

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

Becoming a Better Chromatographer
Educational Webinar Series
January 31, 2024

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GC/MS Applications Scientist



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



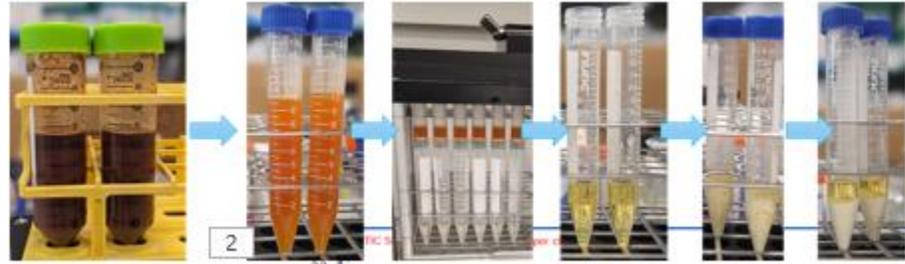
[Rev Environ Health. 2009 Oct–Dec; 24\(4\): 303–309.](#)

Pesticide Testing



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

Pesticide Analysis Workflow



Sample preparation



GC/MS analysis



Data Analysis & Reporting

GC/MS & LC/MS Analysis



Sample



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

Application Note
Food & Beverage Testing

Agilent
Trusted Answers

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 food matrices by GC/MS/MS. The authors discuss the importance of method development, including the choice of carrier gas, column, and detection method. The note highlights the benefits of using hydrogen as a carrier gas and the importance of maintaining the recommended column configuration. The authors also discuss the importance of the choice of the mass spectrometer (MS) electron ionization (EI) source hardware developed for use with hydrogen carrier gas. The 20 m x 20 m (0.18 mm x 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 conditions was 10-fold higher than that achieved with helium. The ability to use the same MRMs, collision energies, and retention times greatly simplified the transition from helium to hydrogen.

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Application Note
Food & Beverage Testing

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Trusted Answers

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



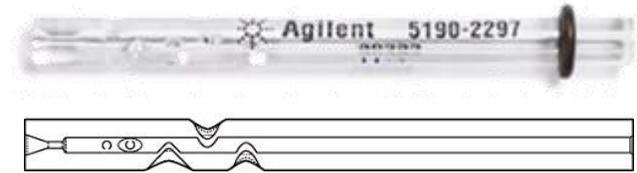
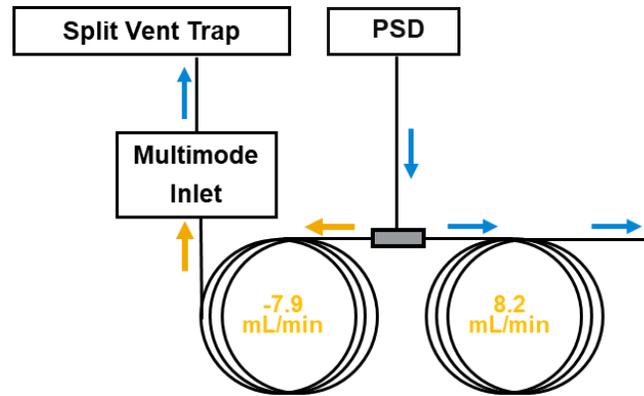
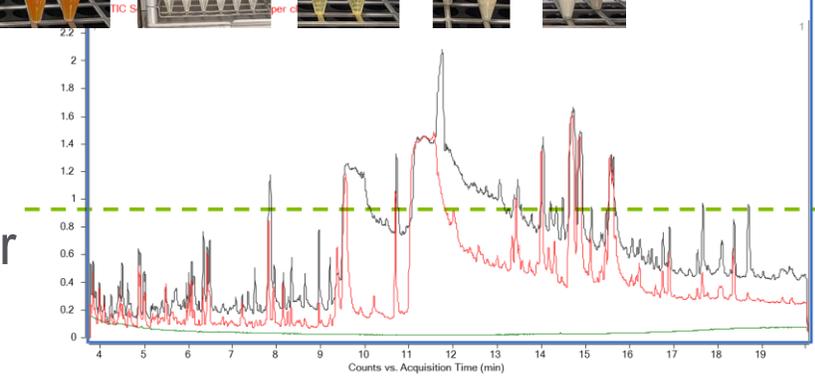
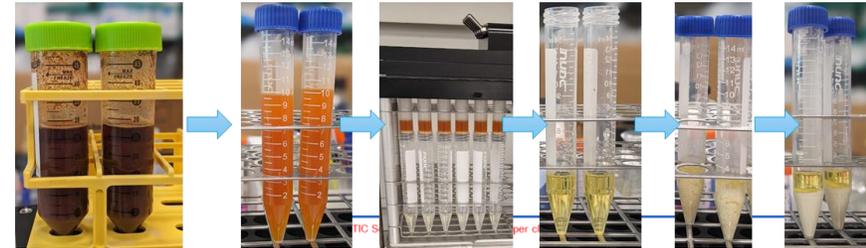
Authors
Anastasia A. Andrianova,
Bruce D. Quimby, and
Limian Zhao
Agilent Technologies, Inc.

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 x 20 m (0.18 mm x 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 conditions was 10-fold higher than that achieved with helium. The ability to use the same MRMs, collision energies, and retention times greatly simplified the transition from helium to hydrogen.

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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

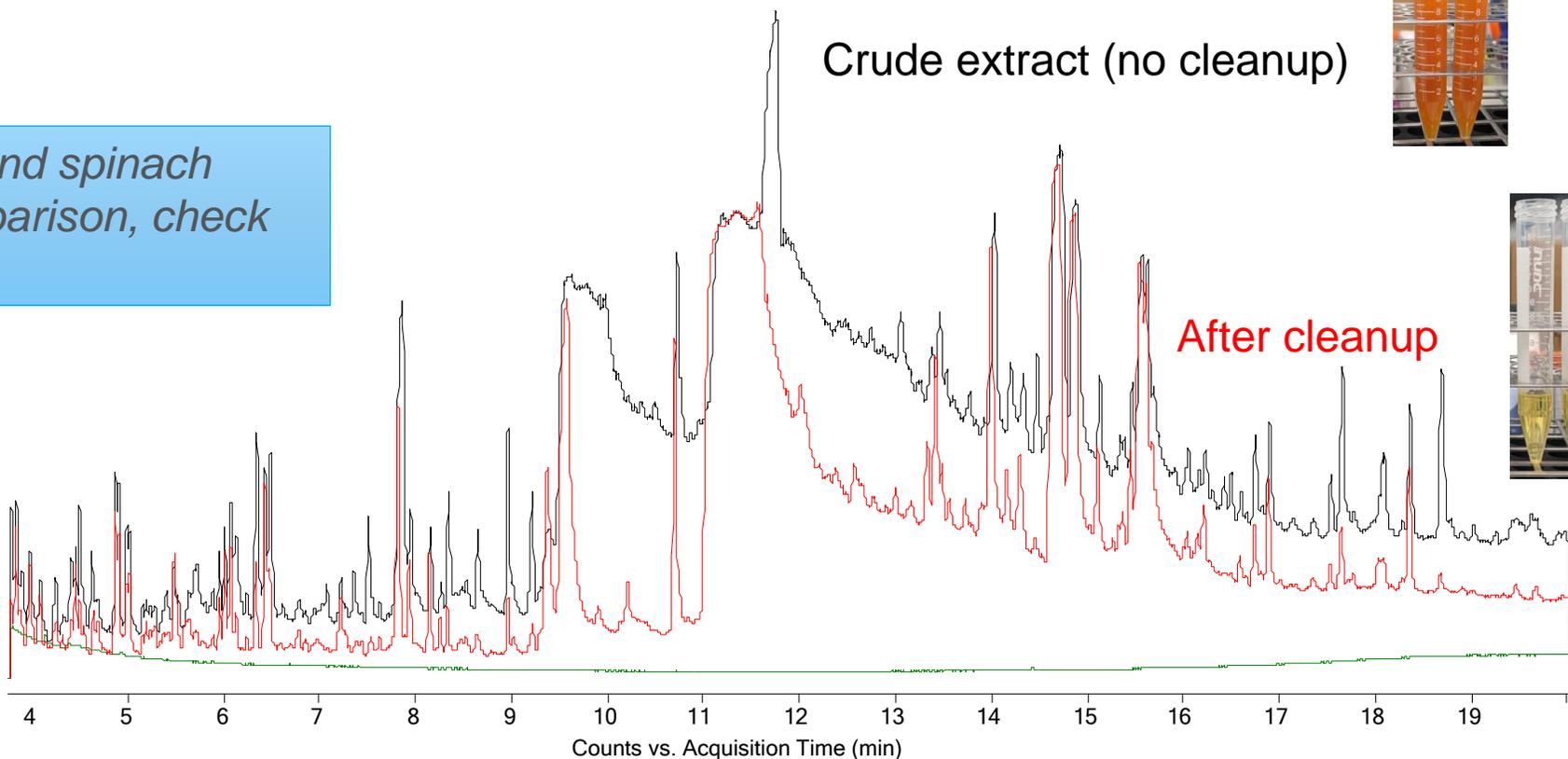


1. Effective Sample Extraction and Matrix Cleanup



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

NEW



Captiva EMR Passthrough Selection Guide



Captiva EMR-HCF
High Chlorophyll Fresh
• Spinach, arugula, chard



Captiva EMR-GPF
General Pigmented Fresh
• Berries, peppers, broccoli



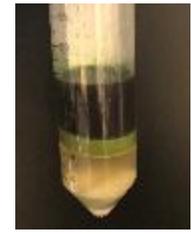
Captiva EMR-GPD
General Pigmented Dry
• Spices, seasoning, herbal medicine



Captiva EMR-LPD
Low Pigmented Dry
• Nuts, tobacco, light pigmented spices

Simplified Passthrough Workflow

Baby spinach



Blackberry



Almond flour



Cinnamon powder



Standard QuEChERS extraction

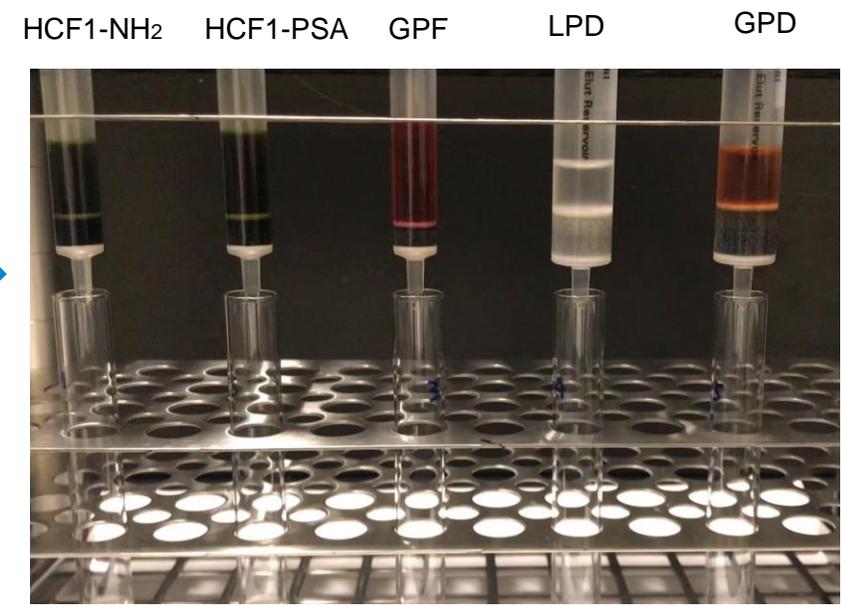


Crude ext. loading



Gravity elution or w/ low level external force

Captiva EMR cartridges



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

Application Note
Food & Beverage Testing

Agilent
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Determination of Multiclass, Multiresidue Pesticides in Bell Peppers

Using Captiva EMR–GPF passthrough cleanup by LC/MS/MS and GC/MS/MS

Author
Lemian Zhao
Agilent Technologies, Inc.

Abstract
This application note presents the development and validation of a multiresidue method for the analysis of pesticide residues in a mixed bell pepper matrix composed of different color bell peppers. The method uses extraction with the Agilent Bond Elut QuEChERS ADAC extraction kit, followed by Agilent Captiva Enhanced Matrix Removal–General Pigmented Fresh (EMR–GPF) passthrough cleanup, and then LC/MS/MS and GC/MS/MS detection, separately. The novel sample preparation workflow provides efficient and selective matrix cleanup, delivered a fast, simplified, and convenient one sample preparation for both LC/MS/MS and GC/MS/MS analysis. Compared to traditional dispersive SPE (dSPE) cleanup, the Captiva EMR–GPF passthrough cleanup delivers highly efficient and selective matrix/pigment removal, improves target recovery and reproducibility, and reduces the matrix effect and interferences. For analysis of a large panel of pesticides (240 pesticides) on both LC/MS/MS and GC/MS/MS, the workflow showed that 98% target were within the acceptance recovery window (60 to 120%), 99% target were within the RSD acceptance window (≤20%), and 94% targets gave out good calibration linearity ($R^2 > 0.99$ in the calibration range).

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Application Note
Food & Beverage Testing

Agilent
Trusted Analysis

Determination of Over 300 Pesticides in Cinnamon

Using Captiva EMR–GPD passthrough cleanup and LC/MS/MS and GC/MS/MS detection

Author
Lemian Zhao and
Anastasia Andrianova
Agilent Technologies, Inc.

Abstract
This application note presents the development and optimization of a multiresidue method for the analysis of pesticide residues in cinnamon powder. The method involves sample extraction with the Agilent Bond Elut QuEChERS ADAC extraction kit, followed by passthrough cleanup with Agilent Captiva Enhanced Matrix Removal–General Pigment Dry (EMR–GPD), then LC/MS/MS and GC/MS/MS analysis. The newly developed method provided efficient matrix removal, acceptable target quantitation results, and low failure rate for analysis of a large panel of pesticides in

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2. Evaluation of the Matrix in Full Scan

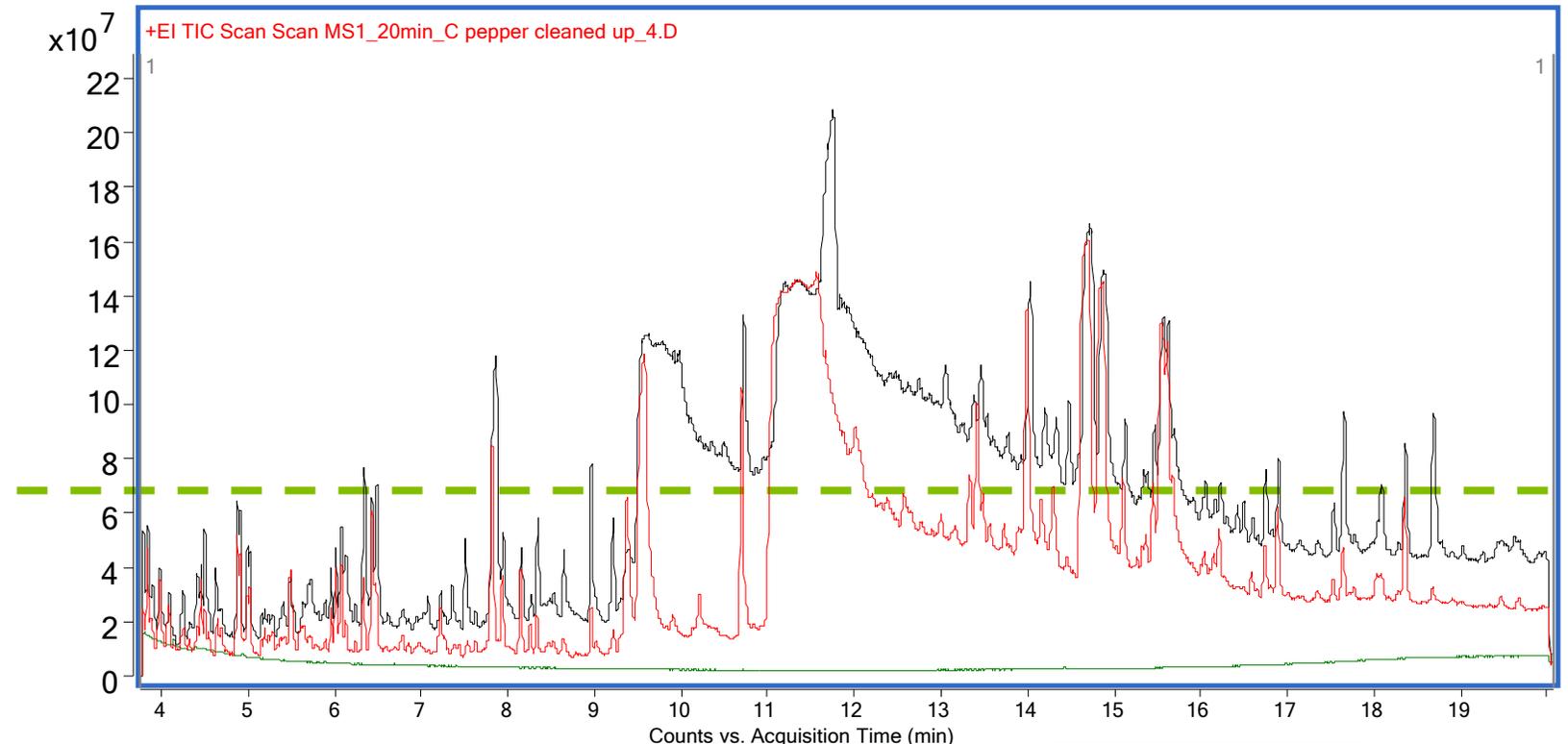


Adequate sample preparation (especially with the 7010C)
Sometimes dilution may yield better sensitivity and enhance robustness



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

If TIC > 7×10^7
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



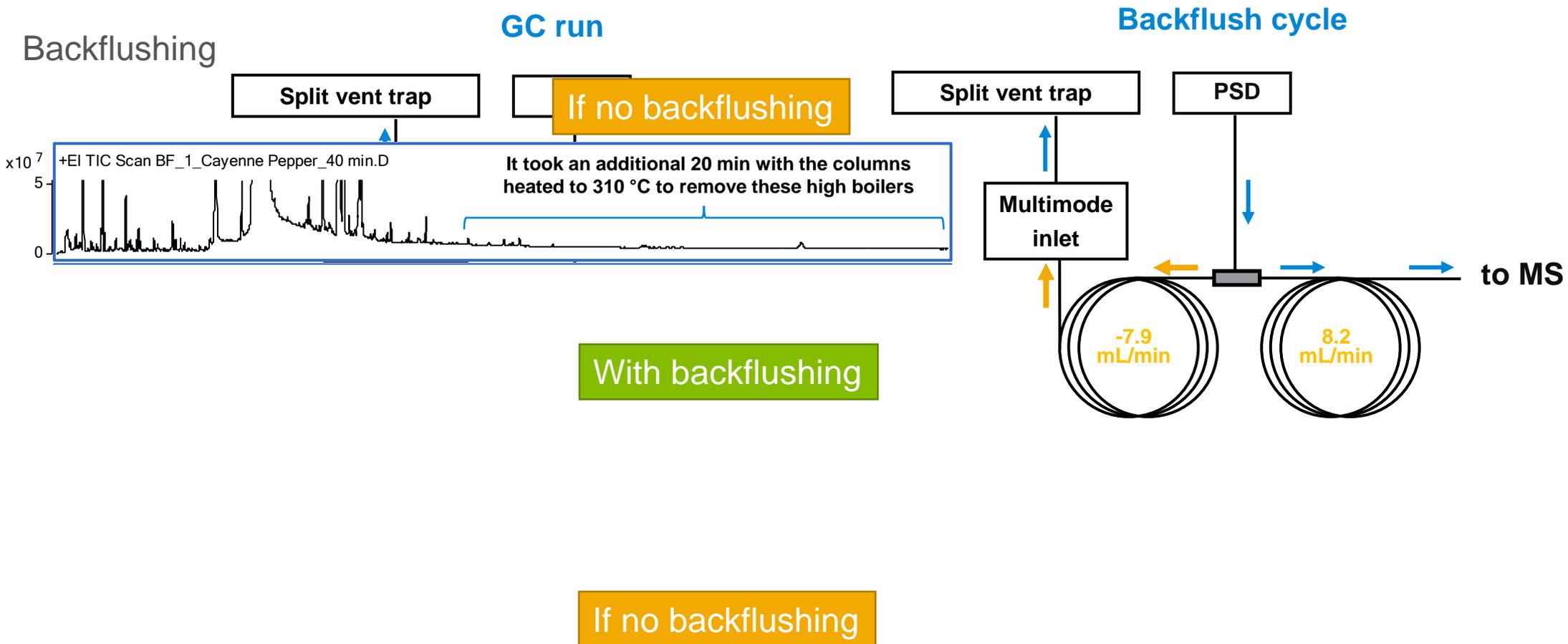
Evaluation of in-source loading of the matrix in full scan:
Sometimes less is more



Backflushing

3. Midcolumn Backflushing

3



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



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



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



Backflushing



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)
Sometimes dilution may yield better sensitivity and
enhance robustness

3

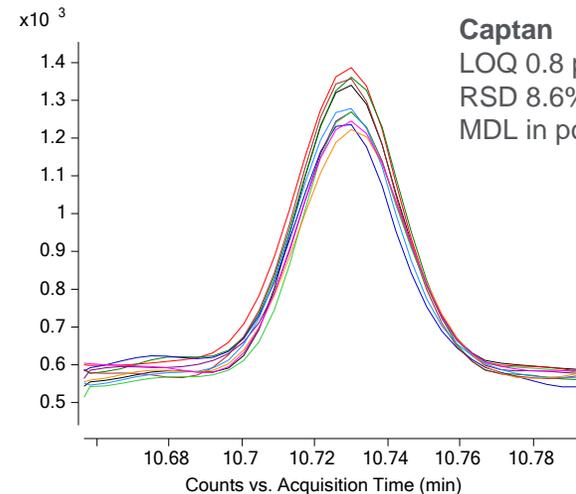
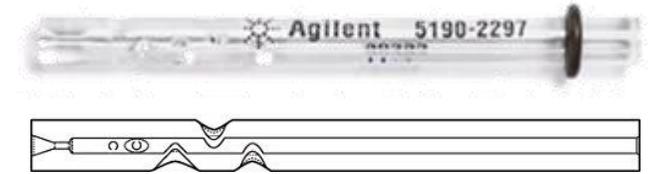
Backflushing

4

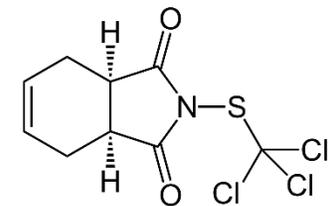
Keep the leaks out

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



Results

App note 5994-4965EN

Application Note
Food & Beverage Testing



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



Authors

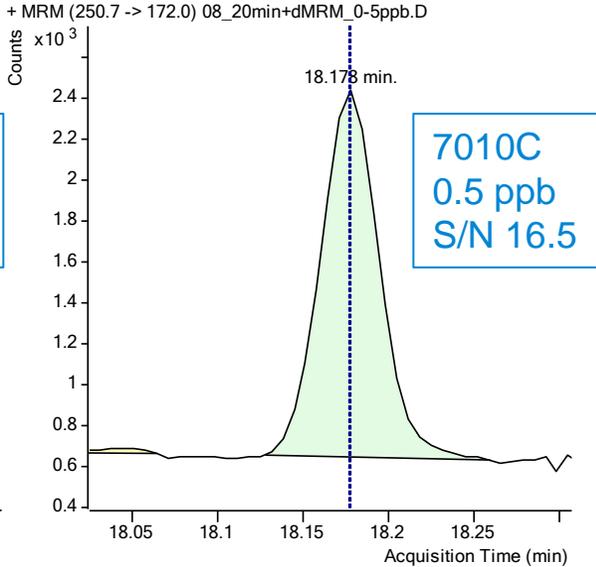
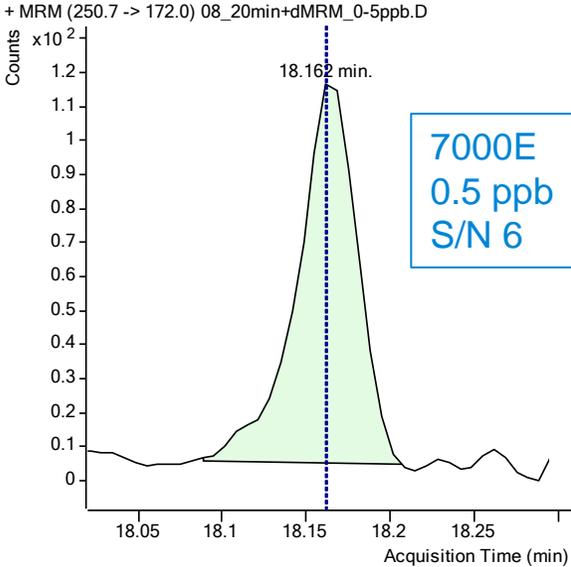
Anastasia A. Andrianova and
Limian Zhao
Agilent Technologies, Inc.

Abstract

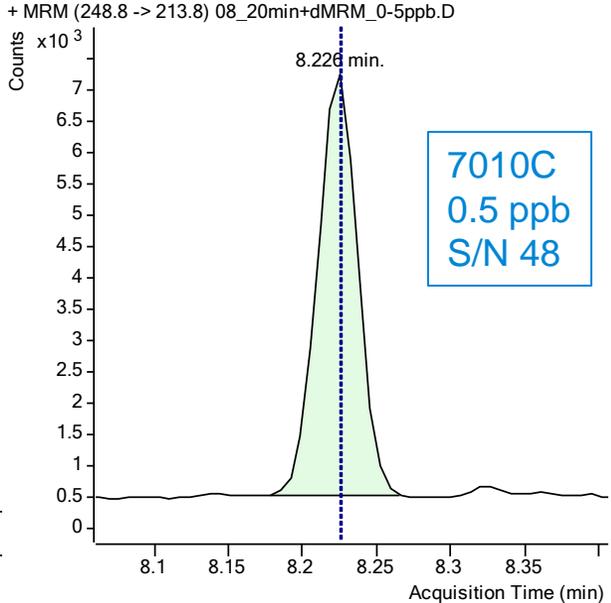
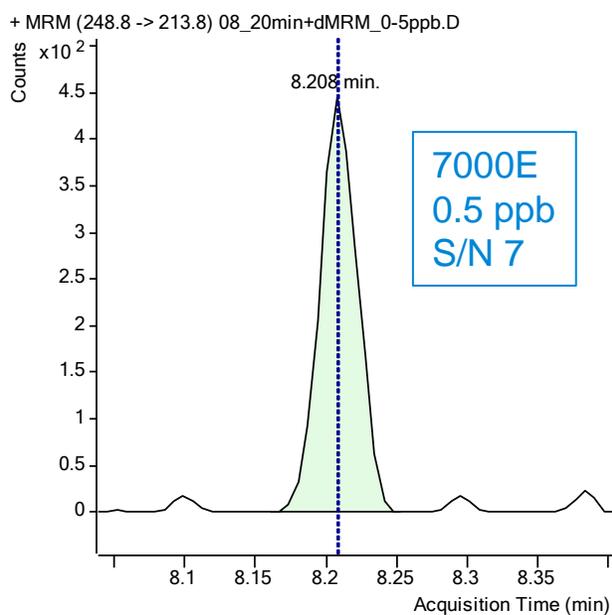
This application note describes five best practices to enhance analytical performance in the analysis of over 200 pesticides in challenging matrices including spinach, walnut, and cayenne pepper. The novel Agilent Captiva EMR passthrough cleanup procedure following the Agilent QuEChERS extraction enabled 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



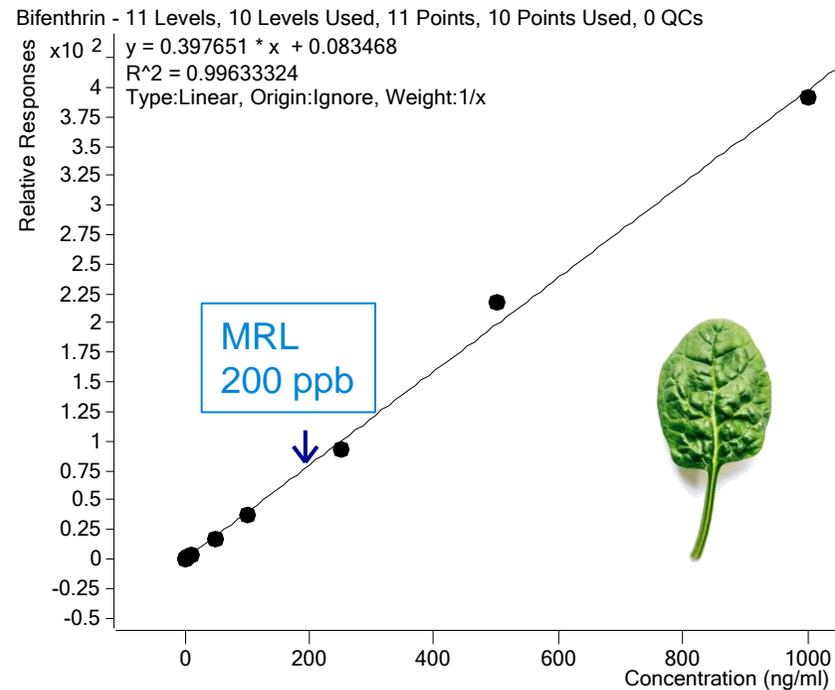
Pentachloronitrobenzene: No MRL in walnut
But regulated in many vegetables and fruits
(20 ppb – 1 ppm)
Cannot be done with LC/MS



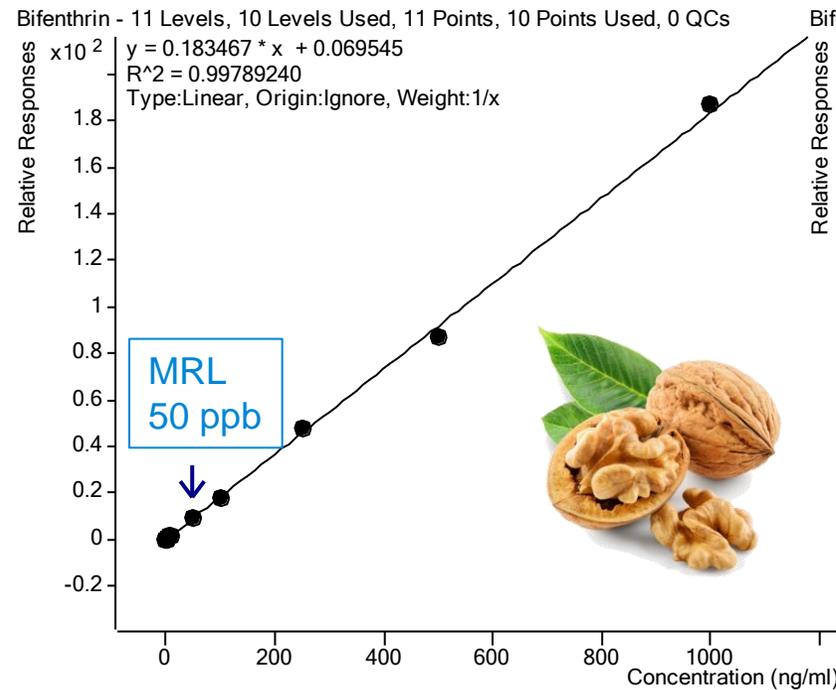
Calibration Performance Over a Wide Dynamic Range with the 7000E GC/TQ

Bifenthrin: encompassing varying MRLs in different commodities

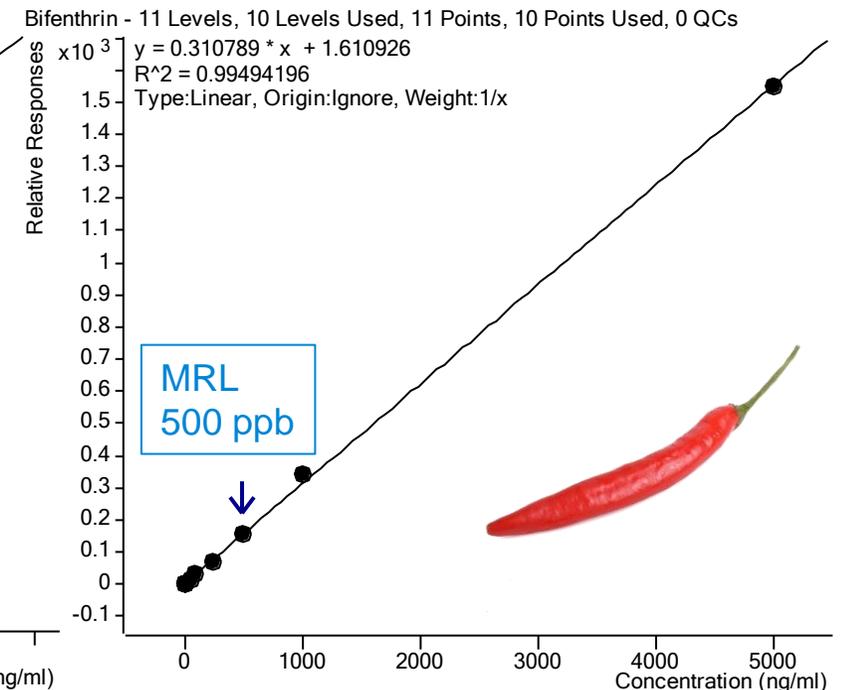
Spinach



Walnut



Cayenne pepper

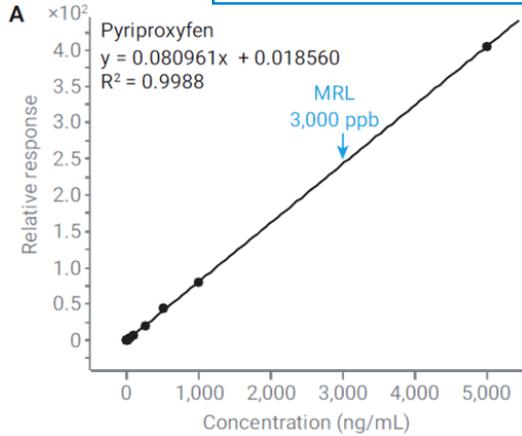


Calibration Over a Wide Dynamic Range with the 7000E and 7010C GC/TQ

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

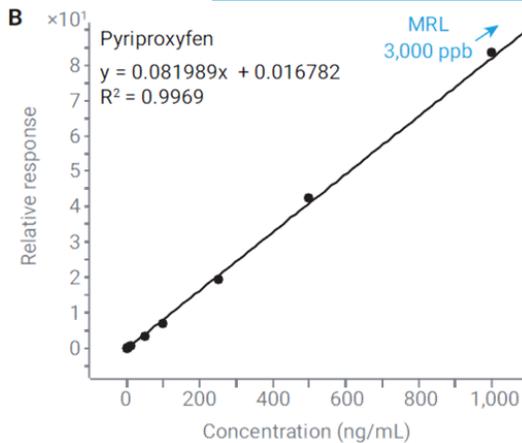


7000E: 0.1-5,000 ppb



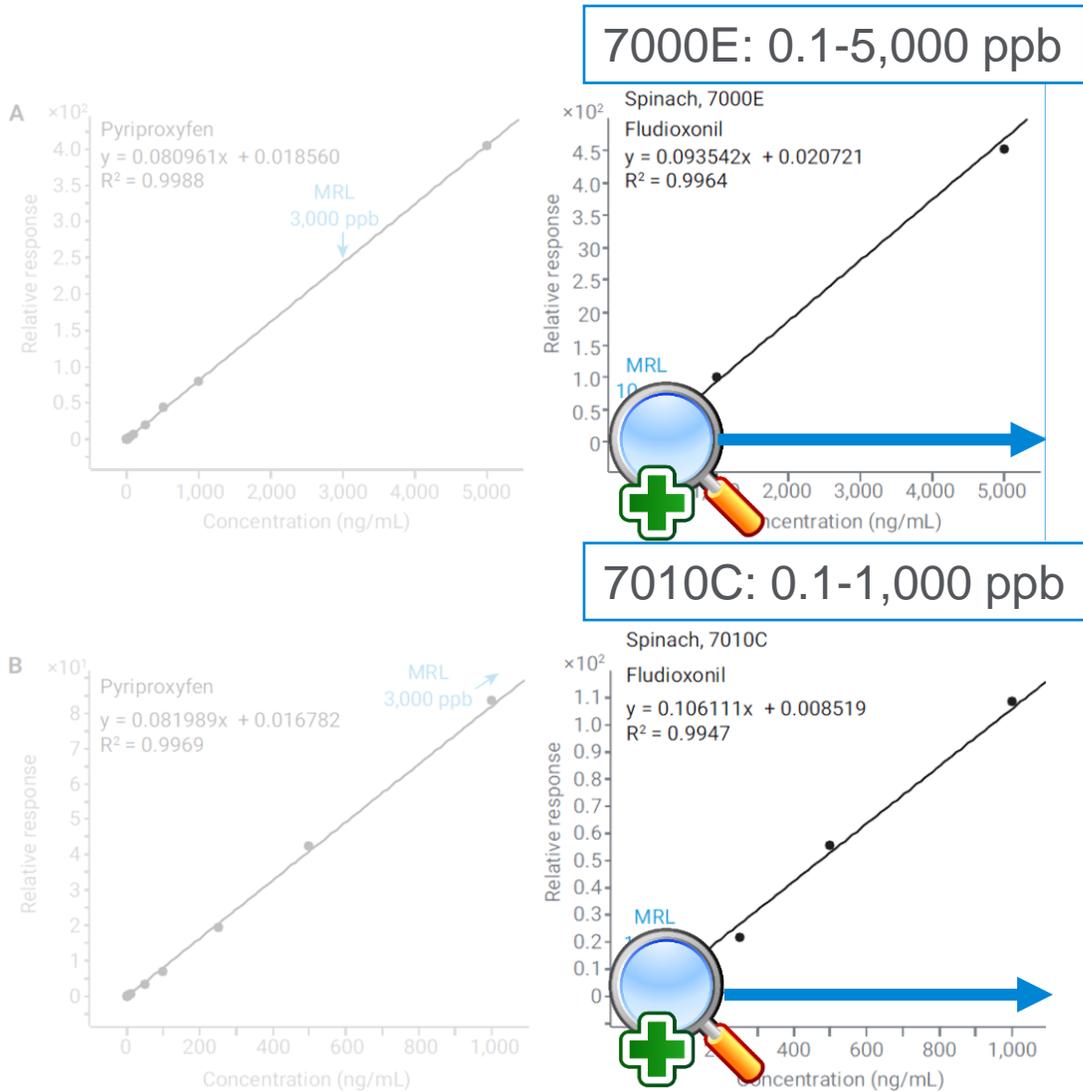
Pyriproxifen:
MRL in spinach 3,000 ppb

7010C: 0.1-1,000 ppb



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

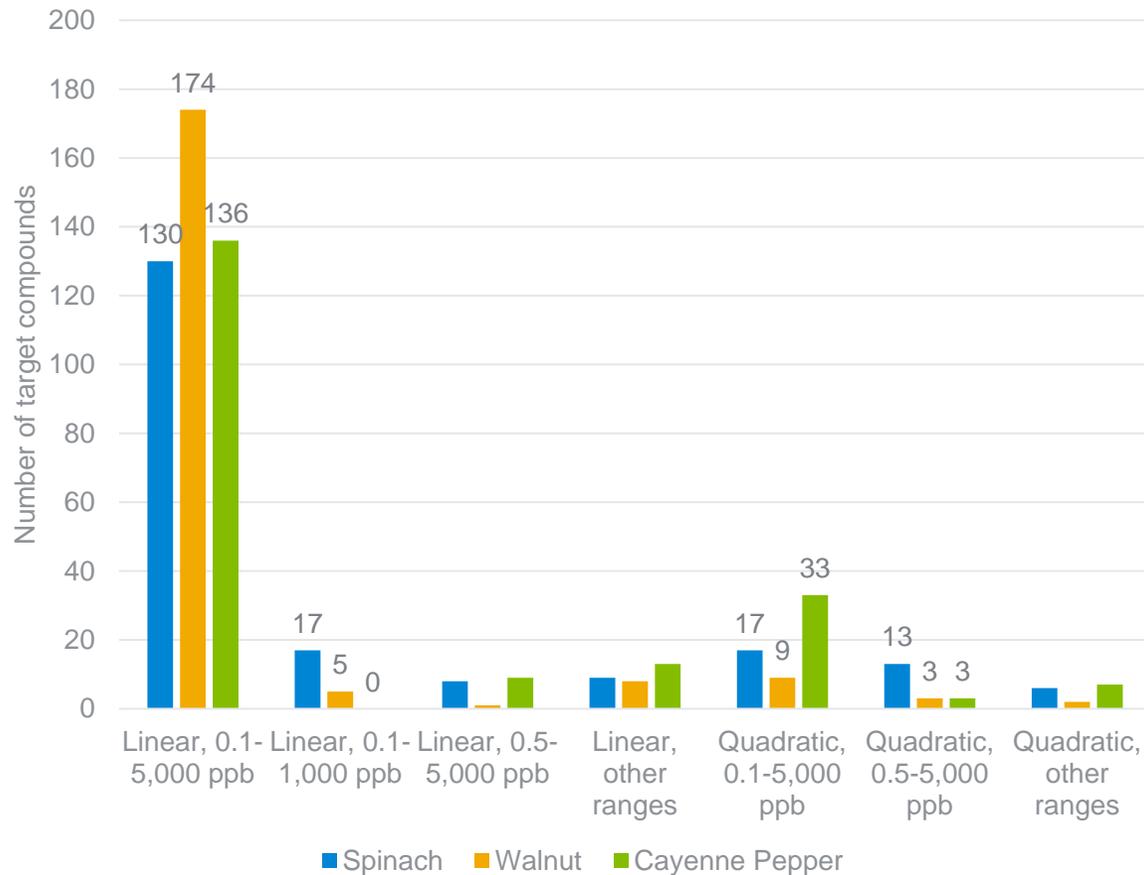
Pyriproxyfen and fludioxonil: widely different MRLs in spinach (3,000 and 10 ppb)



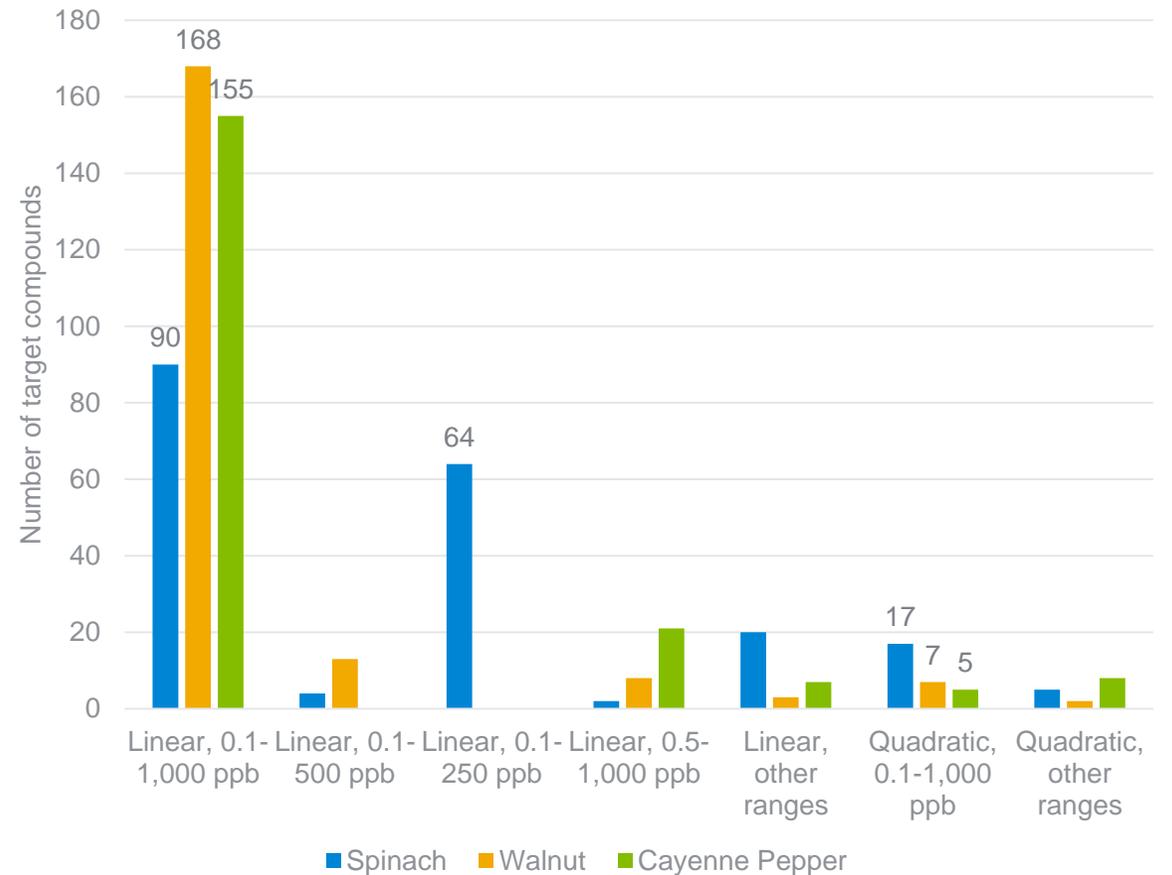
Fludioxonil:
MRL in spinach 10 ppb

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

Number of compounds with R2>0.99 and their calibration ranges with the 7000E GC/TQ

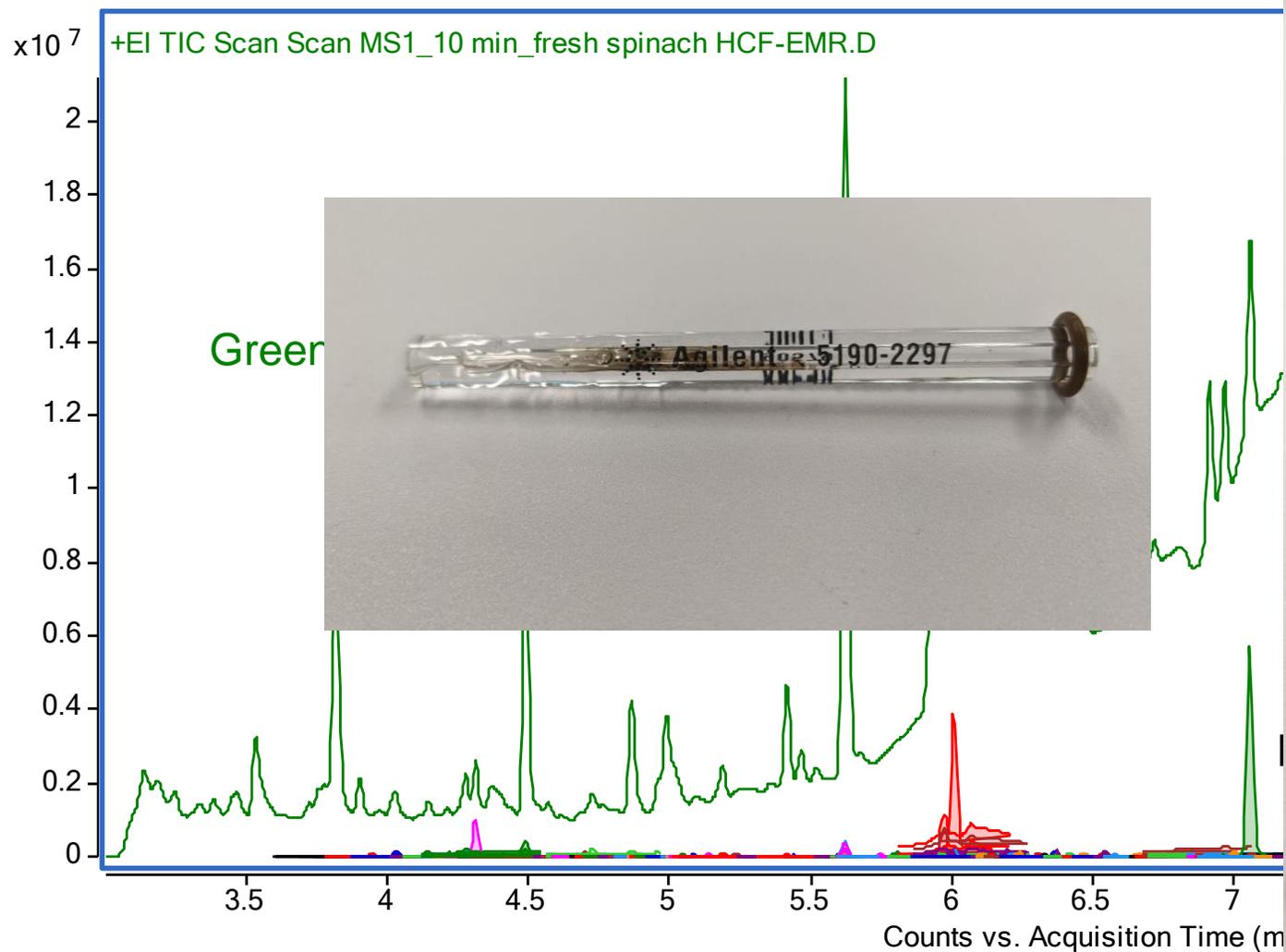


Number of compounds with R2>0.99 and their calibration ranges with the 7010C GC/TQ



Spinach QuEChERS Extract – for Longevity Study

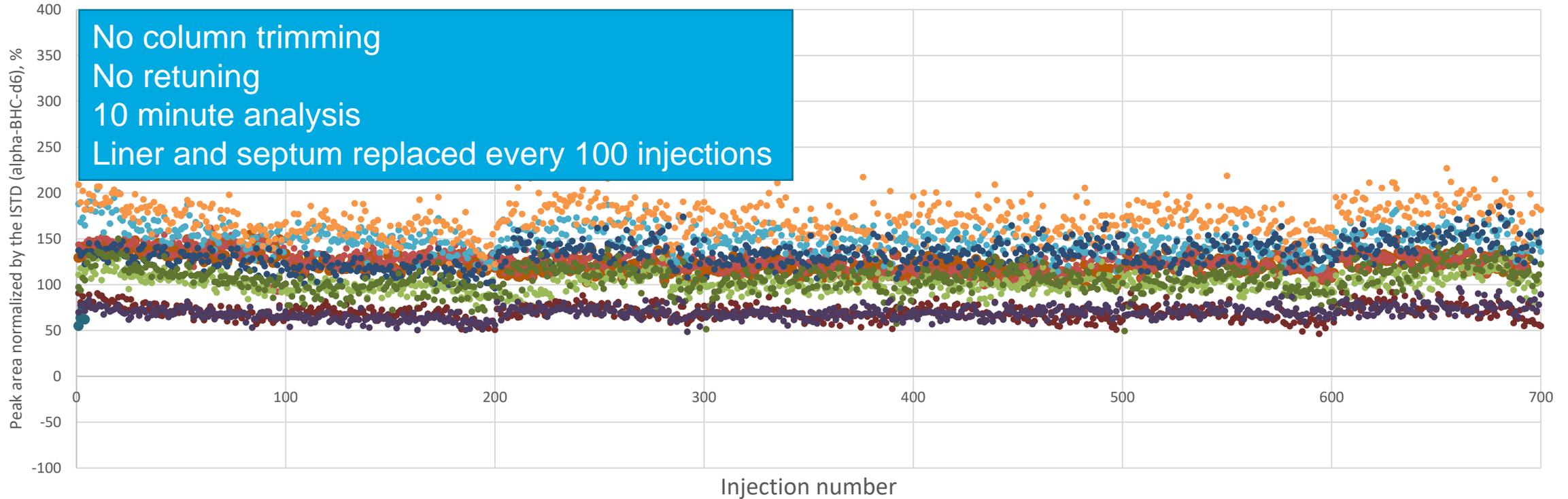
7000E (pesticides spiked at 20 ppb), 10 minute analysis



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

Area normalized by alpha-BHC-d6, %



- BHC-alpha (benzene hexachloride), 8%
- Pirimiphos-methyl, 9%
- Bupirimate, 11%
- Metalaxyl, 10%
- BHC-beta, 9%
- Bromophos-ethyl, 10%
- Chlorthiophos, 11%
- Atrazine, 11%
- Prothiofos, 10%
- Fluquinconazole, 13%

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

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, target analyte recovery, and improved calibration. Calibration orders of magnitude higher than conventional GC/MS systems (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.

5994-4965EN

A Fast and Robust GC/MS/MS Analysis of 203 Pesticides in 10 Minutes in Spinach



Authors

Anastasia A. Andrianova,
Bruce D. Quilty,
and Limian Zhao
Agilent Technologies, Inc.

Abstract

This application note describes two approaches for achieving robust, multiresidue pesticide analysis in 10 minutes by GC/MS/MS, while maintaining sufficient chromatographic resolution for the analysis of over 200 pesticides in spinach, a challenging high chlorophyll, fresh matrix. First, the conventional 15 × 15 m (0.25 mm × 0.25 µm) midcolumn backflush configuration was used with an accelerated oven ramp, yielding an analysis time of 10 minutes. Second, a midcolumn

5994-4967EN

million (ppb). Method robustness was shown with 700 consecutive injections of a spinach extract, spiked with pesticides at 20 ppb, that spanned over 175 hours of continuous running of the GC/TQ.



How About Hydrogen Carrier Gas?

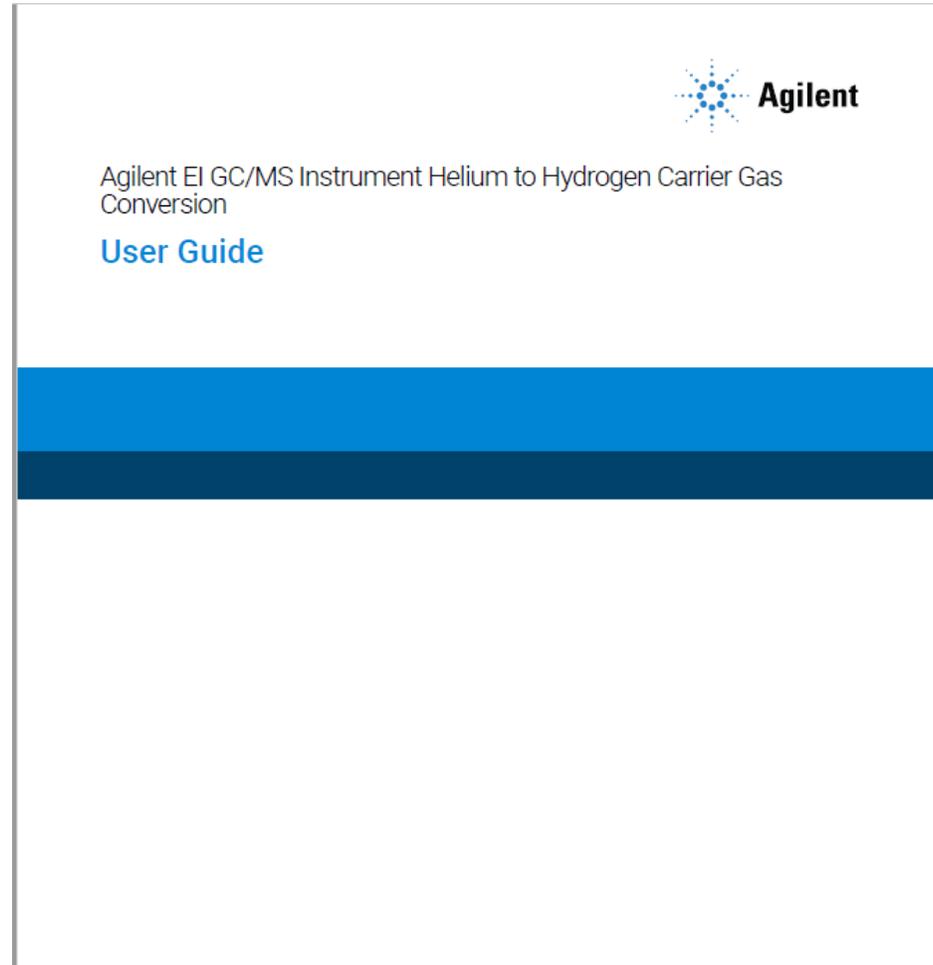
Hydrogen As a Carrier Gas in GC/MS/MS

- 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 H₂ carrier.
- Essential read before converting to H₂.

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](#)

SeparationScience
PREMIER LEARNING FOR ANALYTICAL SCIENTISTS

On-Demand Presentation

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

On-Demand

Key strategies for pesticide analysis utilizing hydrogen as the carrier gas, while maintaining sensitivity that allows for meeting the MRLs.

GC/MS Recipe for Success with Hydrogen



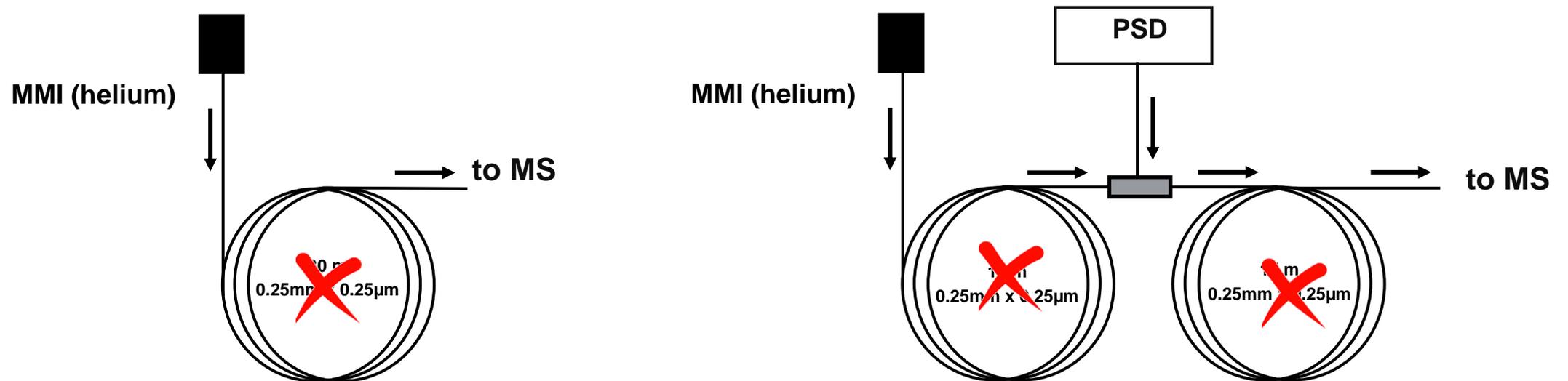
- H₂ carrier gas
- HydroInert Source optimized for use with hydrogen
- 20 × 20 m (0.18 mm × 0.18 μm) HP-5ms UI
- Starting column flows: 0.9 and 1.1 mL/min
- Retention time lock to chlorpyrifos methyl (9.143 min)
- **Same retention times** with H₂ as with the conventional He method (20 minutes)
- Ability to perform 10 minute analysis with excellent resolution

The screenshot shows the top of an Agilent application note. The header includes "Application Note" and "Food & Beverage Testing" on the left, and the Agilent logo with "Trusted Answers" on the right. The title of the note is "Hydrogen Carrier Gas for Analyzing Pesticides in Pigmented Foods with GC/MS/MS". Below the title is a photograph of various fresh fruits and vegetables. The "Authors" section lists Anastasia A. Andrianova, Bruce D. Quimby, and Limian Zhao from Agilent Technologies, Inc. The "Abstract" section begins with "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 transition. The resulting chromatographic resolution achieved under the optimal conditions was comparable to that achieved with helium. The use of hydrogen as the carrier gas provided a 10-fold increase in the range of analyte detection when compared to helium. The use of hydrogen as the carrier gas with the HydroInert source 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." A blue box with the number "5994-6505EN" is overlaid on the abstract text.

GC Configuration and Method Considerations

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

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

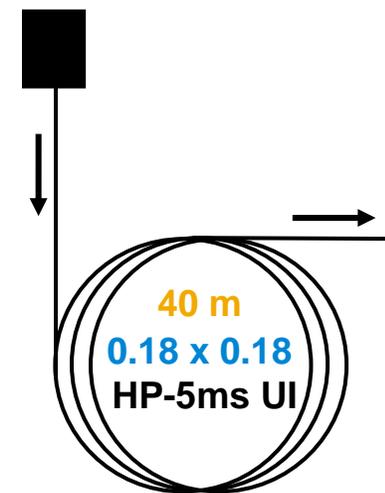
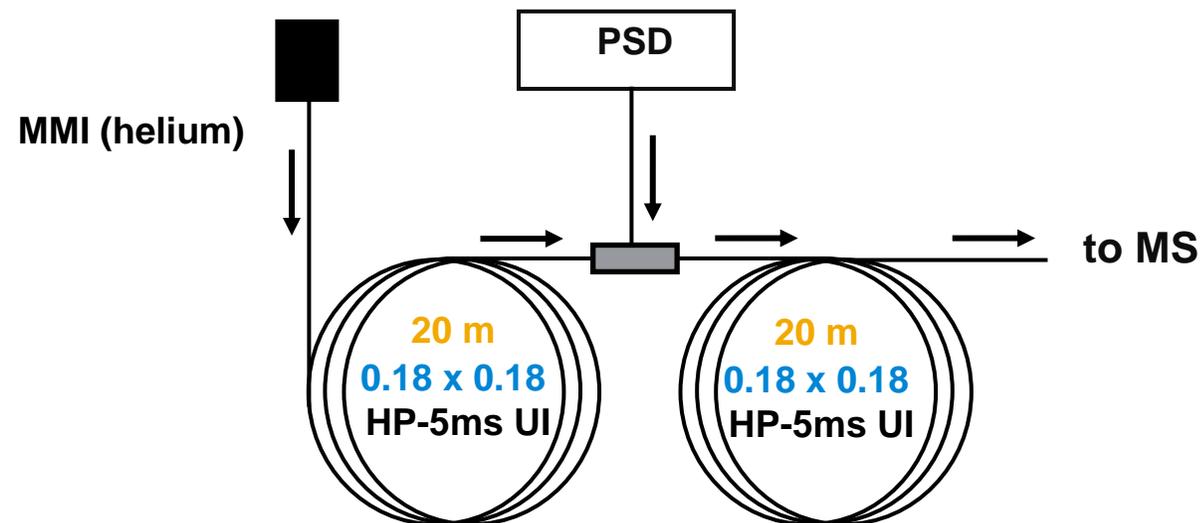


GC Configuration and Method Considerations

20 x 20 m
0.18 mm x 0.18 μ m

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 μ m \rightarrow 20 m, 0.18 mm x 0.18 μ m



GC Configuration and Method Considerations

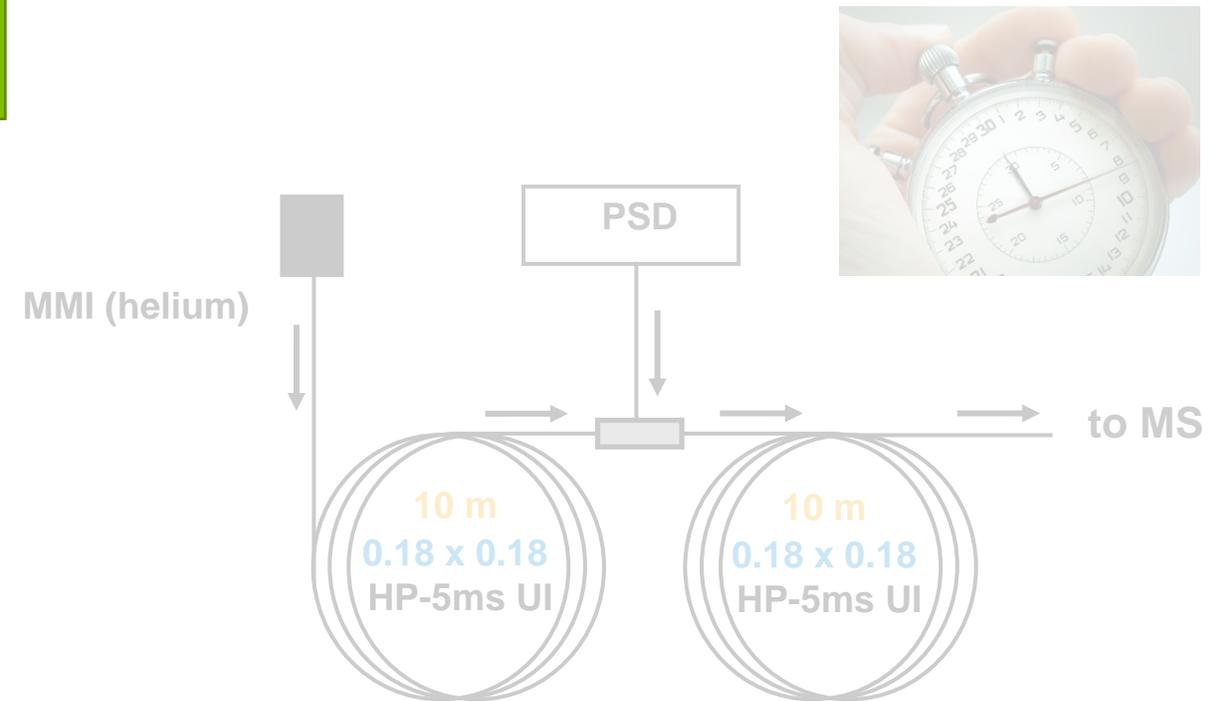
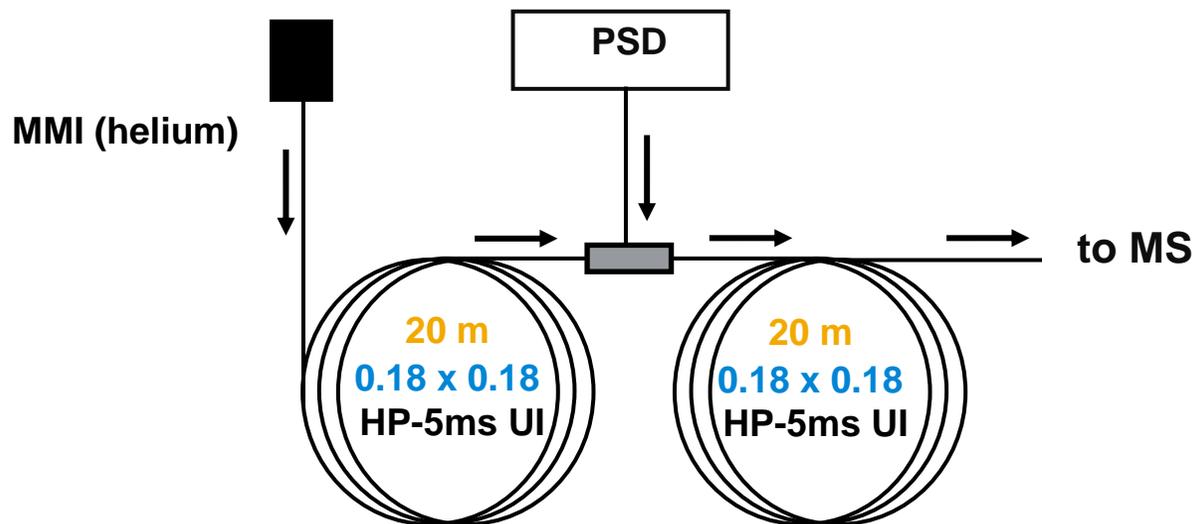
20 x 20 m
0.18 mm x 0.18 μ m

Compatible with H_2 carrier gas
Analysis time **20 minutes**

10 m x 10 m
0.18 mm x 0.18 μ m

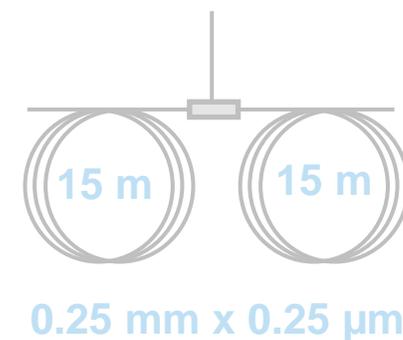
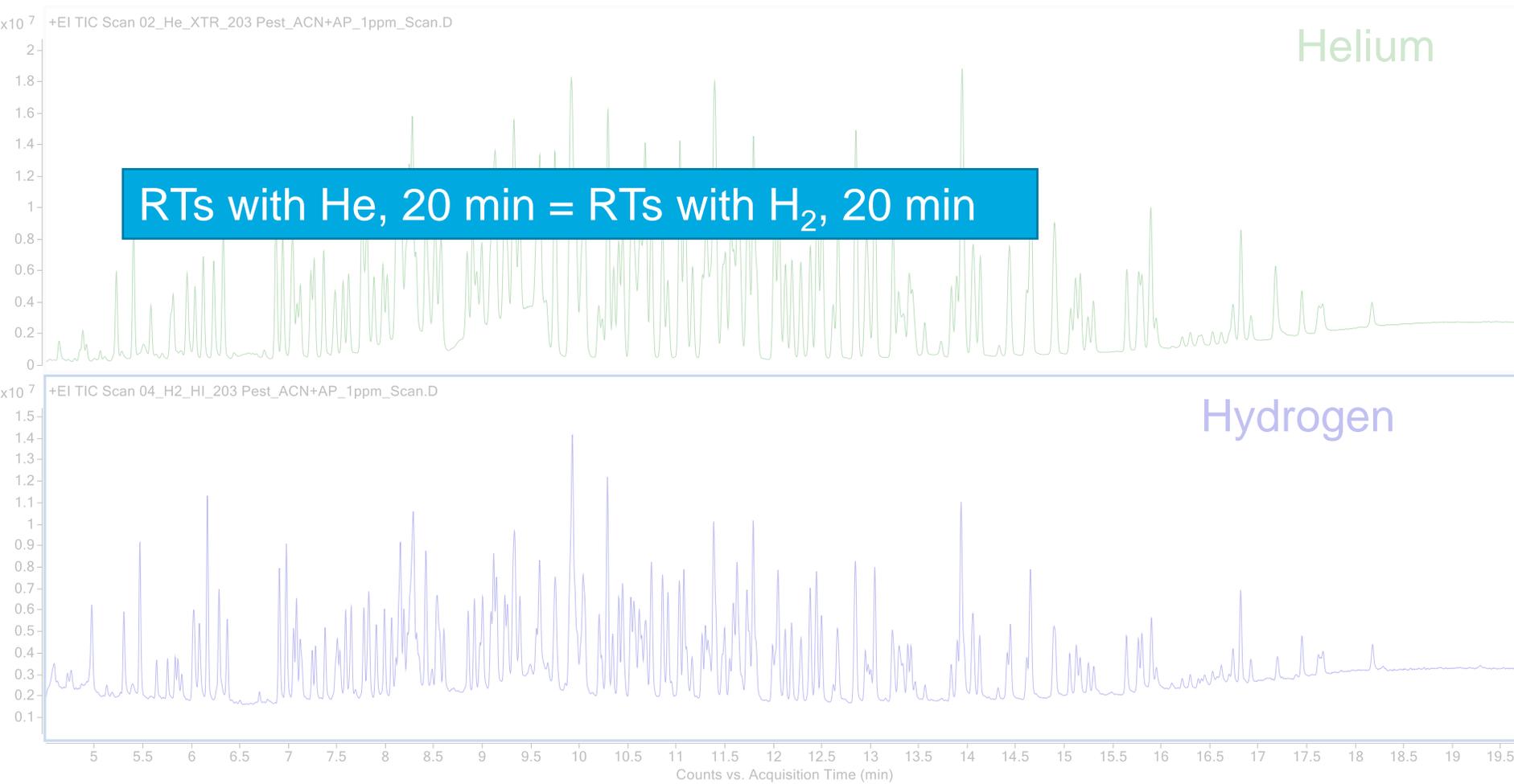
Compatible with H_2 carrier gas
Analysis time **10 minutes**

Maintain the same RTs and elution order
30 m, 0.25 mm x 0.25 μ m \rightarrow 20 m, 0.18 mm x 0.18 μ m

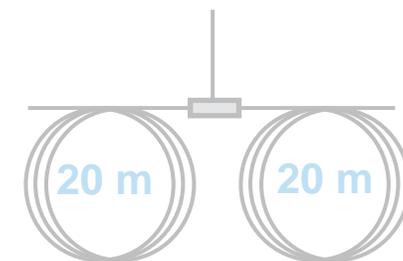


What Happens to the Retention Times and Resolution?

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



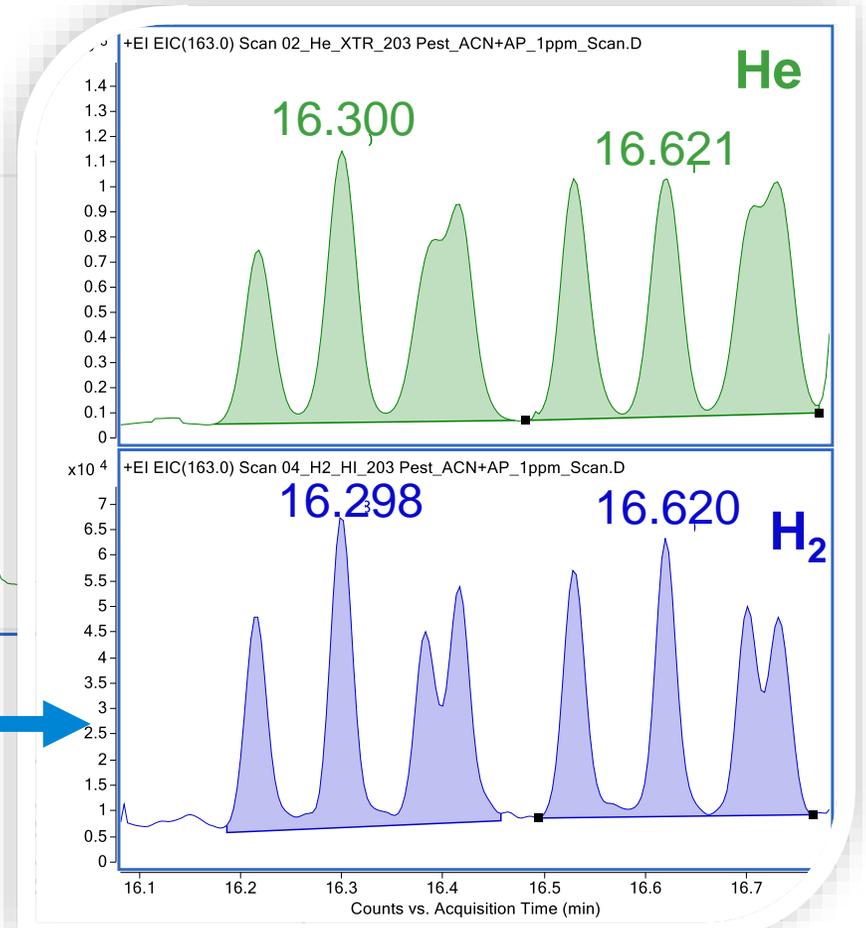
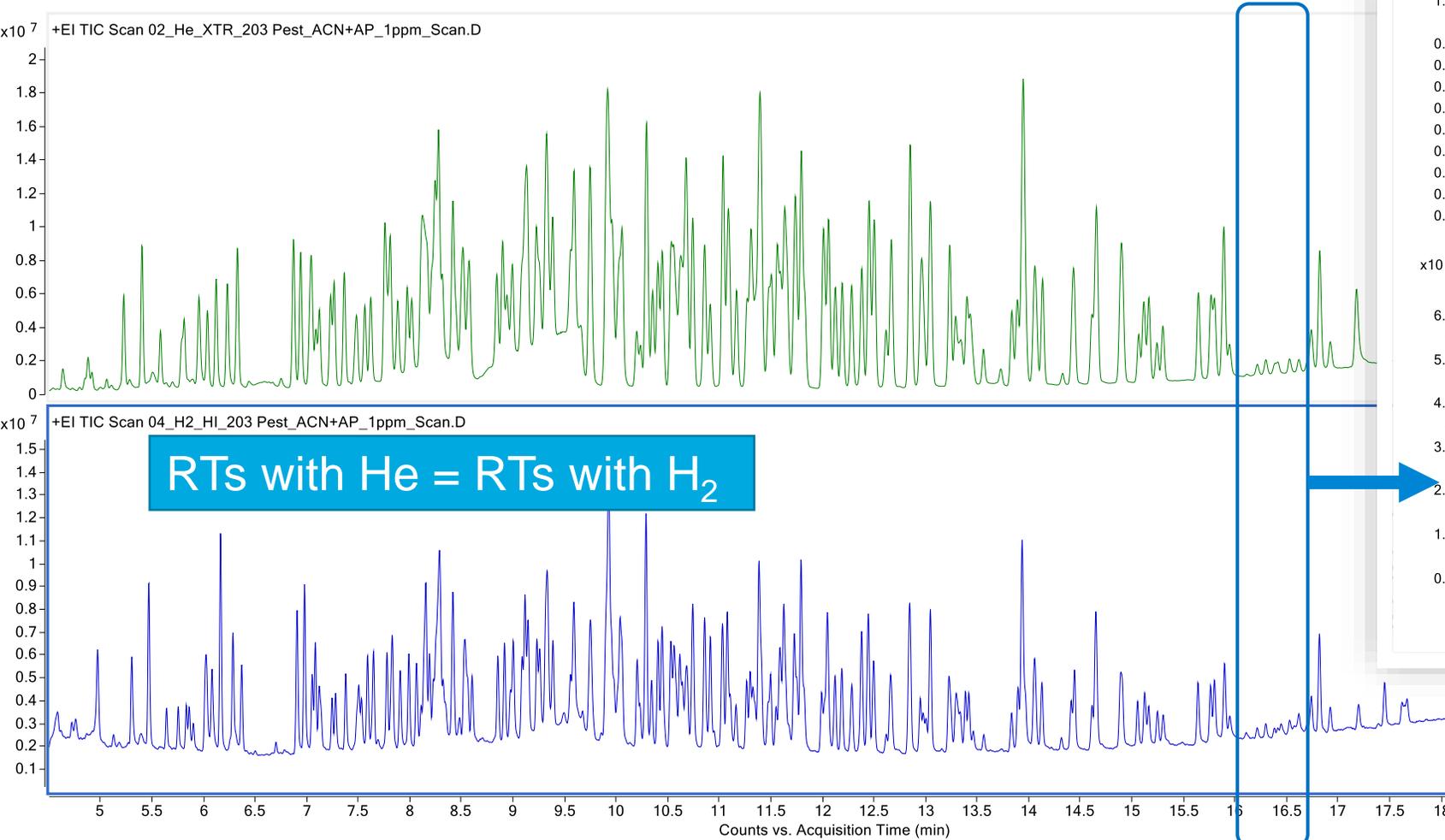
0.25 mm x 0.25 µm



0.18 mm x 0.18 µm

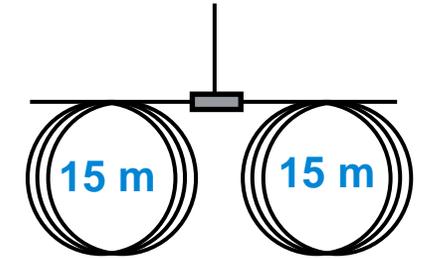
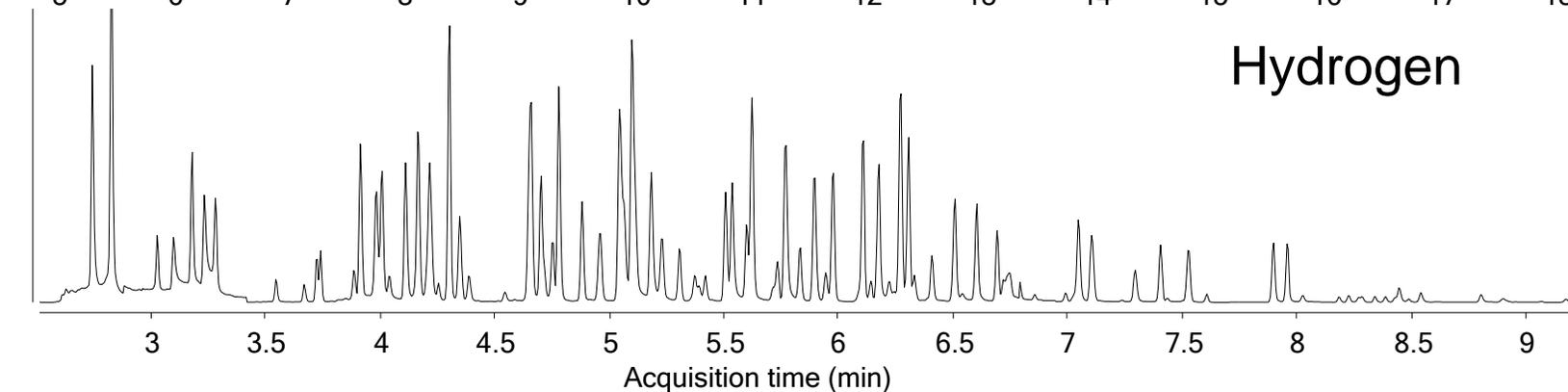
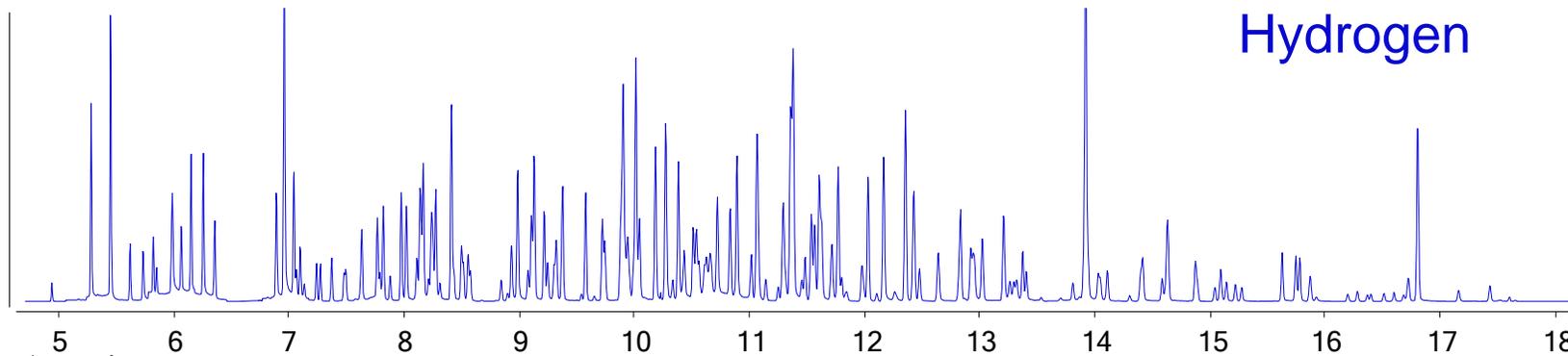
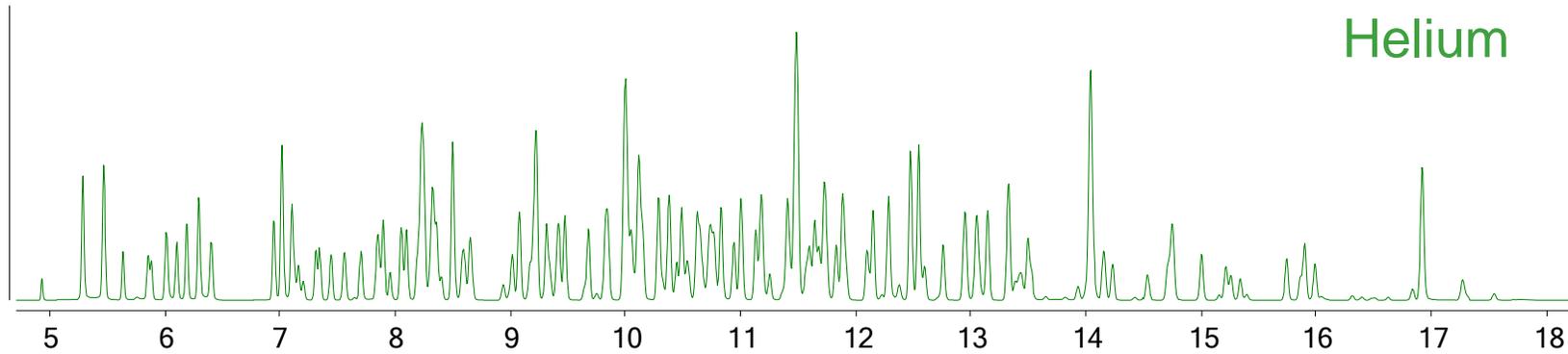
Superior Resolution with Hydrogen

EIC 163

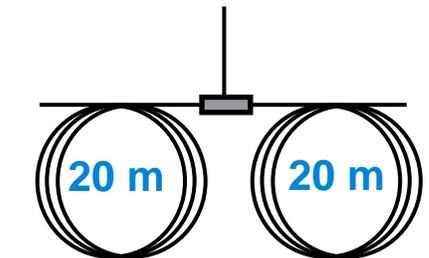


Cyfluthrins **Cypermethrins**

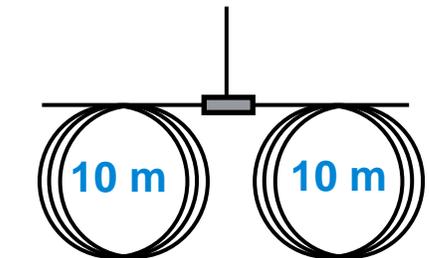
Proof of Concept: 10 Minutes with Hydrogen



0.25 mm x 0.25 μ m

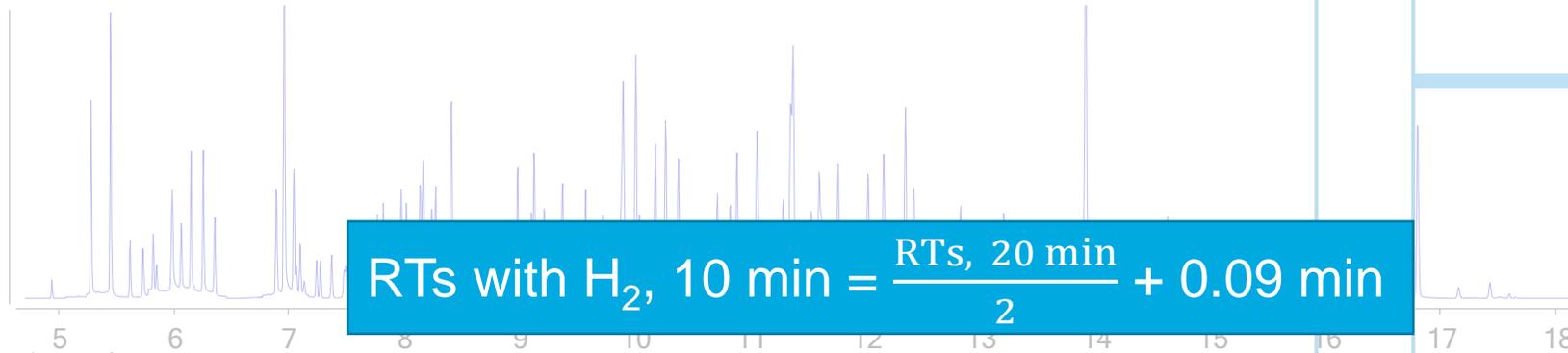
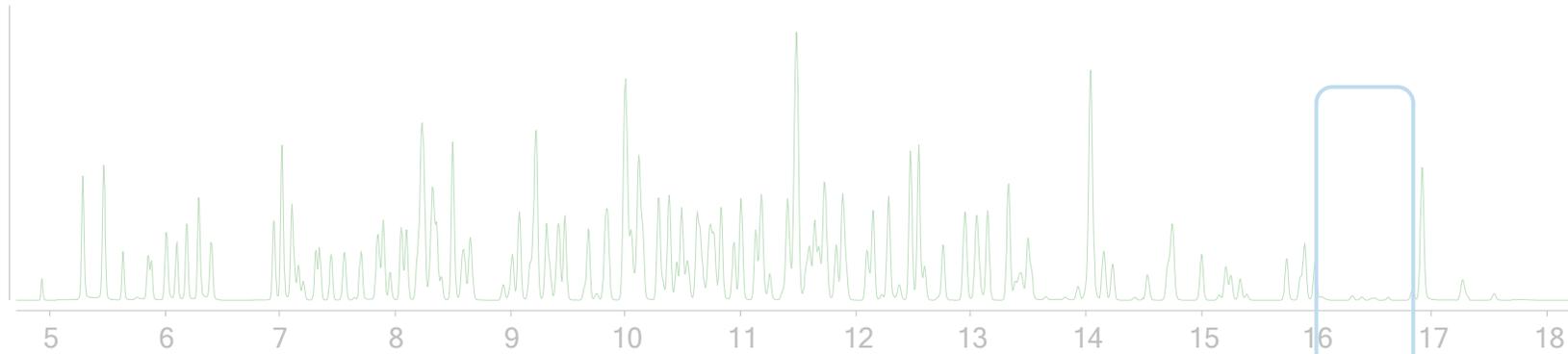


0.18 mm x 0.18 μ m

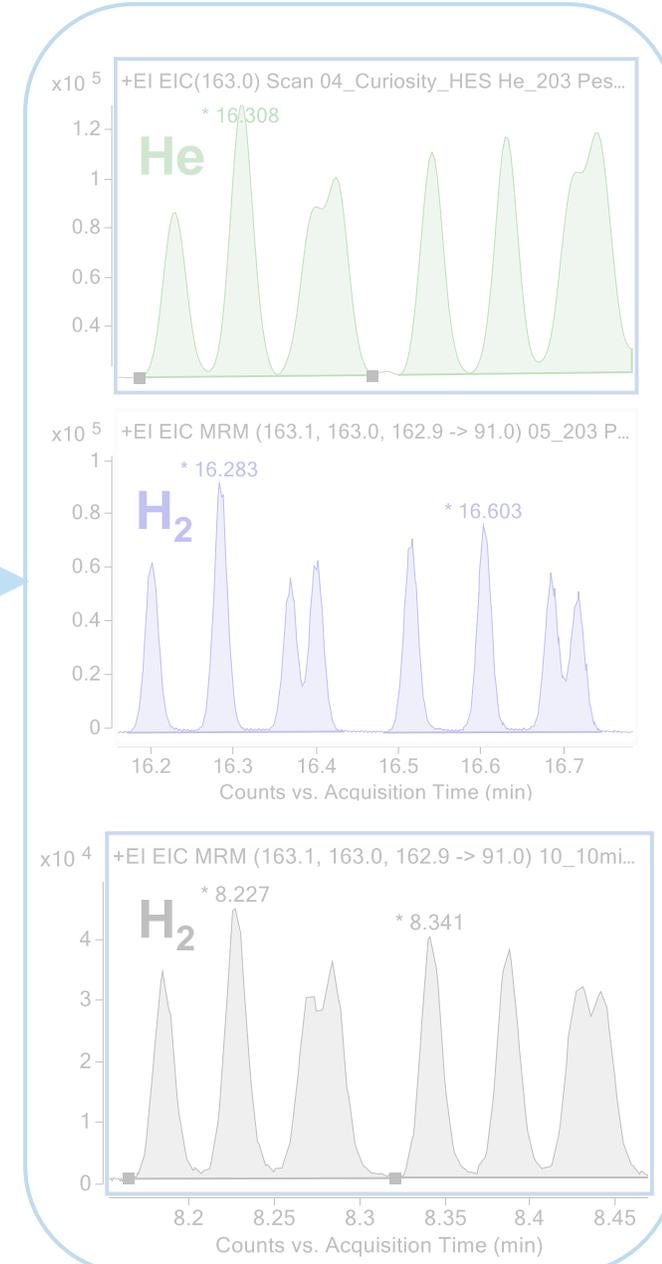
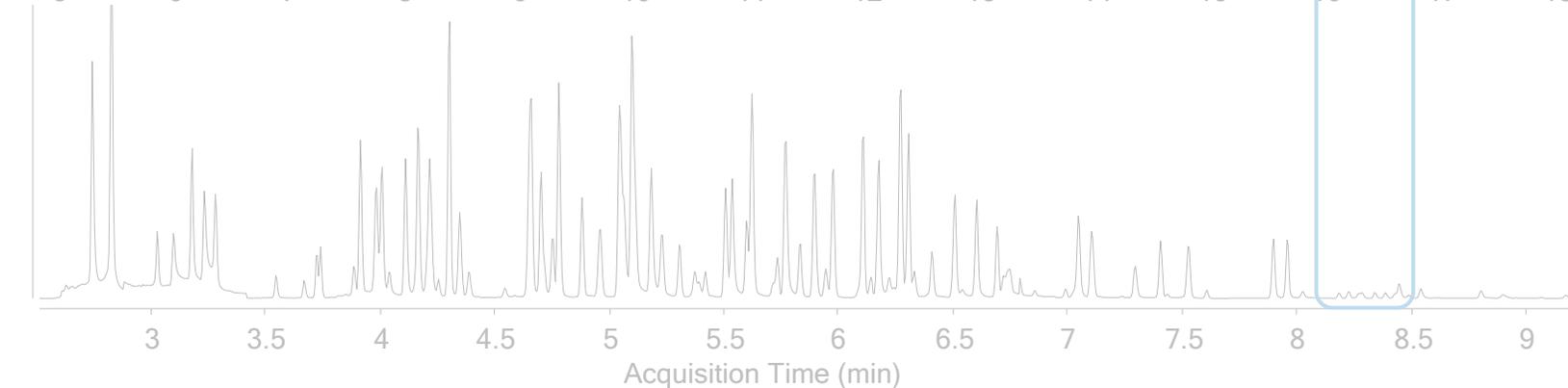


0.18 mm x 0.18 μ m

10 Minutes with Hydrogen and Still Good Resolution



RTs with H₂, 10 min = $\frac{\text{RTs, 20 min}}{2} + 0.09 \text{ min}$



Electron Ionization MS Sources

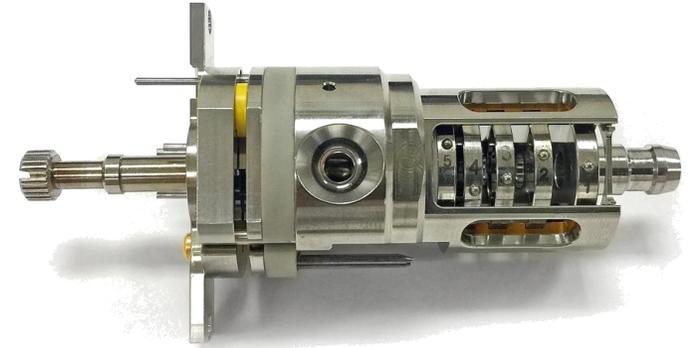
Conventional EI Extractor
(Inert Plus) Source



HydroInert
EI Source

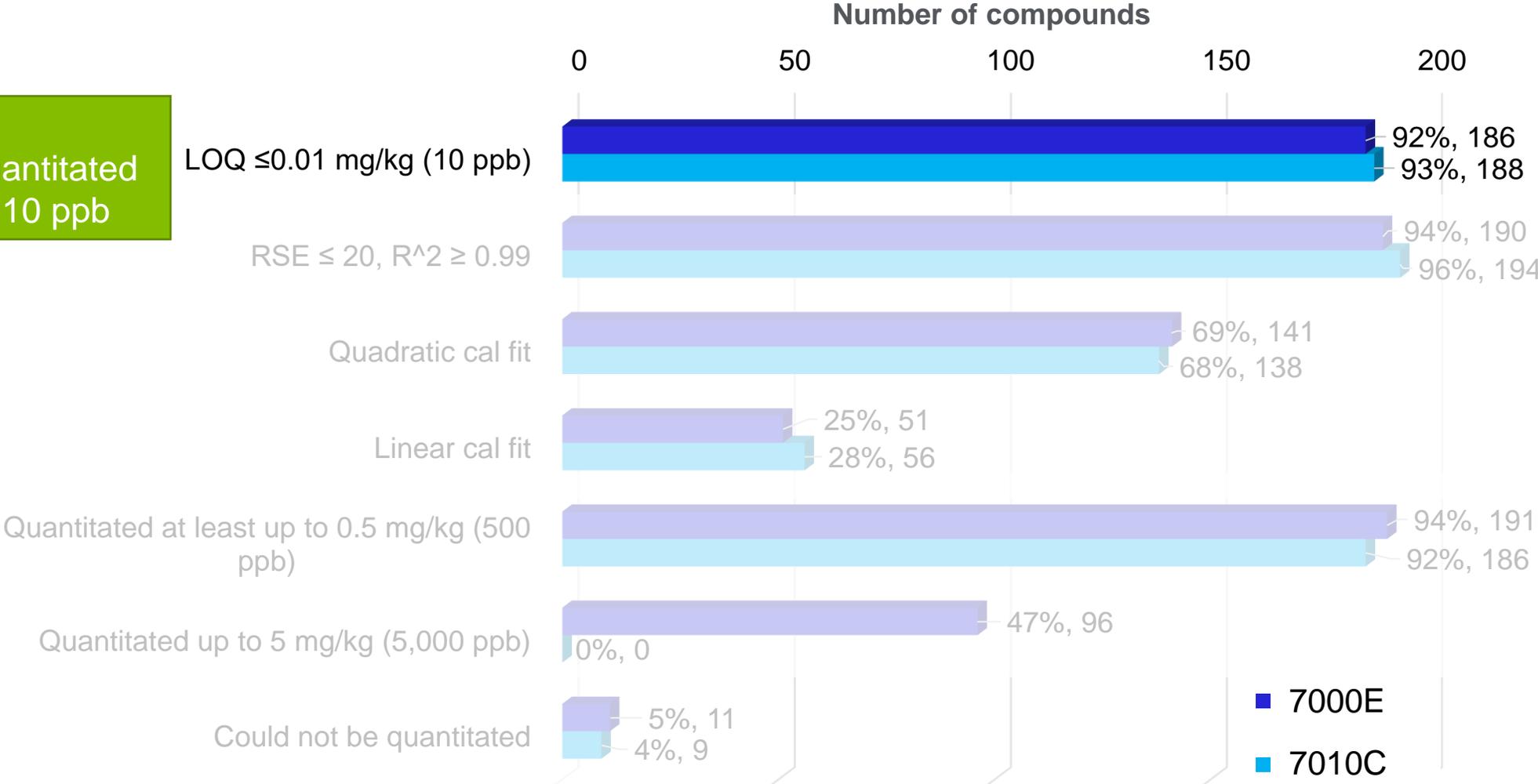


High Efficiency (HES)
EI Source



Calibration Performance in Spinach QuEChERS Extract for 203 Pesticides

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



Summary of Analyzing Pesticides with H₂ 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 H₂
- The optimized setup with H₂ **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 H₂.

GC/TQ EI source considerations

The HydroInert EI source:

- Improved sensitivity compared to the standard EI with H₂
- Best spectral fidelity

The HES EI source:

- Best sensitivity observed with H₂

Agilent GC/MS Best Practices

Infographic link

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



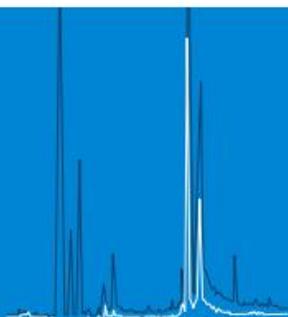
Achieve greater reproducibility



Agilent Captiva EMR HCF2 (5610-2088)
Agilent Captiva EMR GPD (5610-2091)

Screen Sample Matrix

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



Prevent source overload



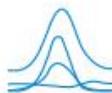
Improve accuracy of analysis



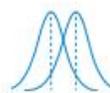
Maintain optimal performance

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



Use Backflush

Mid-column backflushing extends the 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.



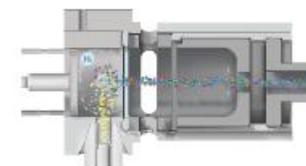
Save time cleaning, reconditioning, and recalibration



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.

