrogen Carrier Gas for Analyzing Pesticides in Pigmented Foods with GC/MS/MS

Authors

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Agilent Technologies, Inc.

Abstract

This application note describes the key strategies for pesticide analysis with gas chromatography/triple quadrupole mass spectrometry (GC/TQ) using hydrogen as the carrier gas while maintaining sensitivity to meet maximum residue limits (MRLs). The key aspects addressed in this work include the recommended column configuration, the optimized injection conditions, and the appropriate choice of the mass spectrometer (MS) electron ionization (EI) source hardware developed for use with hydrogen carrier gas. The 20 m × 20 m (0.18 mm × 0.18 µm) Agilent HP-5ms UI midcolumn backflush configuration allowed for maintaining the same retention times as with helium, leading to time savings associated with method translation. The resulting chromatographic resolution achieved under the optimal

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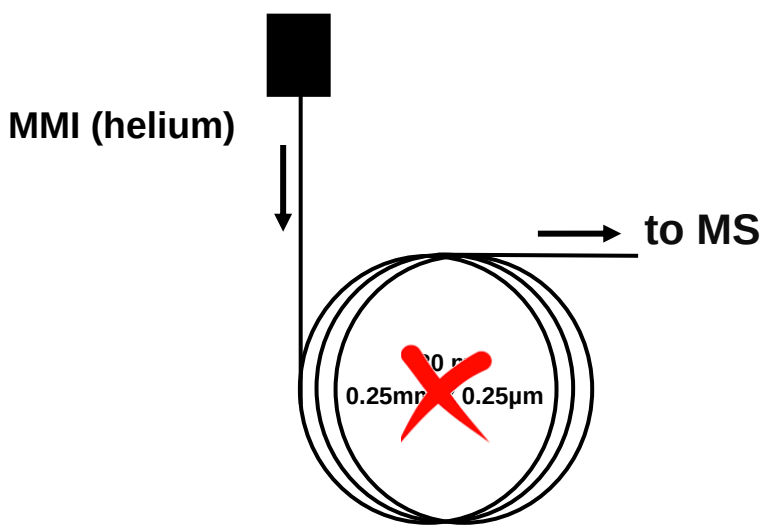
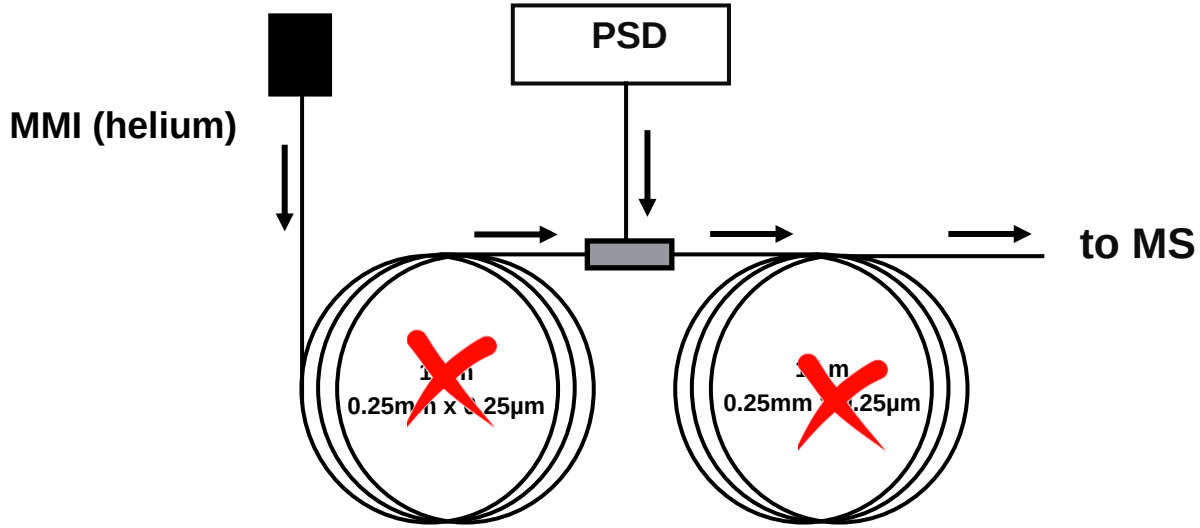
and the Agilent High Efficiency Source (HES) resulted in nearly identical spectra observed with hydrogen and helium, which allowed using the same multiple reaction monitoring (MRM) transitions and collision energies as with helium. The ability to use the same MRMs, collision energies, and retention times greatly simplified the transition from helium to hydrogen.

GC Configuration and Method Considerations

~~Conventional 15 x 15 m (or 30 m)~~
~~0.25 mm x 0.25 µm~~

Cannot be used with H_2 carrier gas
because of insufficient inlet pressure





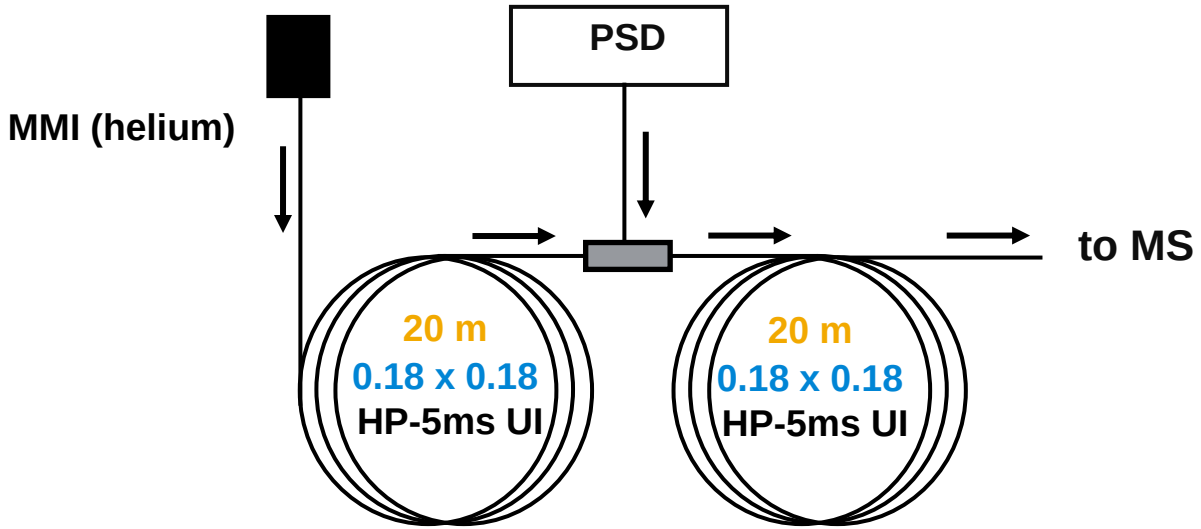
GC Configuration and Method Considerations

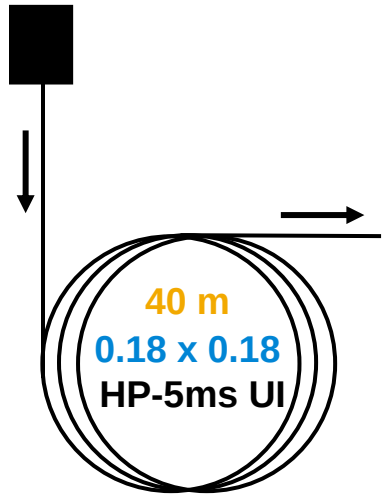
20 x 20 m
0.18 mm x 0.18 µm

Compatible with H_2 carrier gas

Analysis time **20 minutes**

Maintain the same RTs and elution order
30 m, 0.25 mm x 0.25 µm → 20 m, 0.18 mm x 0.18 µm





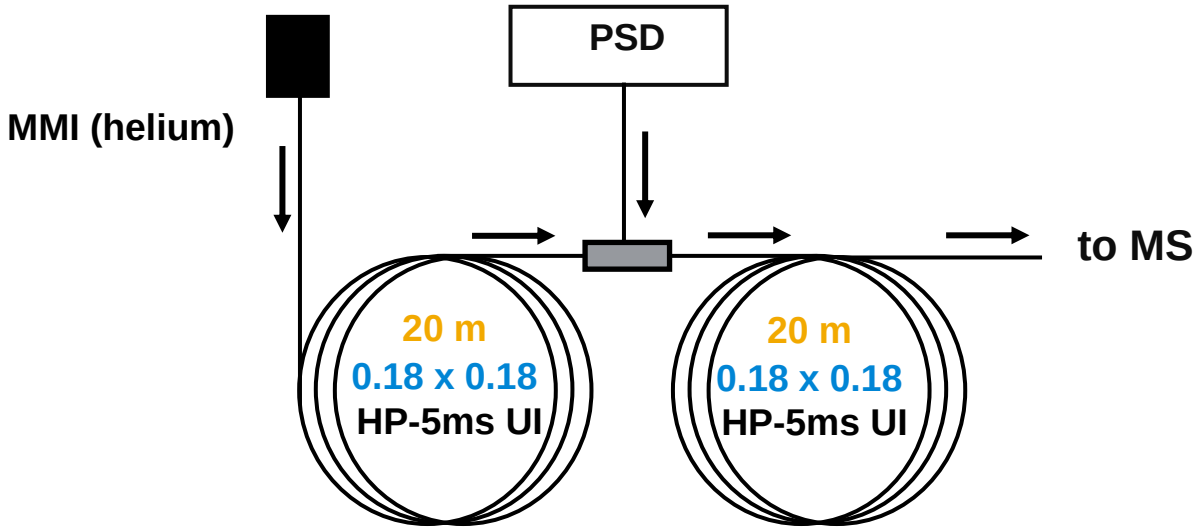
GC Configuration and Method Considerations

20 x 20 m
0.18 mm x 0.18 µm

Compatible with H_2 carrier gas

Analysis time **20 minutes**

Maintain the same RTs and elution order
30 m, 0.25 mm x 0.25 µm → 20 m, 0.18 mm x 0.18 µm



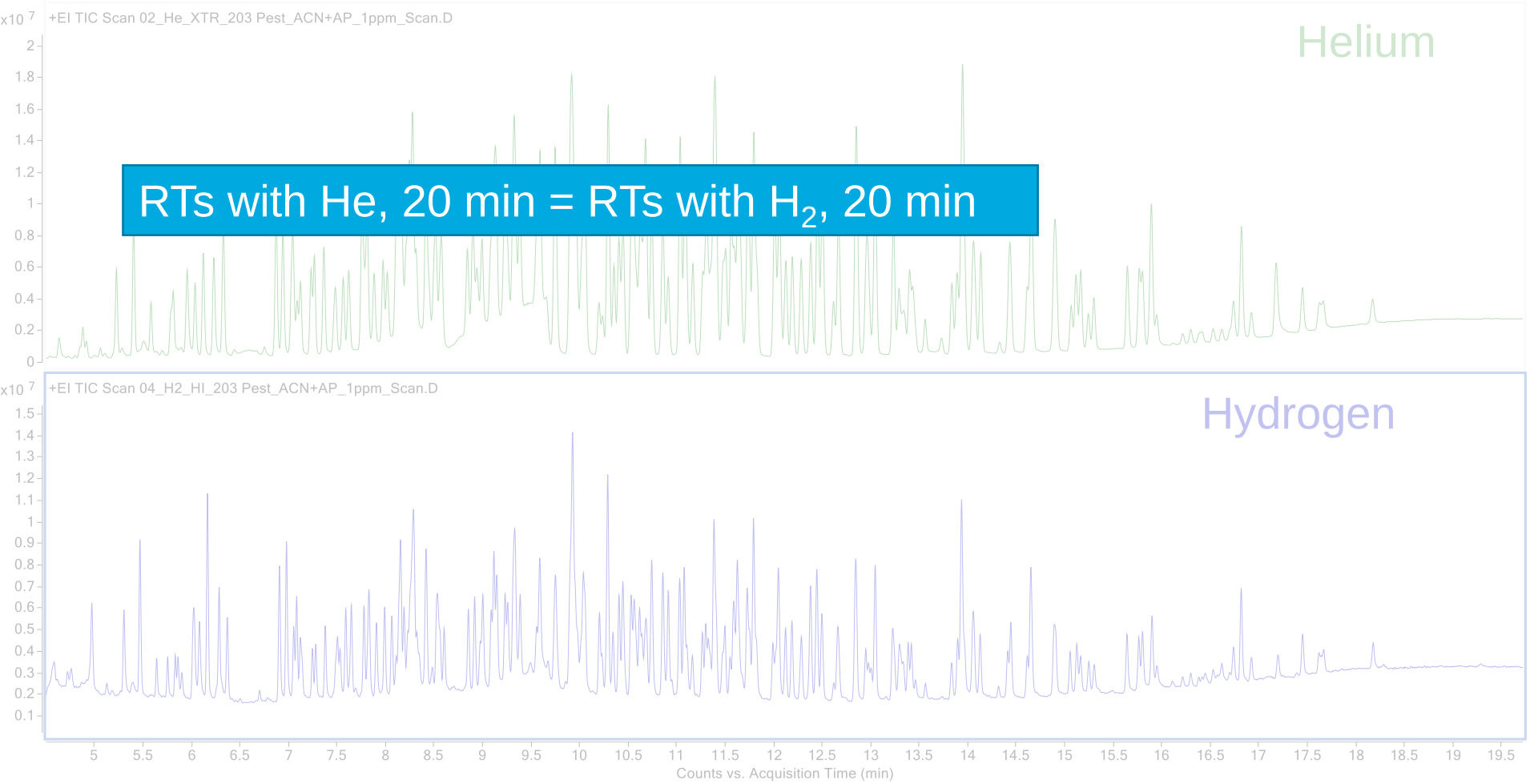
10 m x 10 m
0.18 mm x 0.18 µm

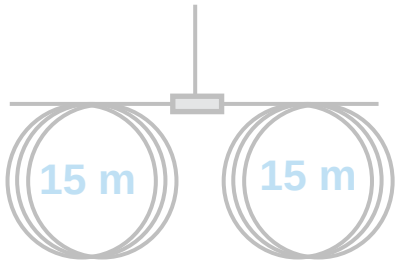
Compatible with H_2 carrier gas

Analysis time **10 minutes**

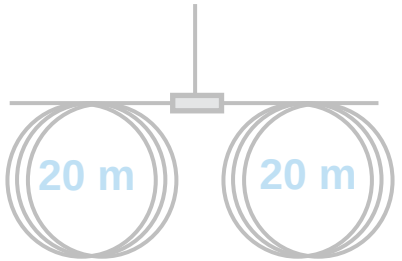
What Happens to the Retention Times and Resolution?

Exact Retention Time Matching Achieved with Method Translation and Retention Time Locking



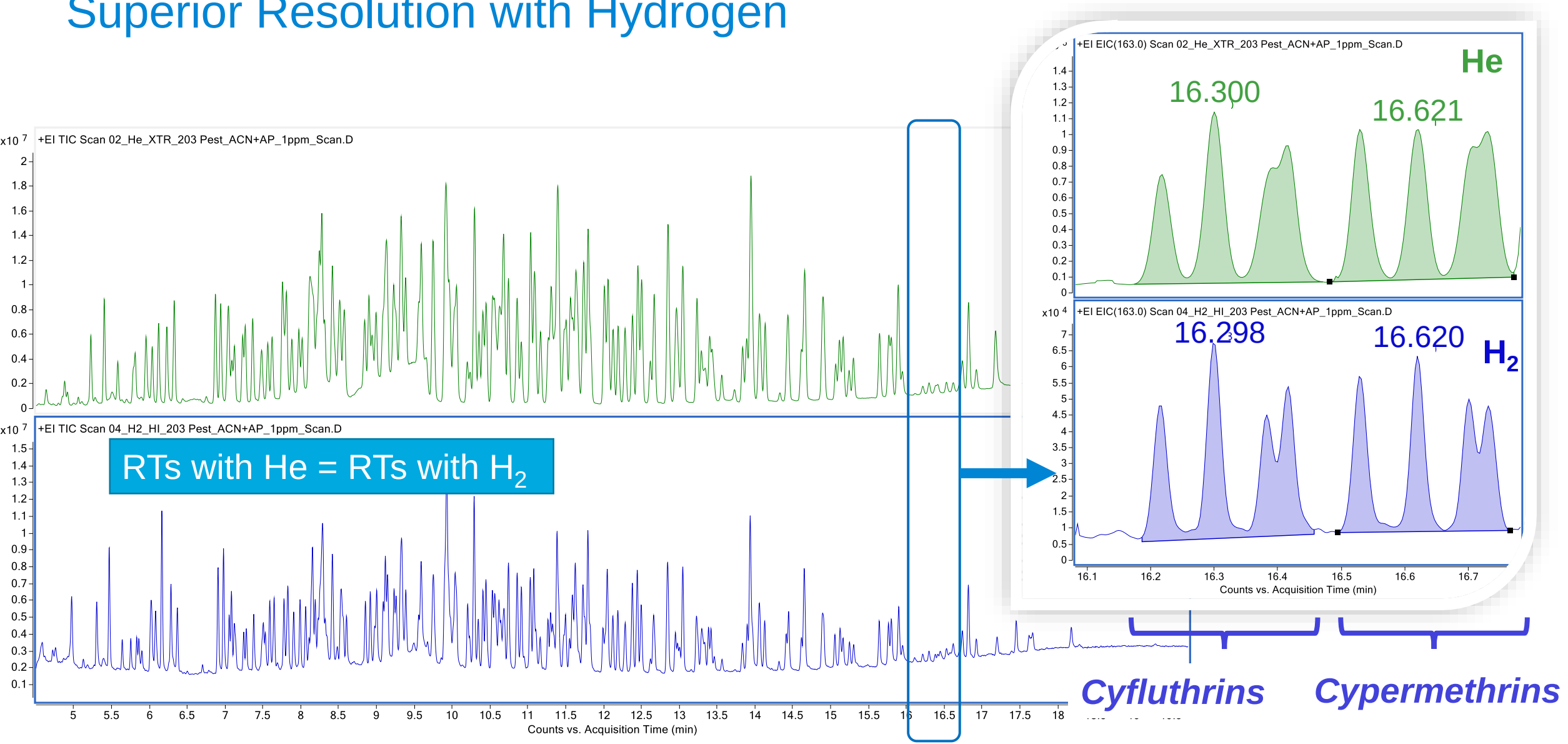


0.25 mm x 0.25 µm

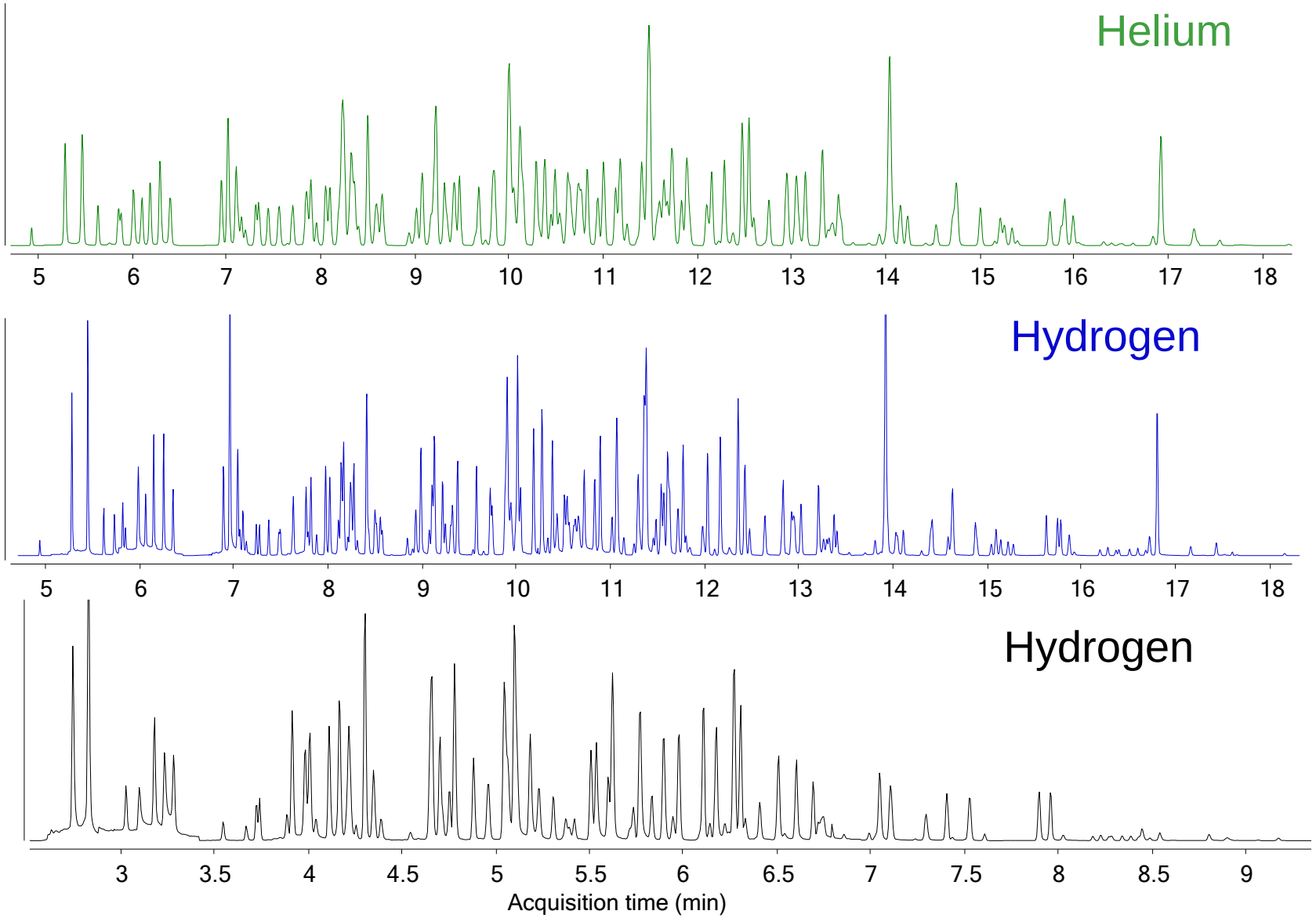


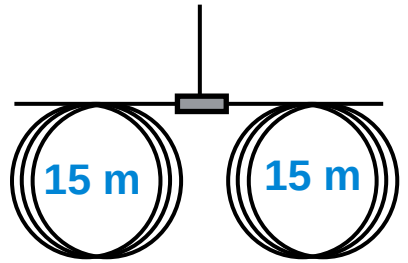
0.18 mm x 0.18 µm

Superior Resolution with Hydrogen

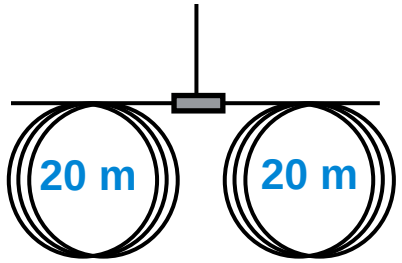


Proof of Concept: 10 Minutes with Hydrogen

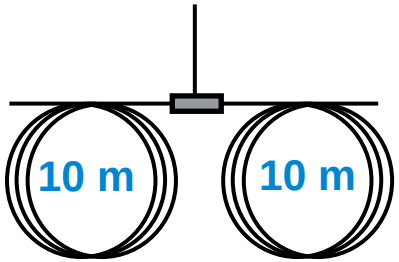




0.25 mm x 0.25 µm

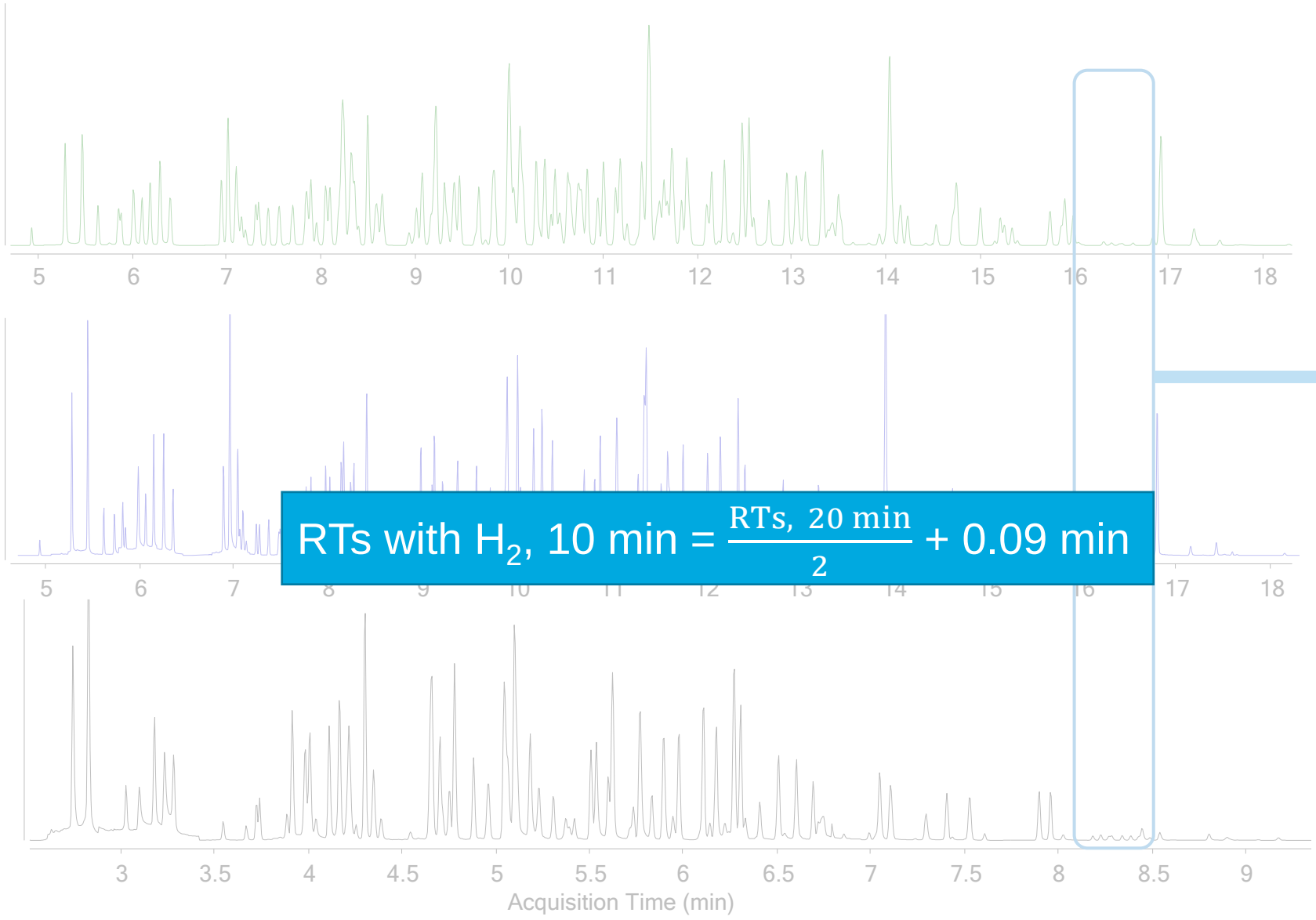


0.18 mm x 0.18 µm

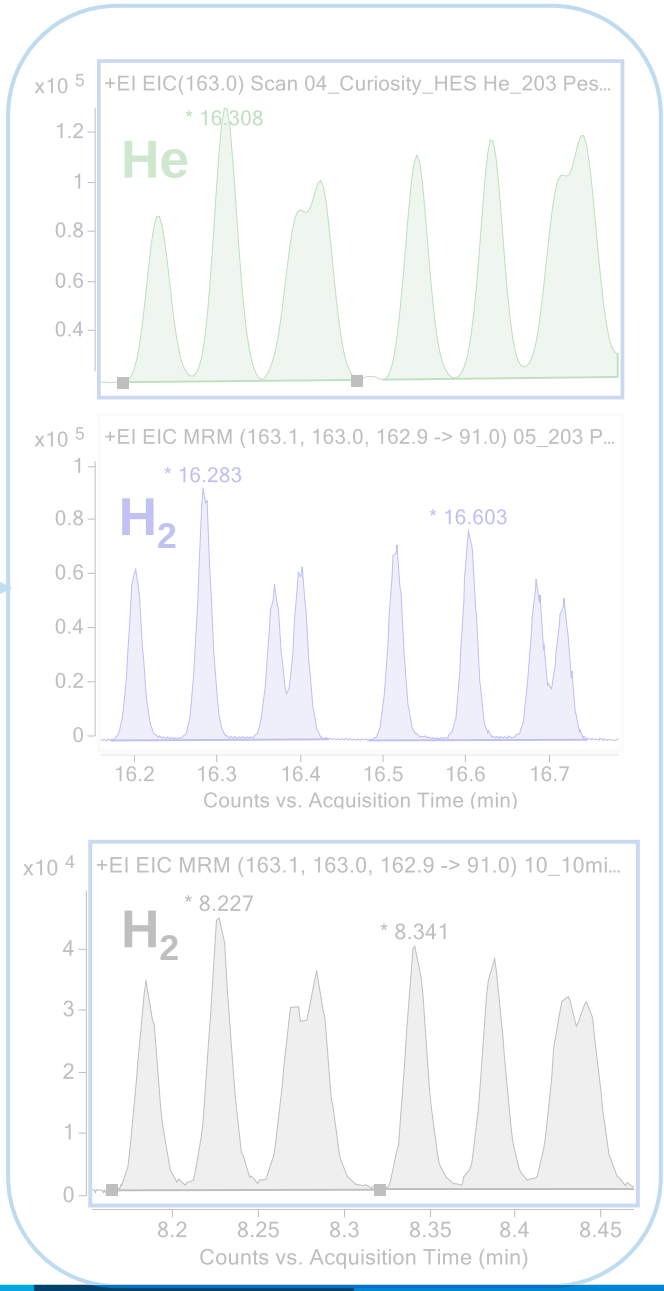


0.18 mm x 0.18 µm

10 Minutes with Hydrogen and Still Good Resolution



$$\text{RTs with } H_2\text{, 10 min} = \frac{\text{RTs, 20 min}}{2} + 0.09 \text{ min}$$

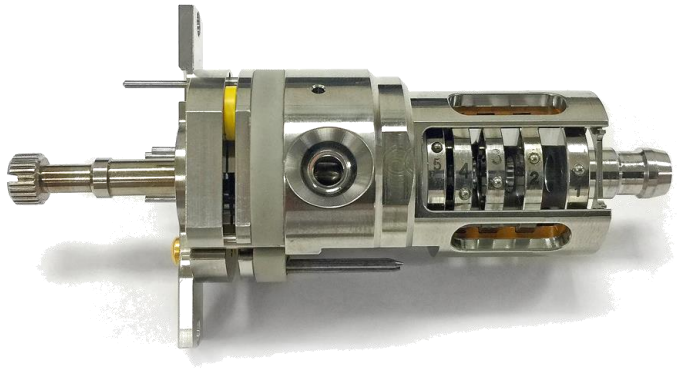


Electron Ionization MS Sources

Conventional EI Extractor (Inert Plus) Source

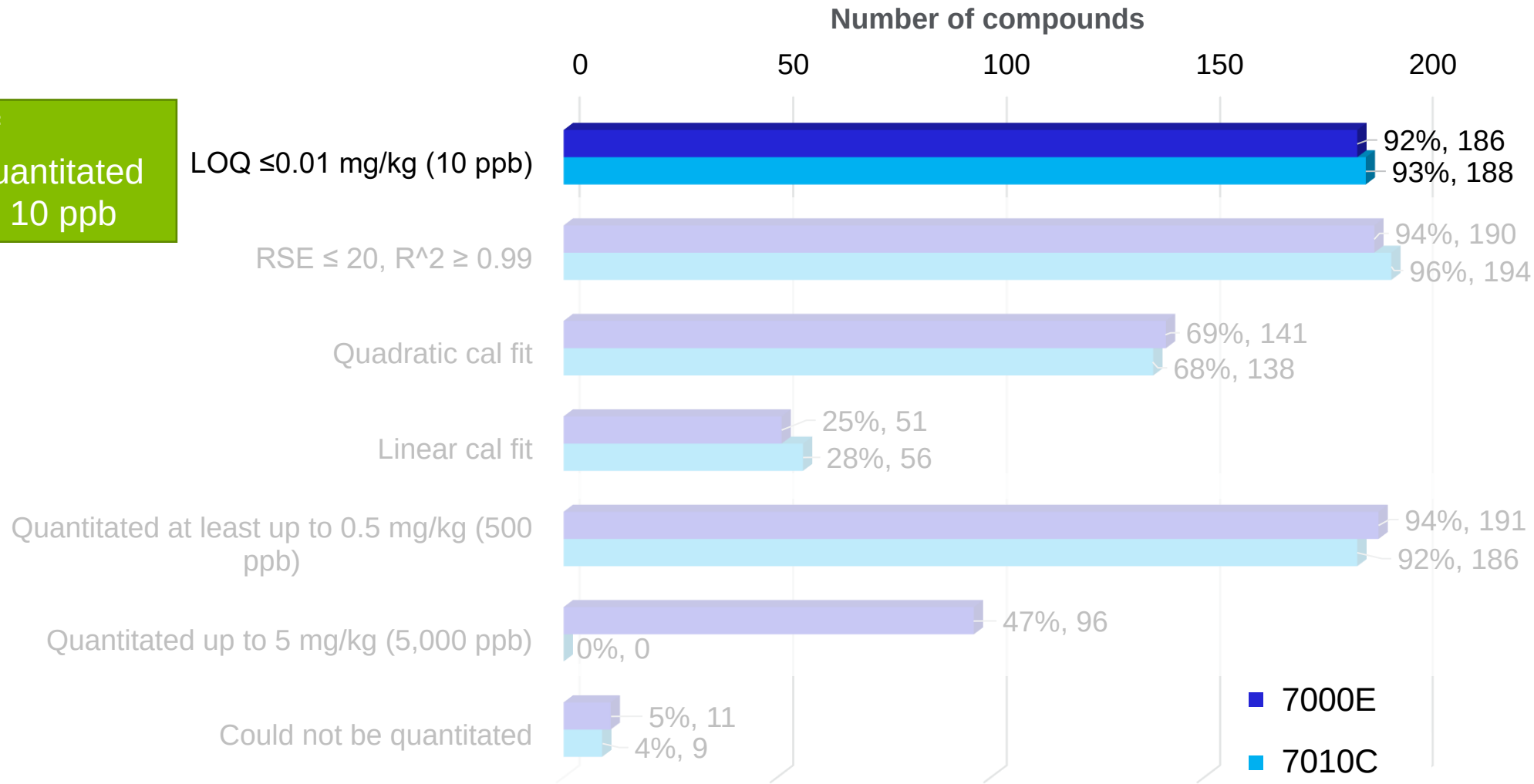
HydroInert EI Source

High Efficiency (HES) EI Source



Calibration Performance in Spinach QuEChERS Extract for 203 Pesticides

Over 92% of pesticides quantitated at (or below) 10 ppb



Summary of Analyzing Pesticides with H_2 Carrier Gas

- **Over 90%** of the evaluated **pesticides could be detected** at or below the default MRL of **10 ppb** in the vial
- However, just like with He, some pesticides may be more challenging to analyze at low concentrations
- Using **optimized GC conditions (injection, column set)** is essential when using H_2
- The optimized setup with H_2 **improved chromatographic resolution** and allowed for **precise matching of retention times** with He
- The same MRM transitions, with the same collision energies for the targets eluting at the same retention times as with He, could be used with H_2.

GC/TQ EI source considerations

The HydroInert EI source:

- Improved sensitivity compared to the standard EI with H_2
- Best spectral fidelity

The HES EI source:

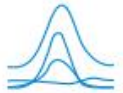
- Best sensitivity observed with H_2

Agilent GC/MS Best Practices

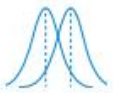
Infographic link

Dilute More, Inject Less

The GC/MS High-Efficiency Source (HES) is designed for ultimate sensitivity where a little goes a long way.



Significantly reduce interferences from matrix background



Peaks with horizontal line

GC/MS operation with excellent ultra-trace level sensitivity

Perform Sample Cleanup

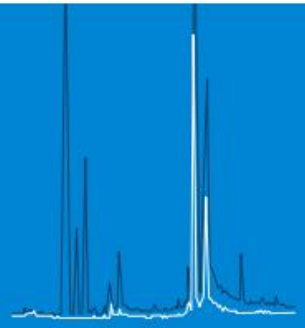
Sufficient sample preparation and sample cleanup is crucial to getting the most out of any GC/MS analysis.

Lessen in-source matrix loading and target interferences

Enhance signal-to-noise ratios and accuracy

Achieve greater reproducibility

Screen Sample Matrix



Performing matrix screening in full scan data acquisition mode facilitates the evaluation of in-source matrix loading.

Prevent source overload

Improve accuracy of analysis

Maintain optimal performance

Use Backflush

Mid-column backflushing extends t operation of the GC/MS system.

Reduce analysis time

Extend column life

Significantly reduce carryover

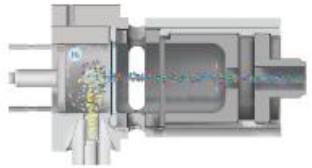
Implement JetClean

Patented JetClean technology uses a gentle flow of hydrogen through the source.

Save time cleaning, reconditioning, and recalibration

Achieve more consistent responses for target analytes

Keep the GC/MS source clean for increased sample throughput



Check for Leaks

To improve your GC/MS analysis, preventing leaks is critical. Agilent offers hardware and software tools to aid in identification of leaks at their source.

The Agilent CrossLab CS Electronic Leak Detector tool detects leaks of various gas types.

Leak test software functionality for GC/TQ identifies the source of leaks in real time when using a leak testing gas.


Q&A