Application Note

Food & Beverage Testing

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

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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 conditions with hydrogen surpassed that with helium. The optimized injection conditions included solvent vent mode, a 2 mm dimpled liner, and the use of analyte protectants. The analyte response with hydrogen was enhanced on average 10-fold when using the optimized conditions compared to using hydrogen carrier gas with the injection conditions, commonly used with helium. Both the Agilent HydroInert 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.

The resulting method allowed for quantitation of over 90% of the 203 target pesticides at or below the default MRL of 10 parts per billion (ppb) in the pigmented spinach matrix with both the HydroInert and the HES sources. The method detection limits (MDLs) for compounds susceptible to reactions with hydrogen, and hence, presenting the biggest challenge to the analysis with hydrogen, were in the sub-ppb range, with the HES enabling higher sensitivity and lower MDLs. The calibration performance was demonstrated over a broad range of concentrations, meeting the SANTE/11312/2021 guidelines. The relative standard error (RSE) for over 94% of 203 targets was below 20%. Even the compounds most prone to reacting with hydrogen, such as tecnazene, could be accurately quantitated over the ranges of 0.5 to 5,000 ppb and 0.1 to 1,000 ppb with the HydroInert and HES sources, respectively. Finally, simultaneous dynamic MRM and full scan data acquisition mode was demonstrated for accurate quantitation and reliable compound identification. The identification was based on spectral matching with the Agilent 8890/7000E and the Agilent 8890/7010C GC/TQ systems using hydrogen carrier gas.

Introduction

Due to recurring helium shortages and increased prices experienced in the recent years, there is an intensified demand for adapting the GC/MS analysis to hydrogen carrier gas. While helium is the optimal carrier gas for GC/MS, hydrogen has emerged as a viable alternative. Hydrogen brings chromatographic benefits to the analysis if proper measures are taken to translate the method.[1,2] Additionally, hydrogen emerges as a renewable and cost-effective alternative for sustainable laboratory practices. However, unlike helium, hydrogen is not chemically inert. This lack of inertness raises concerns as hydrogen can potentially react with target analytes, matrix components, or solvents. Such reactions can lead to compound degradation, chromatographic issues like peak tailing, distorted ion ratios in the mass spectrum, compromised library matching, and decreased sensitivity. Therefore, the transition from helium to hydrogen carrier gas requires due diligence. The EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion Guide[1] provides detailed instructions for method conversion from helium to hydrogen carrier gas. The user guide outlines considerations and procedures for hydrogen safety necessary to make the transition to hydrogen carrier gas successful.

Since the introduction of the HydroInert source, several applications have been implemented successfully with hydrogen carrier gas. Those applications included analysis of semivolatile organic compounds with GC/MS[3] and GC/MS/MS[4], volatile organic compounds[5], polycyclic aromatic hydrocarbons (PAHs) in environmental samples with GC/MS[6] and GC/MS/MS[7] and PAHs in infant formula with GC/MS[8], flavor and fragrance GC/MS analysis[9], and the EPA TO-15 analysis.[10] Analyzing pesticides poses its own set of challenges, even when using helium as the carrier gas, due to the diverse and labile nature of many pesticides and the complex matrices they are found in. The best practices in sample preparation and GC/MS/MS analysis of pesticides with helium carrier gas have been described in previous work.[11] This application note describes the key strategies for analyzing pesticides with hydrogen carrier gas while delivering high-quality uncompromised results. The components enabling successful analysis of pesticides with hydrogen in foods include:

- Effective sample extraction and matrix cleanup, such as QuEChERS extraction followed by Agilent Captiva enhanced matrix removal (EMR) pass-through cleanup
- Solvent vent injection mode with the 2 mm dimpled liner and the temperature-programmable multimode inlet (MMI)
- Use of the analyte protectants
- Minibore columns with the same phase ratio as those with the helium method (20 m × 20 m, 0.18 mm × 0.18 µm)
- Midcolumn backflush
- Method translation and retention time-locking techniques
- EI sources with reduced or eliminated source reactivity with hydrogen

The novelty of the work involved the evaluation of several EI sources, including the standard Inert Plus Extractor EI source, the HydroInert source, and the HES for pesticides analysis with hydrogen carrier gas. Both the Agilent 8890/7000E and Agilent 8890/7010C gas chromatography/triple quadrupole mass spectrometry (GC/TQ) systems were ideally suited to meet the analytical needs with hydrogen carrier gas.

The resulting method was applied to analyzing a broad panel of 203 GC-amenable pesticides in a spinach QuEChERS extract to demonstrate method sensitivity. The achieved sensitivity was sufficient for quantitating pesticides at the MRLs. Calibration performance was demonstrated over the concentration range up to four orders of magnitude while meeting SANTE 11312/2021 guidelines.[12] Simultaneous dynamic multiple reaction monitoring (dMRM) and scan (dMRM/scan) data acquisition mode was demonstrated for

compound screening via spectral deconvolution and search against spectral libraries, while the dMRM data were used for accurate quantitation. The reduced/eliminated in-source hydrogen reactions with the HydroInert and HES sources significantly improved library match scores and, hence, identity confirmations for untargeted compounds.

Experimental

GC/TQ analysis

The 8890/7000E and 8890/7010C GC/TQ systems (Figure 1A) were used and configured to achieve the best performance with hydrogen carrier gas. The GC was configured with the Agilent 7693A automatic liquid sampler (ALS) and 150-position tray, an MMI operated in solvent vent mode, midcolumn backflush capability provided by an Agilent purged Ultimate union (PUU) installed between two identical 20 m columns (0.18 mm × 0.18 µm), and the 8890 GC pneumatic switching device (PSD) module (Figure 1B). A 40 m column can be used in lieu of two 20 m columns, although without the backflushing capability. Several EI source configurations including the optional 3 mm and 6 mm lenses were evaluated with the 7000E GC/TQ. The best performance with the 7000E GC/TQ was achieved when using the HydroInert source with the default 9 mm lens. The 7010C GC/TQ delivered excellent performance with hydrogen carrier gas when using the standard HES. The best practices when converting the GC/TQ from helium to hydrogen carrier gas described in the Helium to Hydrogen Conversion Guide[1] were followed to ensure safe and successful conversion. The instrument operating parameters are listed in Table 1.

The Method Translation software allows users to port a current GC method to another GC column configuration and/or carrier gas while ensuring that relative retention order is maintained, i.e., peaks elute in the same order.[13,14] It is available among the downloadable GC Tools from the Agilent GC calculators and method translation software page.[15] In this work, the method translation technique was used to determine the approximate hydrogen carrier flow rate for a 20 m × 20 m column configuration. This method translation was used to obtain nominally the same retention times as with the conventional 15 m × 15 m method with helium carrier gas i.e., speed gain of 1. Those flows were 1 and 1.2 mL/min for columns 1 and 2, respectively. Next, retention time locking to chlorpyrifos methyl at 9.143 minutes resulted in precise matching of the retention times between the hydrogen and the conventional 20-minute helium method described in other application notes[11] and in the GC/MS/MS pesticide residue analysis reference guide.[16] Chlorpyrifos methyl is selected as a retention time locking compound because it typically does not present analytical challenges, elutes in the middle of the pesticide chromatographic range, and is commonly used as a process control compound for GC-amenable pesticides used in the Pesticide Data Program laboratories.[16] Retention time locking is a technique that allows a new column or instrument to have retention times that match the retention times provided in the databases, including the MRM database used in this work, or an existing method precisely, allowing methods to be easily ported from one instrument to another and across the Agilent GC/MS and GC/MS/MS instruments globally.

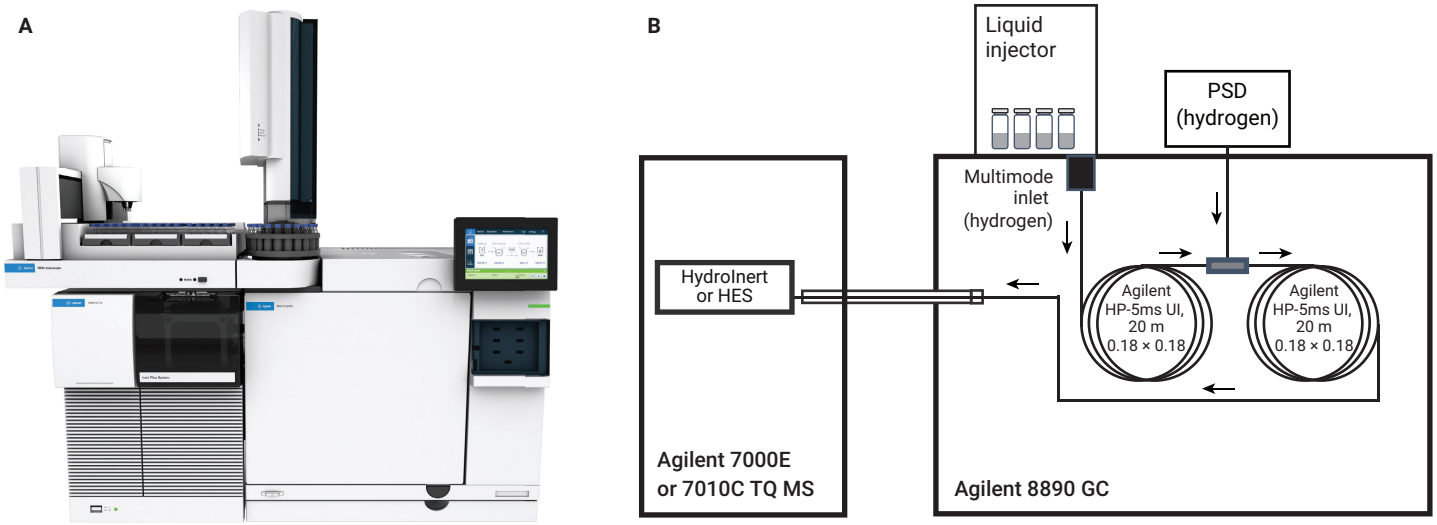

Figure 1. The Agilent 8890/7000E and 8890/7010C GC/TQ system (A) and system configuration (B).

Table 1. Agilent 8890/7000E and 8890/7010C gas chromatograph and mass spectrometer conditions for pesticide analysis with hydrogen carrier gas.

GC	
Model	Agilent 8890 with Fast Oven, Auto Injector and Tray
Inlet	Multimode Inlet (MMI)
Mode	Solvent Vent
Purge Flow to Split Vent	60 mL/min at 2.56 min
Septum Purge Flow	3 mL/min
Vent Flow	100 mL/min
Vent Pressure	5 psi until 0.06 min
Septum Purge Flow Mode	Switched
Cryo	On (Air)
Cryo Use Temperature	200 °C
Injection Volume	2.0 µL
L1 Airgap	0.2 µL
Gas Saver	Off
Inlet Temp	60 °C for 0.06 min, then to 280 °C at 600 °C/min
Postrun Inlet Temperature	310 °C
Postrun Total Flow	25 mL/min
Carrier Gas	Hydrogen
Inlet Liner	Agilent Ultra Inert 2 mm dimpled liner
Inlet Liner Part Number	5190-2297
Oven	
Initial Oven Temperature	60 °C
Initial Oven Hold	1 min
Ramp Rate 1	40 °C/min
Final Temp 1	170 °C
Final Hold 1	0 min
Ramp Rate 2	10 °C /min
Final Temp 2	310 °C
Final Hold 2	2.25 min
Total Run Time	20 min
Postrun Time (Backflush Duration)	1.5 min
Equilibration Time	0.5 min
Column 1	
Type	Agilent HP-5ms UI (p/n 19091S-577UI)
Length	20 m
Diameter	0.18 mm
Film Thickness	0.18 µm
Control Mode	Constant flow
Flow	1.0 mL/min (nominal before retention time locking)
Inlet Connection	Multimode inlet (MMI)
Outlet Connection	PSD (PUU)
PSD Purge Flow	5 mL/min
Postrun Flow (Backflushing)	–6.260 mL/min

Column 2	
Type	Agilent HP-5ms UI (p/n 19091S-577UI)
Length	20 m
Diameter	0.18 mm
Film Thickness	0.18 µm
Control Mode	Constant flow
Flow	1.2 mL/min (nominal before retention time locking)
Inlet Connection	PSD (PUU)
Outlet Connection	MSD
Postrun Flow (Backflush Duration)	6.406 mL/min
MSD	
Model	Agilent 7000E or 7010C
Source	HydroInert (G7006-67930) or HES
Vacuum Pump	Performance turbo
Tune File	Atunes.eiex.jtune.xml or Atunes.eihs.jtune.xml
Solvent Delay	3.75 min
Quad Temperature (MS1 and MS2)	150 °C
Source Temperature	280 °C
Mode	dMRM; Scan (45-450 *m/z*; 220 ms); dMRM/Scan (200 ms)
He Quench Gas	Off
N_2 Collision Gas	1.5 mL/min
Collision Energies	Same as listed for helium in P&EP 4.0
MRM Statistics	
Total MRMs (dMRM mode)	614
Minimum Dwell Time	3 ms
Minimum Cycle Time	69.8 ms
Maximum Concurrent MRMs	52
EM Voltage Gain Mode	10
Scan Parameters	
Scan Type	MS1 Scan
Scan Range	45 to 450 *m/z*
Scan Time	220 ms
Step Size	0.1 amu
Threshold	0
EM Voltage Gain Mode	1
Agilent MassHunter Workstation	– MassHunter Acquisition software for GC/MS systems 10.2 – MassHunter Quantitative 10.1 – Unknowns Analysis Quantitative Analysis 10.1 – MassHunter Qualitative 10

The precise matching of the retention times between the hydrogen carrier method and the Agilent MassHunter Pesticide & Environmental Pollutant MRM database (P&EP 4, part number G9250AA) allowed for creating the MS method seamlessly and enabled great time savings. The database includes up to 9 MRM transitions for each of over 1,100 compounds and their retention times for the 20-minute analysis with helium or hydrogen. The use of P&EP 4 increased the ease and speed of setting up a targeted dynamic MRM (dMRM) method.

Acquiring data in dMRM mode enabled the capability for large multi-analyte assays and accurate quantitation of narrow peaks by an automated and most efficient dwell time distribution. The dMRM capability resulted in successful analysis for a large panel of 203 pesticides with 614 total MRM transitions and up to 52 concurrent MRMs. Furthermore, dMRM allowed the analyst to add and remove additional analytes with ease.

Full scan data acquisition mode was used for evaluating mass spectra with hydrogen carrier gas and for the initial screening of the matrix extract. This screening was used to evaluate the in-source loading and for monitoring the efficiency of the sample cleanup procedure that followed the QuEChERS extraction. Either a blank matrix, a representative sample, or a matrix-matched calibration standard can be used for initial screening.

Additionally, simultaneous dMRM/scan data acquisition mode enabled simultaneous targeted quantitation of a large multi-analyte assay and full scan data acquisition for unknown identification and retrospective analysis within one analytical run.

Agilent MassHunter Workstation revisions 10.1 and 10.2 including MassHunter Acquisition for GC/MS 10.2, MassHunter Quantitative Analysis 10.1, including Unknowns Analysis, and MassHunter Qualitative Analysis 10.0 packages were used in this work.

Sample preparation

A sample preparation workflow chart is shown in Figure 2. The sample preparation included two major steps: sample extraction by traditional QuEChERS extraction, followed by Captiva enhanced matrix removal (EMR) pass-through cleanup. The Captiva EMR–High Chlorophyll Fresh with NH_2 (Captiva EMR–HCF1) cartridge was used for high chlorophyll fresh matrix (spinach). The new sample preparation workflow demonstrated as a simplified procedure with improvement on both sample matrix removal and targets quantitation data quality.

As shown in Figure 2, samples were first extracted using the traditional Agilent Bond Elut QuEChERS EN extraction kit (part number 5892-5650CH). Homogenized fresh spinach

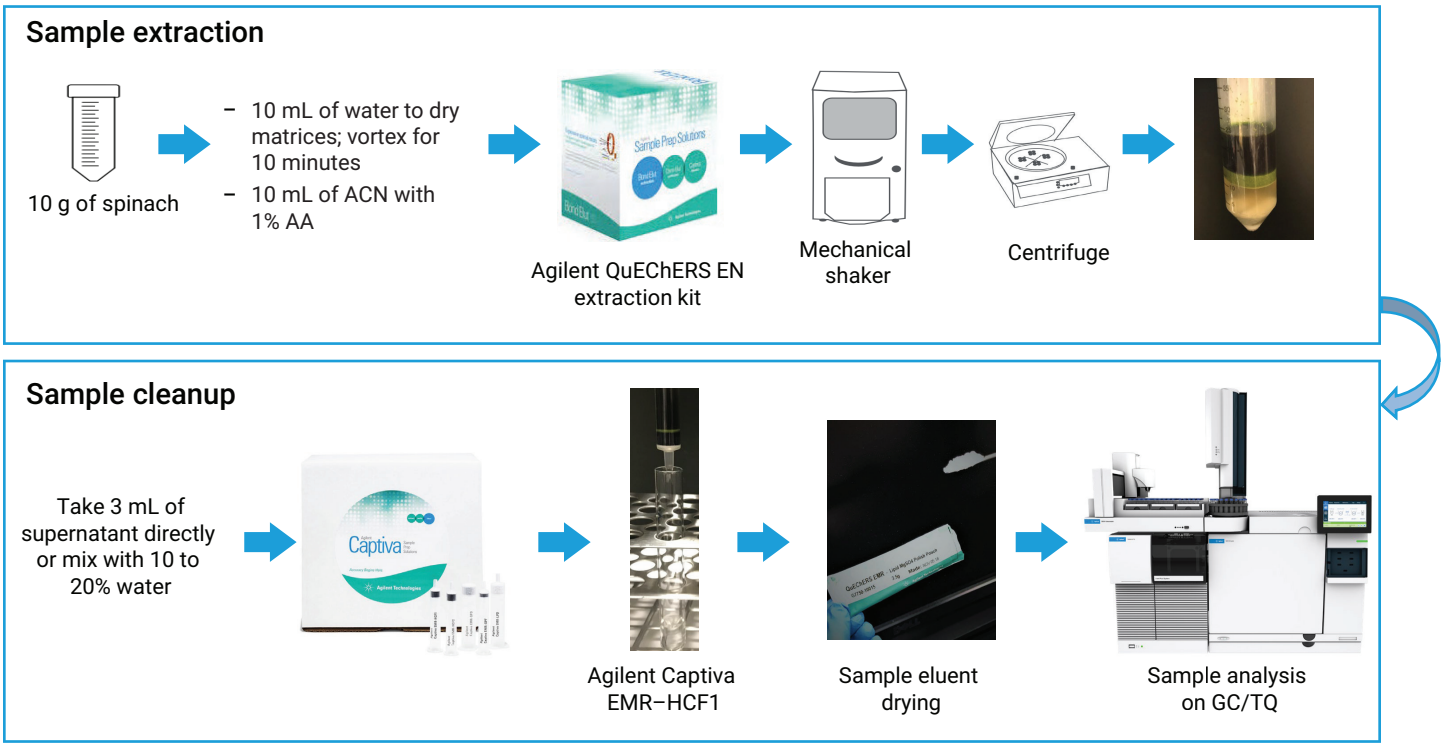

Figure 2. Sample preparation flowchart including traditional Agilent QuEChERS extraction, followed by Agilent Captiva EMR pass-through cleanup.

(10 g) was used for extraction. The 10 mL of acetonitrile (ACN) with 1% acetic acid was then added, followed by extraction. After extraction, 3 mL of crude extract was transferred to an Agilent Captiva EMR–HCF1 cartridge (part number 5610-2088) for pass-through cleanup. The Agilent positive pressure manifold 48 processor (PPM-48; part number 5191-4101) was used for Captiva EMR pass-through cleanup processing. The sample eluent was collected and further dried by anhydrous $MgSO_4$ (Agilent part number 5982-0102). Samples were then ready for GC/TQ analysis.

Analyte protectants

Analyte protectants (APs) were added to all the samples so that the stock solution of the APs comprised 10% of the injected sample volume. The stock solution of the APs consisted of 3-ethoxy-1,2-propanediol (ethylglycerol) at 10 mg/mL, D-sorbitol at 1 mg/mL, L-gulonolactone at 1 mg/mL dissolved in ACN with 1% acetic acid and 12% of water (v/v). This mixture was found to be the most promising AP combination as reported in the peer-reviewed literature.[17] The APs can be added via sandwich injection using the Agilent 7693A automatic liquid sampler as described in the previously published application notes.[18,19] When using the APs, it is recommended that one of the syringe wash solvents comprises of ACN/isopropanol mixture 1:1 (v/v) to prevent syringe plunger stickiness. The polytetrafluoroethylene (PTFE) tipped plunger syringes (10 µL) also helped in this respect (Agilent part number G4513-80220).

Matrix-matched calibration

Calibration performance was evaluated using a series of matrix-matched calibration standards ranging from 0.1 to 5,000 ppb (w/v), including 0.1, 0.5, 1, 5, 10, 50, 100, 250, 500, 1,000, and 5,000 ppb. The GC multiresidue pesticide kit (part number 32562, Restek, Bellefonte, PA, USA) containing 203 compounds, regulated by the FDA, USDA, and other global governmental agencies, was used for preparing matrix-matched calibration standards. The concentrations expressed in ppb (w/v) correspond to the pesticide concentration in the injected sample. The QuEChERS sample preparation procedure resulted in a dilution factor of 1. Hence, the reported concertation in ppb in the sample corresponds to µg/kg in the original commodity. The standard α-BHC-d6 (Agilent QuEChERS IS standard number 6, part number PPS-610-1) at a final concentration of 50 ppb in vial was used as the internal standard for quantitation of the target pesticides.

The developed method calibration performance was validated with both HydroInert and HES sources according to the analytical method validation and performance criteria outlined in SANTE 11312/2021.[12] A multilevel calibration that included up to 11 levels was used. An appropriate calibration function, either linear or quadratic, guided by the lower value of the relative standard error (RSE) was used. A weighting factor of 1/x allowed for maintaining accuracy across the entire calibration range. The deviation of the back-calculated concentrations of the calibration standards from the true concentrations, using the calibration curve in the relevant region, did not exceed ±20%.

Method detection limits

There are many alternative procedures to estimate the MDL. The approach used in this study was to perform eight injections of a matrix-matched calibration standard to assess the uncertainty in the measuring system.[20] This approach is recommended by The Official Journal of the European Communities, Commission Decision of 12 August 2002; Implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results in the EU[21] and the EPA Guidelines Establishing Test Procedures for the Analysis of Pollutants in the US.[22] The concertation selected for the multiple injection trials was 1 ppb for most compounds. For compounds with higher limits of quantitation, eight trials were performed at the concentration of 5 ppb. The calculated MDLs were obtained by applying the formula shown in Equation 1.

$$MDL = s \cdot t(n - 1, 1 - alpha = 99) = s \cdot 2.998$$

Equation 1.

Where:

t (n – 1, 1 – alpha) = t value for the 99%, which is 2.998

Confidence level with n – 1 degrees of freedom

n = number of trials (8)

s = standard deviation of the eight trials.

The calculated MDL < spike level < 10x calculated MDL equation was used to evaluate the empirically determined MDL and ensure its validity.

Results and discussion

Increased chromatographic resolution while maintaining retention times with hydrogen

To assess the feasibility of analyzing pesticides using hydrogen carrier gas, a panel of 203 GC-amenable pesticides was evaluated in a pigmented spinach matrix. Increased chromatographic resolution was achieved when using the recommended minibore column configuration. The configuration was comprised of the two 20 m columns (0.18 mm × 0.18 µm) with hydrogen carrier gas, resulting in a 20-minute analysis compared to the conventional 20-minute analysis with helium carrier gas (Figure 3). It is noted that the oven program used with hydrogen was the same as with helium. The combination of method translation followed by retention time locking allowed for transferring the conventional 20-minute analysis with helium carrier gas to hydrogen carrier gas, while maintaining the relative elution order and precisely matching the retention times. The magnified part of the chromatogram shown in Figure 3 demonstrates the increased chromatographic resolution for cyfluthrins and cypermethrins.

The advantages provided by chromatographic resolution include reduced matrix interferences and minimized interference between coeluting analytes, therefore streamlining a complex pesticide residue analysis that often spans over several hundreds of targets.

The ability to precisely predict and match the retention times observed with helium resulted in great time savings and significantly simplified the transition from helium to hydrogen. This prediction provides an advantage in simplifying the conversion of the existing MRM methods from helium and allows for using the retention times from the databases created with helium, such as P&EP 4.

Proof of concept: fast 10-minute analysis with hydrogen

In addition to translating the method from helium to hydrogen, with a speed gain of 1 as presented in Figure 3, it was shown that a faster analysis can be performed with hydrogen. Previously, a fast 10-minute analysis has been demonstrated with helium as published elsewhere.[23] The chromatographic resolution with hydrogen and fast analysis was similar to that observed with the conventional 20-minute analysis with helium. The same minibore 10 m × 10 m (0.18 mm × 0.18 µm) HP-5ms UI column configuration as discussed in the application note on the fast analysis of pesticides with helium[23] was used with hydrogen.

The retention times observed with the 10-minute analysis using hydrogen and a 10 m × 10 m column configuration precisely matched the retention times observed with the 10-minute analysis with helium when using the 10 m × 10 m column configuration reported in the corresponding application note.[23] The method was precisely scaled from the conventional 20-minute analysis using the method translation tool, providing a speed gain of 2. New retention times (RT) were calculated using the following empirical equation: $RT_{new} = RT_{old}/2 + 0.09$ minutes. This formula is only applicable to the 10 m × 10 m method described in this application note.

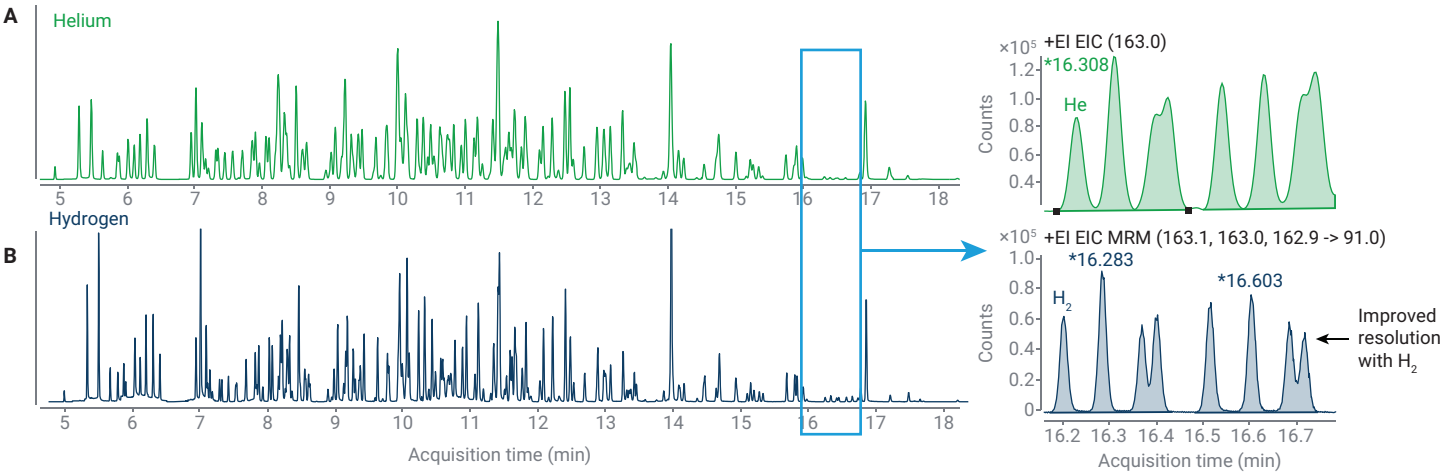

Figure 3. MRM chromatograms for a mixture of (A) 203 pesticides acquired with helium carrier gas with the conventional 20-minute method, (B) 203 pesticides acquired with hydrogen with the 20-minute method using a 20 m × 20 m minibore configuration.

Figure 4 shows an MRM chromatogram acquired for a subset panel consisting of 103 compounds out of 203. The resolution for cyfluthrins and cypermethrins was comparable to that observed with helium and the conventional 20-minute analysis (Figure 3A). Increased chromatographic resolution with hydrogen carrier gas resulted in narrower peaks. Thus, data rate needed to be increased with the fast hydrogen method resulting in shorter dwell times. A fast 10-minute analysis is recommended only when targeting panels of fewer than 200 compounds.

The best practices for pesticide analysis described elsewhere[11] unlocked high analysis ruggedness as demonstrated with 700 consecutive injection of spinach QuEChERS extract using the 10-minute analysis with helium as shown in application note 5991-4967EN.[23] As a result, no additional system maintenance, aside from liner and septum change every 100 injections was needed. The same best practices were implemented in this work ensuring the analysis ruggedness and robustness.

The 20-minute analysis with hydrogen carrier using the 20 m × 20 m (0.18 mm × 0.18 µm) column configuration was used in the rest of this work.

Optimized injection with hydrogen

The injection step is often considered among the most critical and vulnerable stage in the GC/MS analysis of pesticide residue, especially at trace levels. The multimode inlet (MMI) with the programmable temperature injection is commonly used to significantly reduce thermal degradation. It enables effective analyte transfer to the column through rapid temperature and flow programming.[16,24] The solvent vent mode used with the MMI resulted in the elimination of most of the injection solvent through the split vent at a low temperature, permitting the introduction of a larger injection volume. The solvent vent mode resulted in improved peak shapes of early eluting analytes when injecting 2 µL of ACN.

The optimized injection conditions are summarized in Table 1. Starting the injection at a lower temperature of 60 °C and ramping up to 280 °C allowed volatilization of all the target analytes while maintaining their chemical integrity upon introduction to the GC column. A high vent flow of 100 mL/min enabled solvent elimination resulting in improved peak shape, which could be distorted when injecting larger volumes of ACN. Also, in the postrun, the inlet was further heated to 310 °C while backflushing to bake out any matrix residue that may remain in the inlet. This increases maintenance-free operation of the system.

The use of APs provided GC system deactivation in each injection. This resulted in improved ruggedness, that is, long-term repeatability of analyte peak intensities, shapes, and retention times. Moreover, the use of APs helped with equalization of both the matrix-induced response enhancement and matrix-induced response diminishment effects.[16]

The combination of solvent vent injection with the injection volume of 2 µL, an Ultra Inert 2 mm dimpled liner (Agilent part number 5190-2297), and the use of APs resulted in high sensitivity even for challenging pesticides. For example, for tolclofos-methyl, the response was increased 22-fold when comparing the injection of 1 µL in cold splitless mode in solvent to a 2 µL injection in solvent vent mode in the QuEChERS extract with the APs. The average response increase over 203 compounds was 10.9-fold when comparing the optimized 2 µL injection in solvent vent mode in the QuEChERS extract with the APs using the 2 mm dimpled liner to the cold splitless injection with 1 µL injection volume.

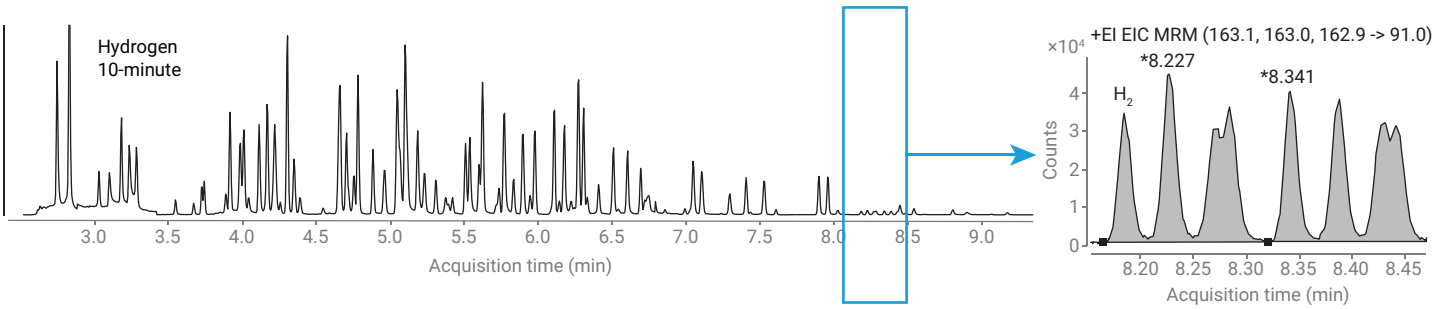

Figure 4. MRM chromatograms for a mixture of 103 pesticides acquired with hydrogen with the 10-minute method using a 10 m × 10 m minibore configuration.

EI source considerations with hydrogen: eliminating in-source reactions to preserve sensitivity and spectral fidelity

Hydrogen carrier gas is expected to provide advantages for chromatographic separation. However, hydrogen could present a challenge for detection when a mass spectrometer is used. Because hydrogen is not inert, it can react with compounds susceptible to hydrogen reduction in the EI source. If an EI source that does not eliminate source-induced reactivity is used, then chemical transformations will take place leading to:

- Spectral changes with hydrogen compared to helium
  - The existing spectral libraries cannot be used for compound identification
  - Previously developed acquisition methods, including SIM ions and MRM transitions, cannot be consistently used with hydrogen
- Undesirable and uncontrollable reactions
  - Quantitation accuracy and precision could be compromised if in-source reactions occur
  - Calibration linearity is affected
- A need to verify each compound for potential reactivity with hydrogen

When using GC/TQ in the MRM data acquisition mode, minimizing or eliminating the undesirable in-source reaction is important because the ions that are diminished in the spectrum with hydrogen and the ions where abundance increases should not be used as precursor ions in the MRM transitions. The reduced ions will lead to substantially sacrificed sensitivity. The newly formed ions are products of uncontrolled chemical reactions occurring in the source, whose rate may depend upon concentration. Therefore, such ions should not be used for quantitation. This means that the MRMs developed with helium and those available in the databases cannot be used for those compounds that react with hydrogen. Finding suitable precursors for compounds reacting with hydrogen in the source can be extremely challenging because of the unpredictable and uncontrollable nature of the in-source reactions.

For this reason, using the EI sources with reduced or eliminated source reactivity such as HydroInert and HES is essential to minimize or prevent the undesirable in-source reactions when using hydrogen.

It is commonly known and expected that hydrogen carrier gas often reduces sensitivity 2 to 5-fold of standard EI sources.[25] The reduced sensitivity can be a combination of a decreased signal and increased noise and is anticipated even for the compounds that do not interact with hydrogen in the EI source.

For example, chlorpyrifos-methyl does not undergo pronounced reaction with hydrogen in the EI source as evidenced by its mass spectrum unchanged with hydrogen carrier gas. Figures 5A and B show the mass spectra acquired for chlorpyrifos-methyl with helium and hydrogen using the standard Inert Plus Extractor EI source, equipped with the 3 mm extractor lens. In both cases, the spectra largely resemble the library spectrum shown in the mirror plot resulting in good library match scores. Figure 5C shows the quantifying and qualifying MRM transitions for chlorpyrifos-methyl acquired with helium (on the top) and with hydrogen. With the 7000E GC/TQ, chlorpyrifos-methyl can be reliably detected at 5 ppb in spinach extract with hydrogen carrier gas using either the conventional or the HydroInert EI sources. The observed sensitivity in terms of signal-to-noise ratio is comparable to that observed with helium, although slightly decreased. The detection limits with the 7010C GC/TQ were lower than with the 7000E, enabling the detection of chlorpyrifos-methyl at 0.5 ppb with both helium and hydrogen. With every MS EI source tested, a decrease in signal-to-noise ratio was observed with hydrogen near the limit of detection and was less pronounced at higher concentrations. With the HES, the slight decrease in sensitivity towards chlorpyrifos-methyl was noted at 0.5 ppb (Figure 5C). Similar performance was observed for other compounds, whose spectra with hydrogen looked like the spectra with helium.

In summary, the compounds that did not react with hydrogen in the EI source, could be detected with hydrogen. A decrease in signal-to-noise ratio at the low levels, close to the detection limits, was 2 to 5-fold with hydrogen when compared to helium. The 7010 GC/TQ equipped with the HES was more sensitive than the 7000E GC/TQ.

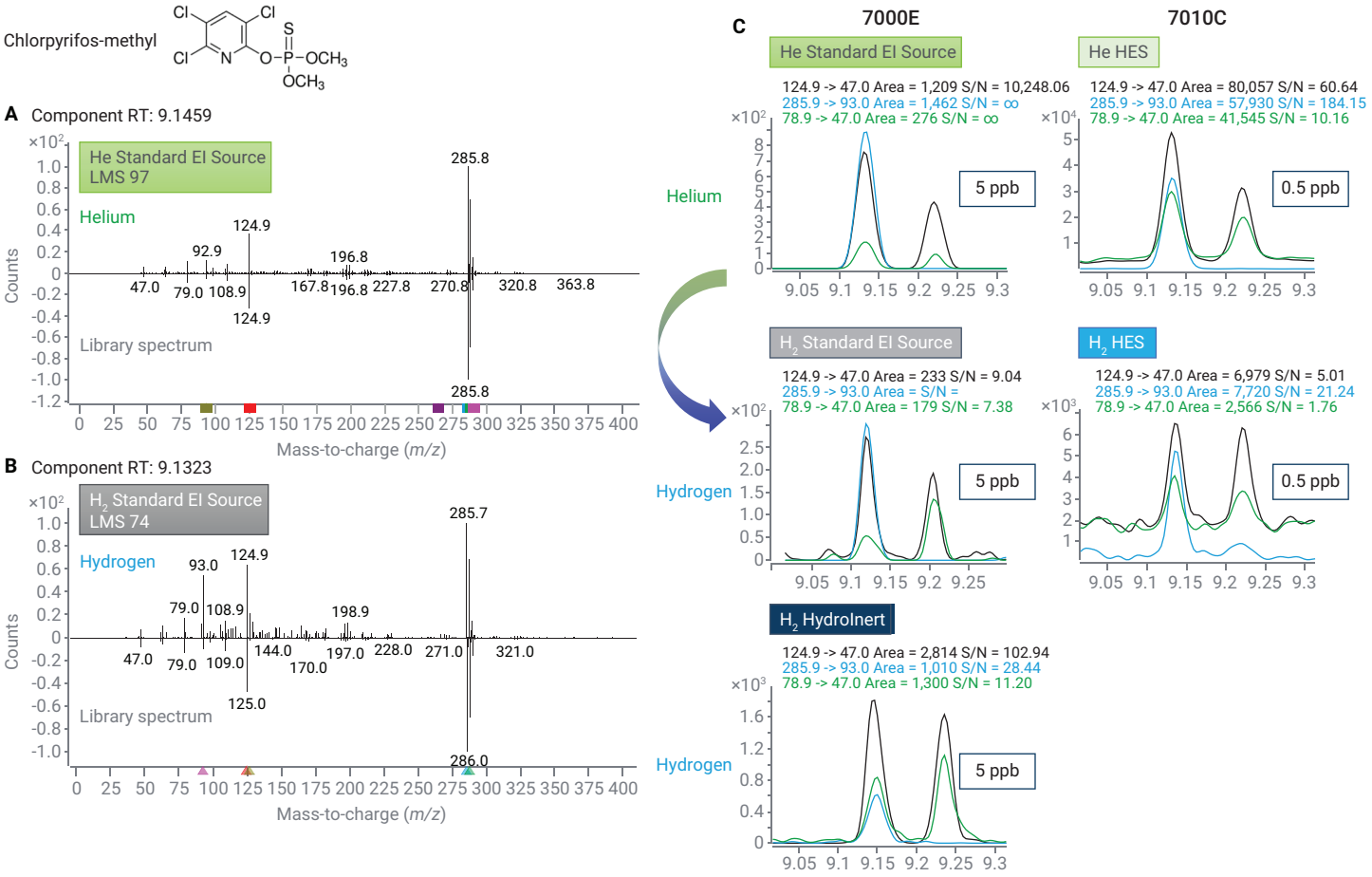

Figure 5. Mass spectra and MRM chromatograms for chlorpyrifos-methyl acquired with helium and hydrogen using the standard EI source, the HydroInert, and the HES.

Unlike chlorpyrifos-methyl, quantitation of compounds susceptible to reacting with hydrogen carrier gas is hindered with a traditional EI source. For example, tecnazene undergoes hydrogenation in a traditional EI source as evidenced by the changed ion ratios of 261 *m/z*, 231 *m/z*, 215 *m/z*, 203 *m/z*, 161 *m/z* (Figure 6B compared to Figure 6A) and the low library match score of 59. Nitro compounds are known to be susceptible to hydrogenation when in the presence of heat, hydrogen, and metal surfaces, and all these factors are present in the standard EI source. There is a large abundance of 231 *m/z* and low 261 *m/z*, indicating conversion of tecnazene to tetrachloroaniline in the source. This conversion is confirmed to occur in the source because the mass spectrum is observed at the retention time of tecnazene, which is well separated from tetrachloroaniline. More information on the in-source conversions is provided in the technical overview of HydroInert source.[26] The resulting diminishment of 261 *m/z*, 259 *m/z*, and 215 *m/z* results in the 100-fold loss of sensitivity when using the standard EI source with hydrogen carrier gas compared to helium. Figure 6E shows that 50 ppb was the lowest concentration at which tecnazene could be detected with hydrogen if using the standard EI source. Substantial sensitivity reduction makes it impossible to analyze tecnazene at the default MRL of 10 ppb with the standard EI source.

Unlike the standard EI source, HydroInert, and HES sources reduce or eliminate source reactivity, hence, minimizing or preventing the undesirable in-source reactions with hydrogen. This is evidenced by the excellent matching of the spectra observed with hydrogen using HydroInert (Figure 6C) and HES (Figure 6D) and the library spectrum acquired with helium resulting in the high library match scores of 94 and 93, respectively. The ability to preserve the intact mass spectrum allowed for using the same MRM transitions as with helium. The sensitivity with hydrogen was sufficient to detect tecnazene at 0.5 ppb in spinach QuEChERS extract with HydroInert and 0.1 ppb with HES (Figure 6E).

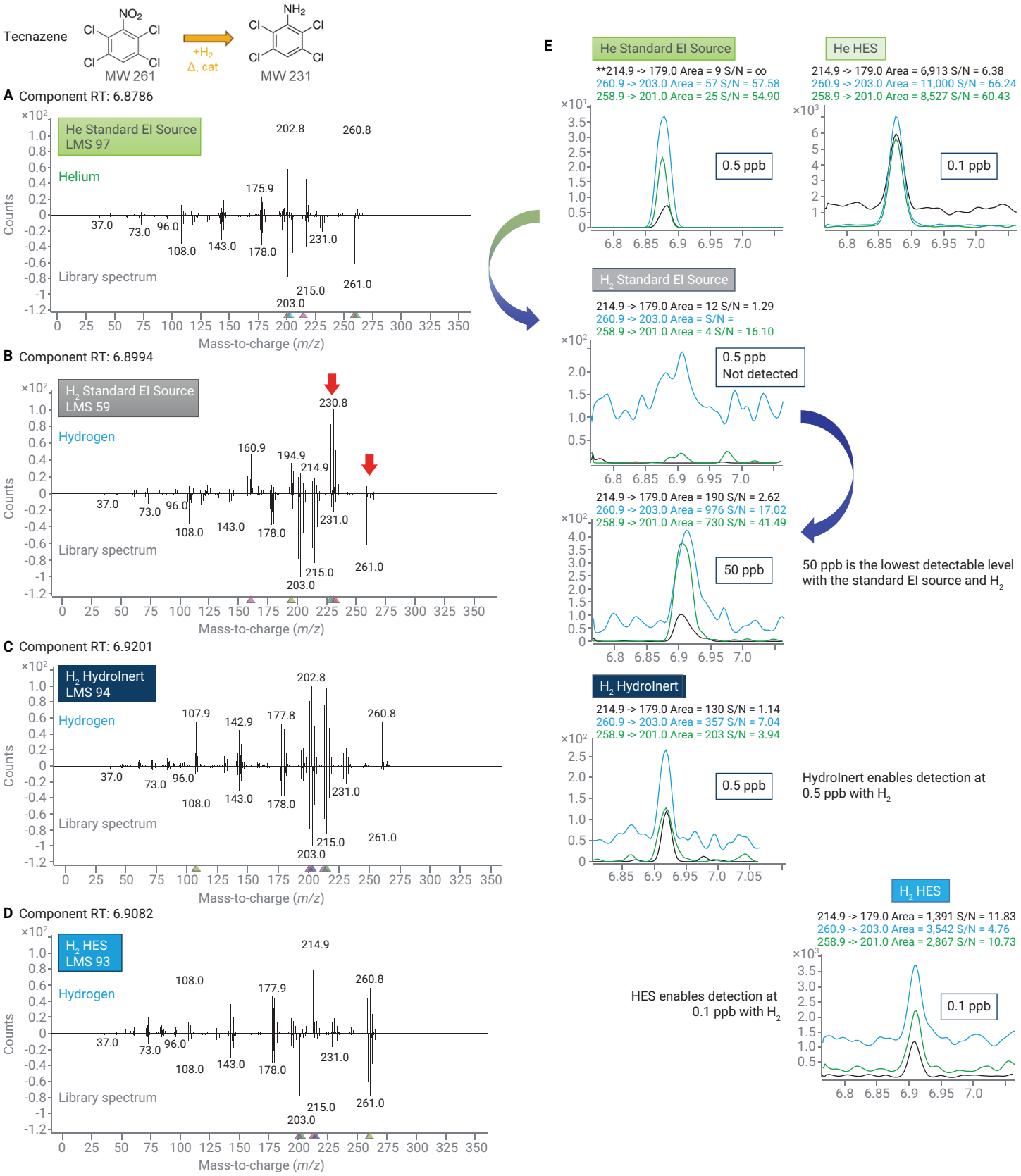

Figure 6. Mass spectra and MRM chromatograms for tecnazene acquired with helium and hydrogen using the standard EI source, the HydroInert, and the HES.

Various EI source configurations were evaluated in this study. It was found that the optional larger diameter extractor lenses (6 and 9 mm) in the standard Inert Plus Extractor EI source did not provide benefits as pronounced as HydroInert source. Among the portfolio of lenses available for HydroInert, the default 9 mm lens was shown to provide the best performance with hydrogen carrier gas in terms of spectral fidelity and sensitivity when compared to the 3 and 6 mm HydroInert lenses. For HES, no source modification was needed.

Both HydroInert and HES demonstrated the capability for successful pesticide analysis by GC/TQ, largely due to prevention of in-source reactions when hydrogen carrier gas is used. The HydroInert source was specifically developed to work with hydrogen carrier gas as it is manufactured from a material more inert than the standard EI source. HydroInert is available with the 7000E GC/TQ and can also be purchased as a replacement source for the 7000C, D, and E GC/TQs. HydroInert should not be used with helium carrier gas as discussed in the technical overview Agilent Inert Plus GC/MS System with HydroInert Source.[26] The HES source was found to minimize the in-source reactions similarly to HydroInert. However, unlike the Inert Plus extractor source design, the standard HES can be used in the GC/TQ with hydrogen providing the inert benefits, maintaining the spectrum fidelity, and enabling best sensitivity with hydrogen carrier gas.

The compounds that, like tecnazene, undergo chemical reaction with hydrogen when a traditional EI source is used could be easily identified by the compromised spectral fidelity expressed in the low library match scores. Fifteen compounds, for which spectra were noticeably distorted with hydrogen and the standard source, are listed in Table 2. These compounds feature diverse functional groups that can undergo hydrogenation, dehydrohalogenation, dehalogenation, double bond reduction, and other undesirable in-source reactions. The library match scores for these compounds were substantially lower with the standard source using hydrogen carrier when compared to helium. This is reflected with yellow shading in Table 2. The spectra for these compounds were restored when using HydroInert and HES sources. The restored spectra allowed for, first, using the MRM transitions developed with helium, and second, preserving sensitivity so that its decrease did not exceed 2 to 5-fold at the levels close to the detection limits. It is of note that like the compounds that did not react with hydrogen, sensitivity decrease for the compounds that undergo hydrogen reduction was most pronounced at low concentration, close to the detection limits. Appendix Figure 1 shows the comparison of the MRM chromatograms for the compounds susceptible to the in-source reactions acquired with helium and hydrogen at their detection limits. The evaluated sources shown in the Appendix Figure 1 are the standard Inert Plus Extractor EI source with a 3 mm lens, HydroInert, and HES with hydrogen, and the standard EI and HES with helium. Appendix Figure 1 provides a comprehensive comparison revealing:

- Substantial sensitivity losses with the standard EI source and hydrogen for the compounds susceptible to reacting with hydrogen
- Sensitivity recovered with HydroInert and HES using hydrogen when compared to the standard EI source
- Sensitivity comparison when transitioning from the standard EI source and helium to HydroInert with hydrogen or from HES with helium to HES with hydrogen
- Comparison of sensitivity between HydroInert and HES with hydrogen

The advantage of preserving the mass spectrum with hydrogen observed with HydroInert and HES resulted in the MDL levels below 1 ppb for the majority of the compounds most susceptible to reacting with hydrogen. The MDLs for those compounds observed with 7000E GC/TQ equipped with HydroInert and the 7010C equipped with HES are provided in Table 2. The MDL measurements were performed using a 1 ppb (w/v) matrix-matched standard for all compounds, except for prothiofos and profenofos, for which a 5 ppb (w/v) matrix-matched standard was used. Using HES enables lower MDLs than HydroInert with hydrogen. Higher sensitivity observed with HES is also demonstrated in Appendix Figure 1, where lower concentrations, often as low as 0.1 ppb, could be detected in spinach extract with HES even for the compounds most susceptible to reacting with hydrogen.

Table 2. Library match scores (LMS) observed for the pesticides most susceptible to reacting with hydrogen observed with helium and hydrogen carrier gasses with GC/TQ operating in scan data acquisition mode. Method detection limits (MDLs) observed with hydrogen using HydroInert and HES in dMRM mode.

Compound	Retention Time (min)	Library Match Scores in Scan MS1					Method Detection Limits (ppb)	
		Helium Carrier Gas		Hydrogen Carrier Gas			Hydrogen Carrier Gas	
		Agilent 7000E, Standard EI Source	Agilent 7010C, HES	Agilent 7000E, Standard EI Source	Agilent 7000E, HydroInert	Agilent 7010C, HES	Agilent 7000E, HydroInert	Agilent 7010C, HES
Tecnazene	6.915	82	84	59	94	93	0.49	0.24
BHC-alpha (benzene hexachloride)	7.623	98	98	81	93	96	0.69	0.20
Dichloran	7.783	89	93	67	90	89	1.00	0.31
BHC-beta	8.019	97	97	77	92	96	0.68	0.24
BHC-gamma (Lindane, gamma HCH)	8.133	80	82	73	69*	91	0.95	0.19
Pentachloronitrobenzene	8.212	91	93	67	91	95	0.31	0.38
BHC-delta	8.502	90	94	74	87	94	0.74	0.31
Heptachlor	9.328	91	88	74	87	93	0.74	0.29
Malathion	9.742	90	90	56	84	76	0.65	0.44
Bromophos-ethyl	11.037	93	90	62	87	92	0.63	0.26
Prothiofos	11.510	95	94	65	92	91	2.52	1.02
Profenofos	11.561	91	87	66	90	85	3.48	2.27
Sulprofos	12.666	98	88	61	87	91	0.87	0.39
Tebuconazole	13.292	93	92	66	89	76	0.58	0.30
Piperonyl butoxide	13.402	92	94	68	92	79	0.84	0.59

* Complete coelution of lindane with terbufos (<1 scan apart) resulted in a lower LMS.

Calibration performance

The developed method calibration performance was validated with both HydroInert and HES sources in accordance the analytical method validation and performance criteria outlined in SANTE 11312/2021.[12] The multilevel calibration was used so that the deviation of the back-calculated concentrations of the calibration standards from the true concentrations using the calibration curve in the relevant region did not exceed ±20%.

It has been demonstrated in literature[27,28] that the correlation coefficient R^2 by itself can be an inconsistent measure of the calibration accuracy. Instead, the residual error at each calibration point can be characterized using percent relative standard error (%RSE) defined as shown in Equation 2:

$$\%RSE = 100 \times \sqrt{\sum_{i=1}^{n} \frac{\left[\frac{x'_i - x_i}{x_i}\right]^2}{n - p}}$$

Equation 2.

Where x_i is the true concentration of each calibration standard

x'_i is the measured concentration of each calibration standard

$\frac{x'_i - x_i}{x_i}$ is the relative error in calculated concentration for each calibration point

n is the number of calibration points used in the curve

(n – p) is the degree of freedom

p is determined by the type of the curve. For linear equations, p = 2 and for quadratic, p = 3.

For 203 evaluated compounds, the calibration RSE values were ≤20 for 190 and 194 compounds corresponding to 94 and 96% of the evaluated compounds with HydroInert and HES, respectively. The accuracy of the back-calculated concentrations of the calibration standards along with the RSE value guided the choice of linear versus quadratic curve fit. For example, tecnazene, the compound that could be severely affected by the in-source reaction with the standard EI source was accurately quantitated over the extended calibration range from 0.5 to 5,000 ppb in spinach QuEChERS extract with a linear calibration fit and the RSE value of 12.8 using the 7000E GC/TQ equipped with HydroInert (Figure 7A). The use of the 7010C GC/TQ with HES resulted in higher sensitivity at lower concentrations, enabling quantitation from 0.1 to 1,000 ppb with a quadratic fit and RSE of 14.4 (Figure 7B) or alternatively from 0.1 to 250 ppb with a linear fit and RSE of 16.6. The calibration ranges reported in this work (Appendix Tables 1 and 2) were selected to cover the widest concentration range because the MRLs may vary over a broad concentration range depending on different pesticides and food commodities. Encompassing a broader calibration range minimizes the need to reinject the samples if the MRLs of the target compounds vary several-fold. If the linearity of calibration is a priority, a narrower concentration range can be considered as discussed with tecnazene.

Less than 5% of the evaluated pesticides, eleven and nine compounds, were found to be problematic to quantitate using hydrogen carrier gas with HydroInert and HES, respectively. Those compounds are marked as not applicable (N/A) in Appendix Tables 1 and 2. Among those compounds were chlorothalonil, dichlofluanid, tolylfluanid, allethrin, captan, folpet, captafol, fenamiphos, iprodione, triflumizole, acequinocyl, and fluvalinate-tau I. Quantitation was not possible either due to insufficient signal or matrix interferences. Additional method optimization, including sample preparation aimed at removing the coeluting matrix interferences would be needed for quantitating these compounds in spinach matrix with hydrogen carrier gas. Other application notes provide the conditions suitable for quantitating these pesticides with either GC/MS/MS using helium carrier gas[11] or LC/MS/MS.[29]

The calibration performance for the evaluated compounds with the 7000E and the 7010C GC/TQ is summarized in Figure 8. The details are provided in Appendix Tables 1 and 2, including the calibration ranges, the calibration function type, the correlation coefficients, and the RSE values. Over 92% of the compounds could be quantitated at or below 10 ppb, which corresponded to the default MRL. This makes the developed method suitable for analyzing the evaluated pesticides at the MRL levels in the pigmented spinach matrix.

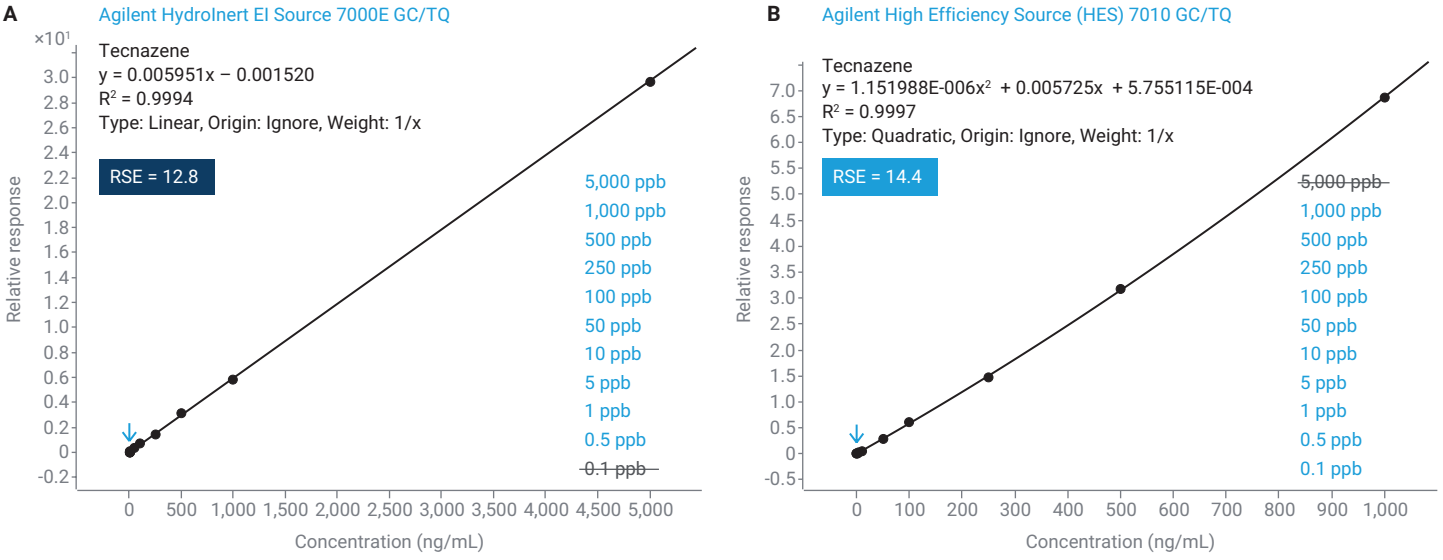

Figure 7. Matrix-matched calibration curves for tecnazene in spinach with the Agilent 7000E and Agilent 7010C GC/TQ with hydrogen carrier gas.

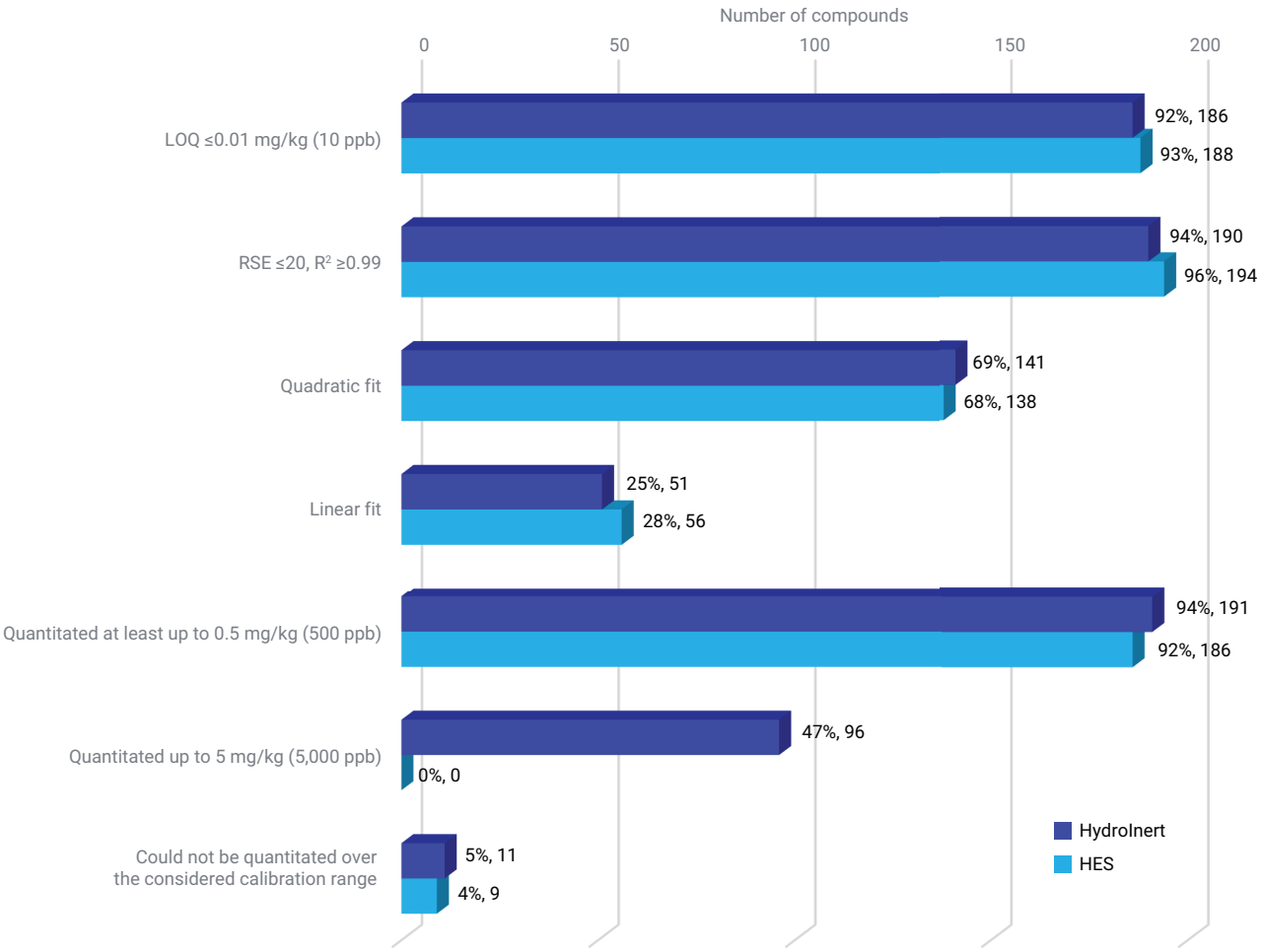

Figure 8. Calibration performance summary for 203 GC-amenable pesticides with the Agilent 8890/7000E and 8890/7010C GC/TQ in spinach using hydrogen carrier gas.

Effect of matrix-derived interferences and in-source loading

Evaluating samples in full scan data acquisition mode facilitates the evaluation of in-source matrix loading. This practice is among five keys to unlocking maximum performance in the analysis of pesticides described in the corresponding application note.[11] Either with helium or hydrogen, every MS source has a limitation on the amount of material present in the source, at any point of time, to maintain the optimal performance. Quantitation accuracy of the analysis can be significantly compromised if the source is overloaded with matrix. Hence, it is essential to analyze matrix in full scan mode to evaluate the total ion chromatogram (TIC) and maintain the optimal GC/TQ performance. The recommendation is to ensure that for the regions where targets elute, the maximum abundance of the base peak chromatogram (BPC) does not exceed 7×10^7 counts when acquiring data in full scan data acquisition mode with gain set to 1. Figure 9 demonstrates the comparison of the spinach and cayenne pepper QuEChERS extracts. The cayenne pepper sample features a higher matrix background compared to spinach, especially eluting between 11 and 14 minutes.

Figure 9B provides the example of quantitating two pesticides, tecnazene and flutolanil in spinach and cayenne pepper extract at 0.5 ppb with the 7010C GC/TQ. Tecnazene, although prone to reacting with hydrogen, had a stable measurable response at 0.5 ppb in the extract. It eluted at 6.91 minutes, with some matrix components coeluting. Flutolanil eluted at 11.42 minutes, during the part of the chromatogram when a lot of background derived from the

matrix was observed in the cayenne pepper extract. As a result, two out of the three ions had detectable interferences in the cayenne pepper extract for flutolanil at 0.5 ppb even in the selective MRM data acquisition mode. Some of the practices that can be used to lower the matrix background include adequate sample cleanup, sample dilution, and smaller injection volume. The latter two approaches often result in better limit of quantitation (LOQs), especially with the HES equipped 7010C GC/TQ system.

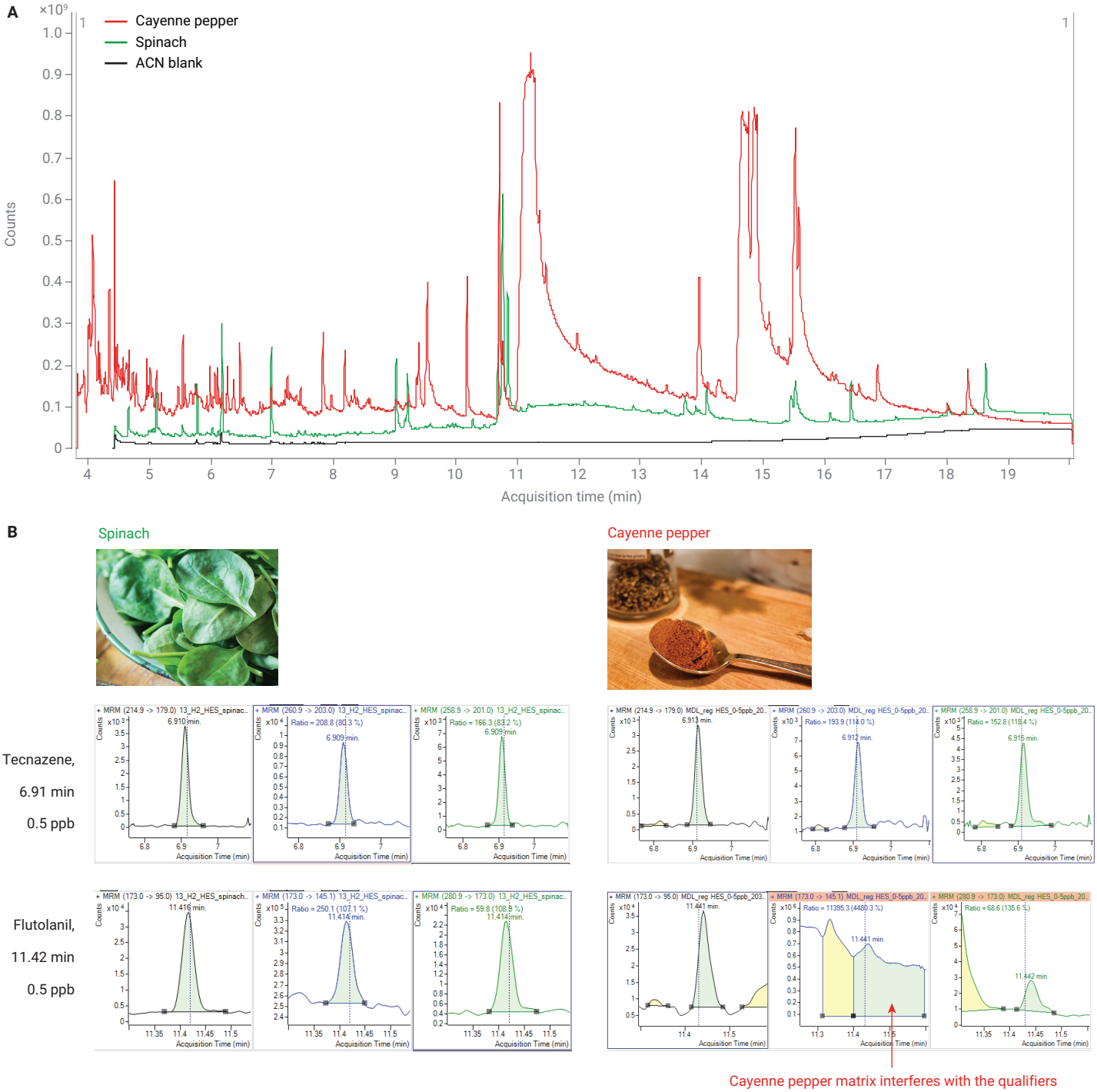

Figure 9. Scan total ion chromatogram (TIC) of the spinach and cayenne pepper QuEChERS extracts, and acetonitrile blank (A). MRM chromatograms for tecnazene and flutolanil in spinach and cayenne pepper extracts at 0.5 ppb acquired with the Agilent 7010C GC/TQ with hydrogen carrier gas (B).

Dynamic MRM/Scan mode: sensitive quantitation with more confidence

The simultaneous dMRM/scan capability available with the 7000E and the 7010C GC/TQs enables identification of the unknown compounds and retrospective analysis, while maintaining sensitivity and dynamic range of the method comparable to a conventional dMRM analysis as described in the application note 5994-4966EN.[30] Full scan data unlocks the opportunity to perform compound screening via spectral deconvolution and component search against GC/MS spectral libraries such as NIST. This functionality is valuable for retrospective analysis, eliminating the need to reanalyze the sample.

The benefit of preserving spectral fidelity provided with HydroInert and HES allowed for identifying the compound based on the spectral match and confirming its identity. Figure 10A illustrates the screening results for spinach extract spiked with a pesticide mixture at 500 ppb with the 7000E GC/TQ equipped with HydroInert using hydrogen carrier gas. The compounds susceptible to reduction with hydrogen presented in Table 2 were among the hits identified in the sample shown in Figure 10A, including prothiofos (LMS 83), sulprofos (LMS 80), tebuconazole (LMS 83), and tecnazene (LMS 82), as shown in the components table. The LMS for tecnazene was 82 and the delta between the observed retention time and the retention time provided in the spectral library was –0.016 minutes. The lower right of Figure 10A shows the spectral information displayed in MassHunter Unknowns Analysis for the hit. The raw mass spectrum appears on the lower right and a mirror plot compares the deconvoluted mass spectrum to the library spectrum. The ratio between 261 *m/z*, 215 *m/z*, and 203 *m/z* in the observed spectrum is similar to how these ions appear in the reference library spectrum confirming that tecnazene does not undergo chemical transformation in the HydroInert EI source with the 7000E GC/TQ.

Figure 10B shows the deconvoluted mass spectrum of tecnazene acquired in the dMRM/scan mode with the 7010C GC/TQ. As with the 7000E and HydroInert, tecnazene's spectrum was preserved intact resulting in a high LMS of 92.

The advantage brought by the simultaneous dMRM/scan functionality is the ability to quantitate the targets within the same run with the screening. Figures 10C and 10D demonstrate the MRM chromatograms for tecnazene at 10 ppb acquired with the 7000E and the 7010C in spinach extract when operating in the simultaneous dMRM/scan using hydrogen carrier gas. In both cases, accurate quantitation resulting in the calculated concentrations of 9.20 and 10.03 ppb was achieved.

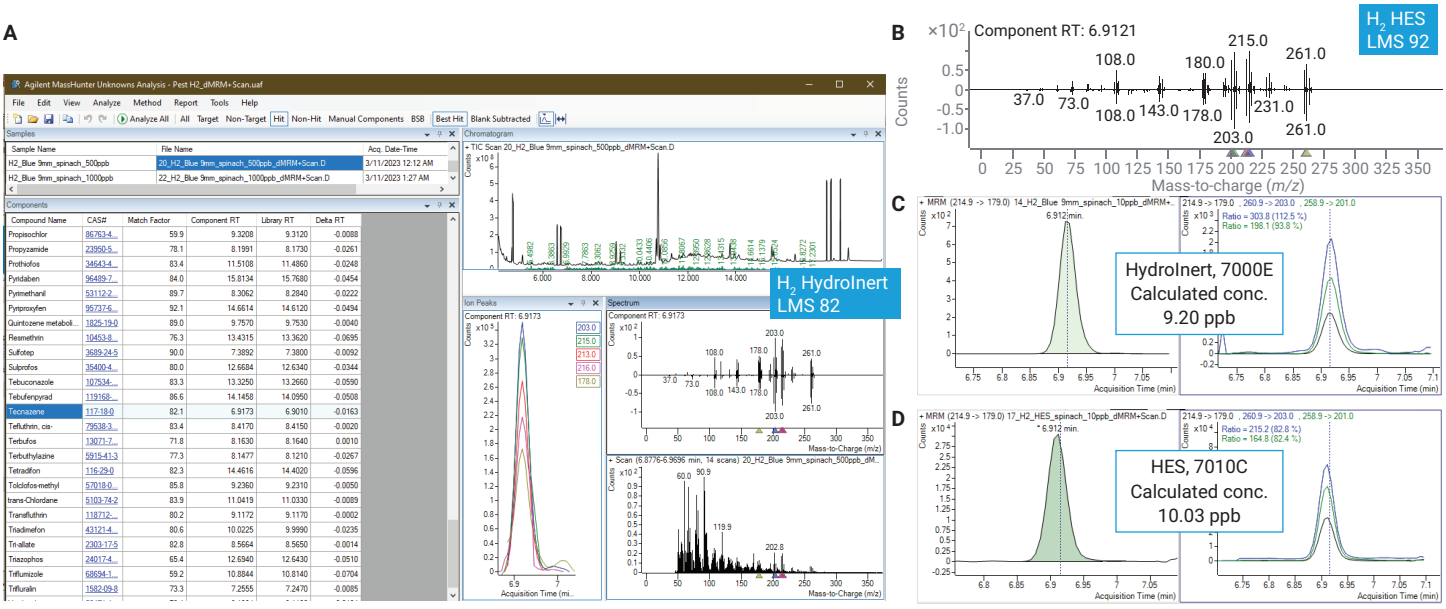

Figure 10. Analysis in simultaneous dMRM/Scan: tecnazene at 500 ppb in the spinach QuEChERS extract analyzed with the HydroInert source (A) and the HES source (B); MRM chromatograms at 10 ppb with the HydroInert (C) and the HES (D).

Conclusion

This application note presents key strategies for pesticide analysis using GC/MS/MS with hydrogen as the carrier gas, while maintaining sensitivity to meet MRLs. The optimized method includes a minibore 20 m × 20 m (0.18 mm × 0.18 µm) column configuration, solvent vent injection mode with the 2 mm dimpled liner, addition of the analyte protectant, and the use of hydrogen compatible electron ionization sources, namely the Agilent HydroInert source and the Agilent High Efficiency Source (HES). The optimized setup with hydrogen showed improved chromatographic resolution and allowed for precisely matching the retention times with helium. The HydroInert and HES sources were shown to provide best sensitivity and preserve spectral fidelity even for the compounds highly prone to reacting with hydrogen in the source by minimizing or preventing such undesirable reactions. As a result, the same MRM transitions, with the same collision energies for the targets eluting at the same retention times as with helium could be used with hydrogen carrier gas, streamlining the transition from helium to hydrogen.

The presented method allowed for quantitation of 92% and 93% of target pesticides at or below 10 ppb in spinach with hydrogen when using the Agilent 8890/7000E and the 8890/7010C GC/TQ systems, respectively. These results were compared to quantitation of 98.5% with helium when using the Agilent 8890/7000E GC/TQ system. The remaining compounds could be successfully analyzed with LC/MS/MS. Sub-ppb level detection limits were achieved, with higher sensitivity using the HES. The method demonstrated accurate quantitation over a broad calibration range with both the 7000E and the 7010C GC/TQ systems. Finally, simultaneous dynamic MRM and full scan data acquisition mode was demonstrated for accurate quantitation and reliable compound identification based on spectral matching.

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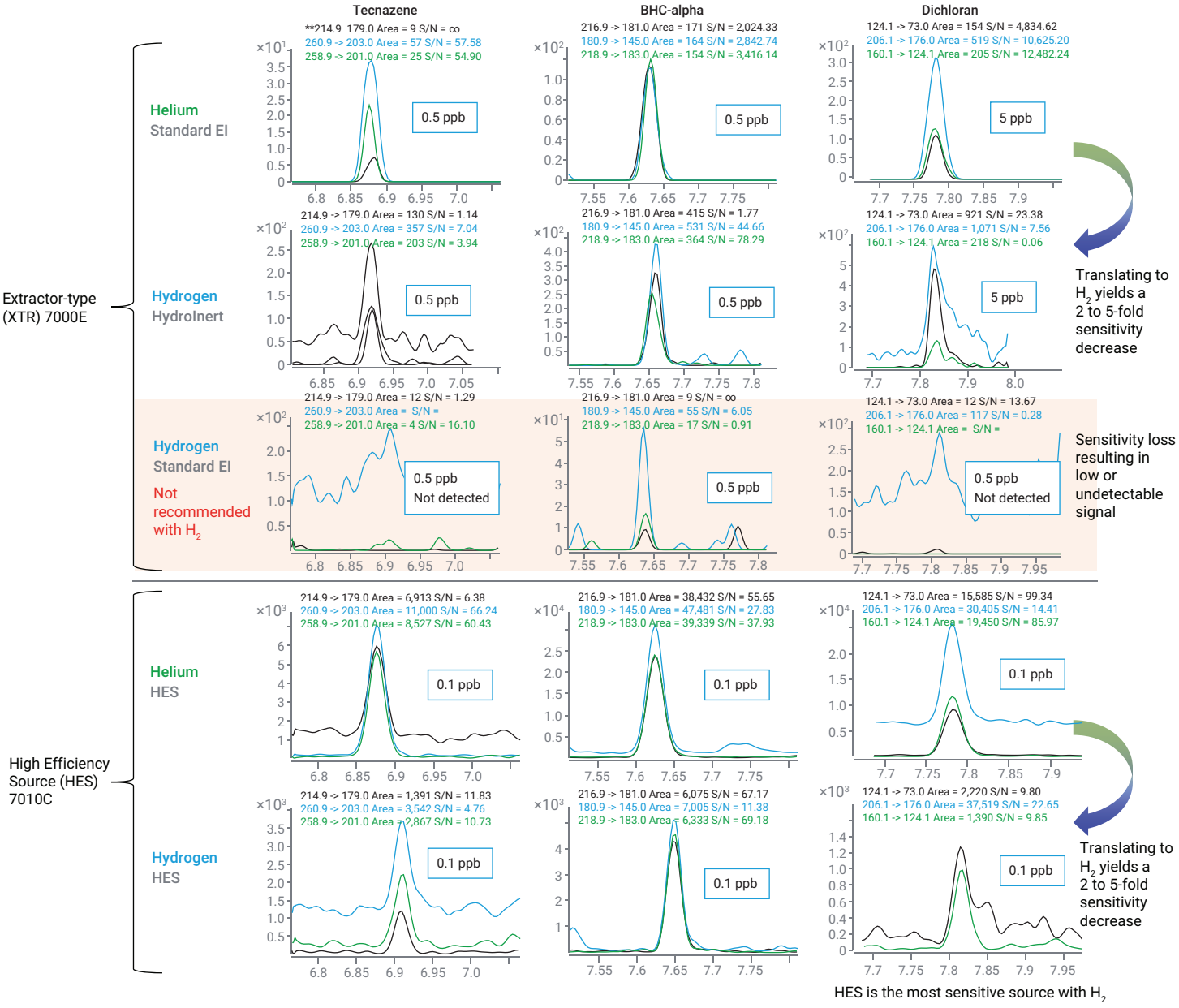
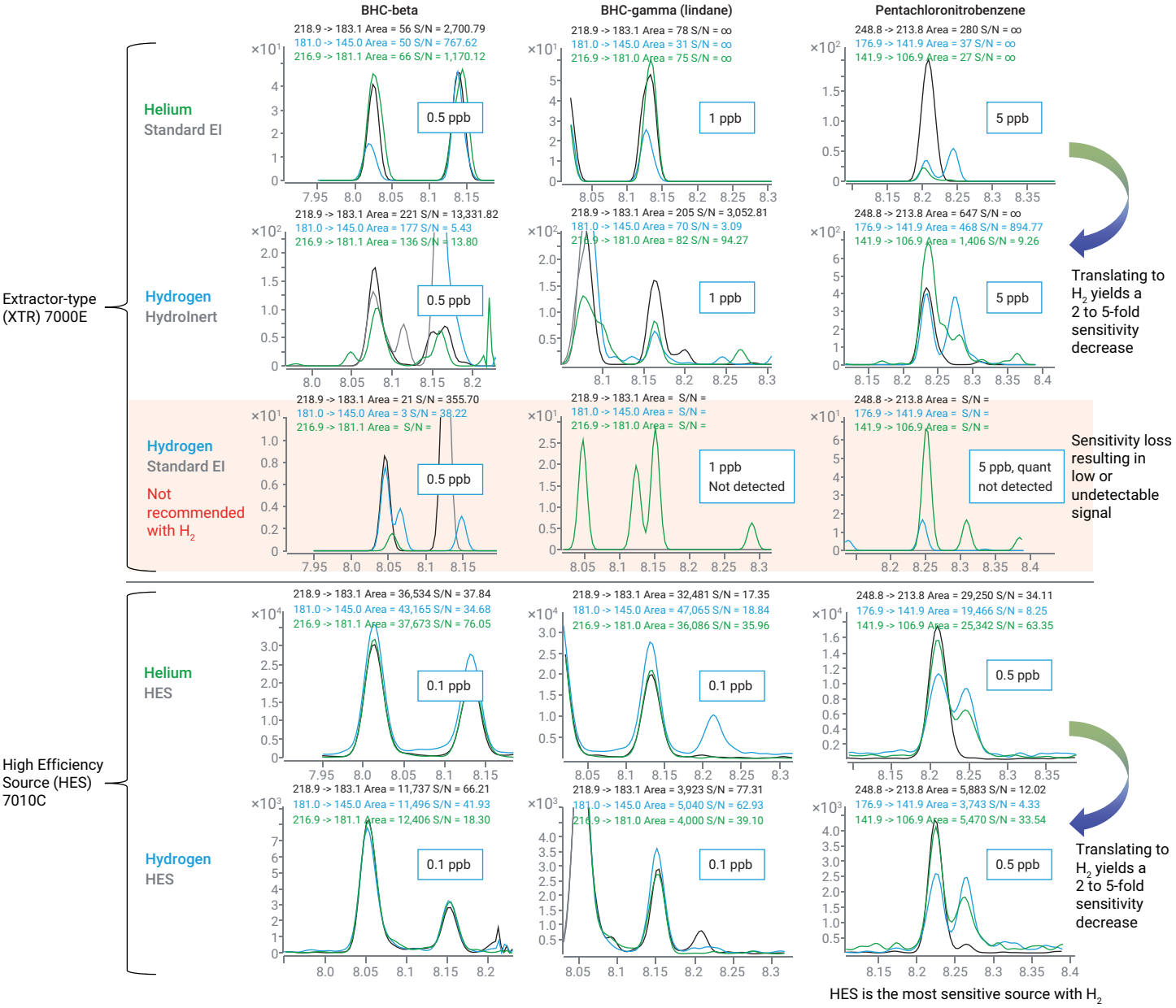
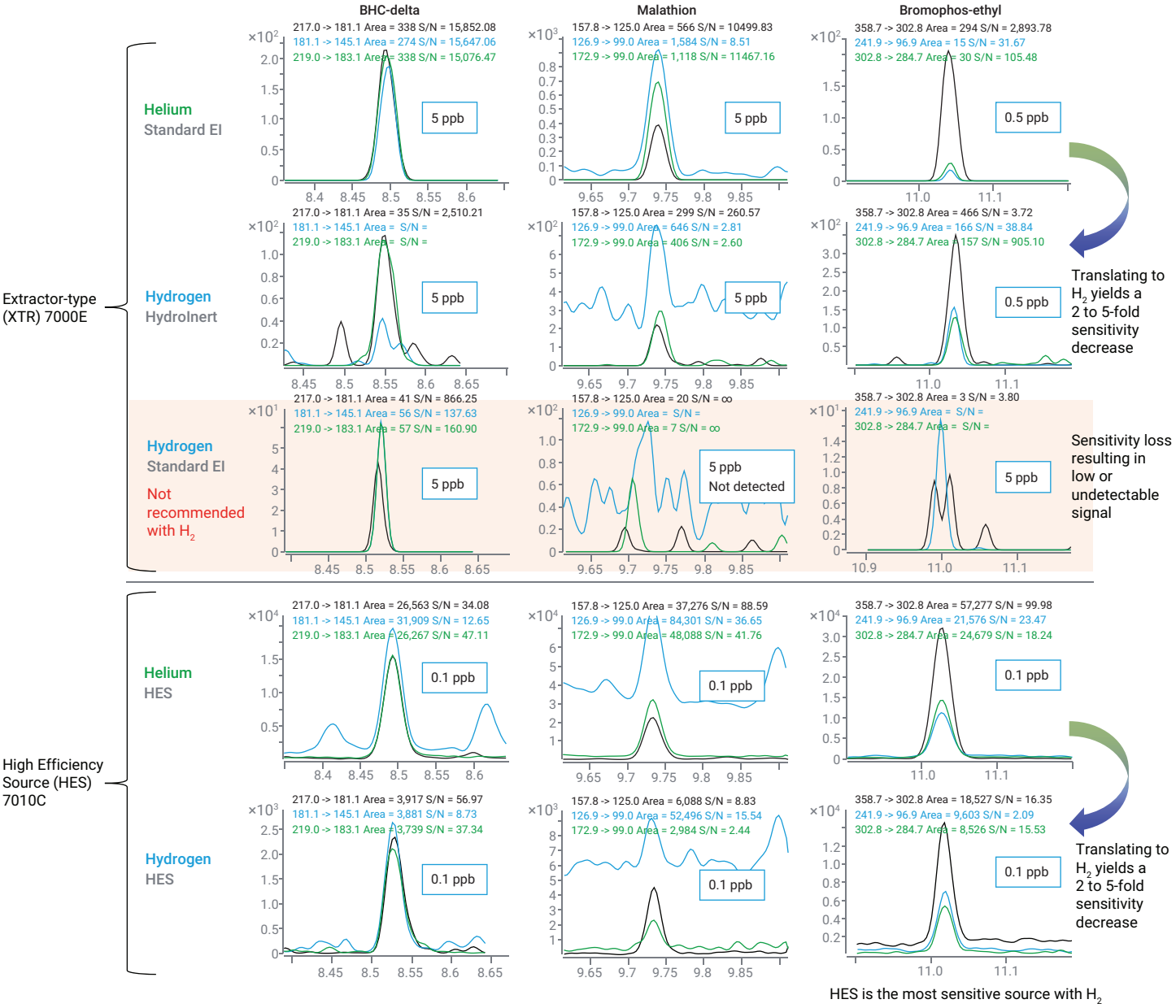
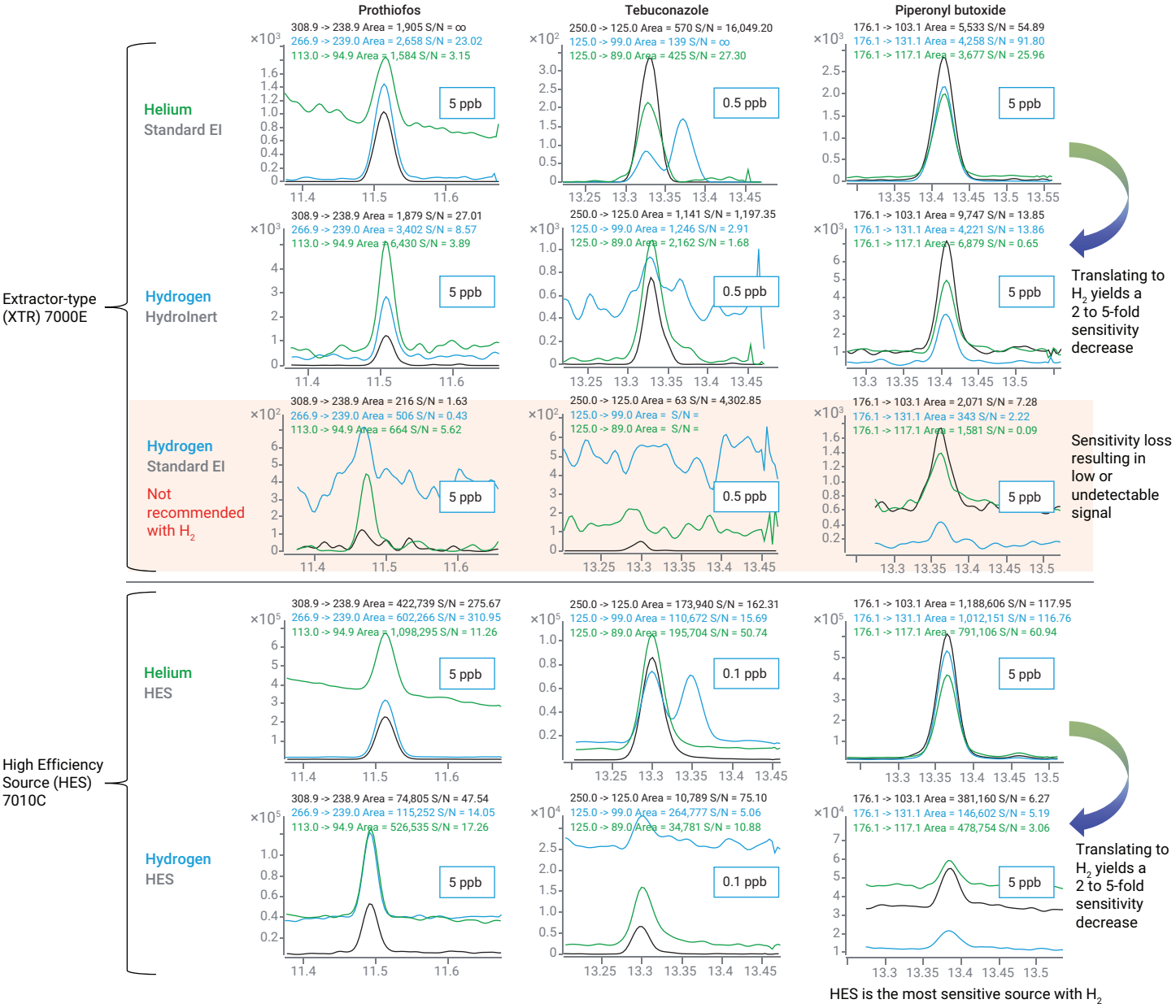
Appendix

Appendix Figure 1. MRM chromatograms for pesticides susceptible to reacting with hydrogen acquired in spinach QuEChERS extract under the optimized injection conditions (2 µL, solvent vent, analyte protectants) with helium and hydrogen carrier gasses using the Agilent 7000E and Agilent 7010C GC/TQ. Identically prepared samples were used for comparison. Black traces correspond to the quantifying MRM transition. The qualifying MRM transitions are blue and green. Continued on subsequent pages.




BHC-beta
BHC-gamma (lindane)
Pentachloronitrobenzene
Extractor-type (XTR) 7000E
Helium
Standard EI
218.9 -> 183.1 Area = 56 S/N = 2,700.79
181.0 -> 145.0 Area = 50 S/N = 767.62
216.9 -> 181.1 Area = 66 S/N = 1,170.12
0.5 ppb
218.9 -> 183.1 Area = 78 S/N = ∞
181.0 -> 145.0 Area = 31 S/N = ∞
216.9 -> 181.0 Area = 75 S/N = ∞
1 ppb
248.8 -> 213.8 Area = 280 S/N = ∞
176.9 -> 141.9 Area = 37 S/N = ∞
141.9 -> 106.9 Area = 27 S/N = ∞
5 ppb
Hydrogen
HydroInert
218.9 -> 183.1 Area = 221 S/N = 13,331.82
181.0 -> 145.0 Area = 177 S/N = 5.43
216.9 -> 181.1 Area = 136 S/N = 13.80
0.5 ppb
218.9 -> 183.1 Area = 205 S/N = 3,052.81
181.0 -> 145.0 Area = 70 S/N = 3.09
216.9 -> 181.0 Area = 82 S/N = 94.27
1 ppb
248.8 -> 213.8 Area = 647 S/N = ∞
176.9 -> 141.9 Area = 468 S/N = 894.77
141.9 -> 106.9 Area = 1,406 S/N = 9.26
5 ppb
Translating to H2 yields a 2 to 5-fold sensitivity decrease
Hydrogen
Standard EI
Not recommended with H2
218.9 -> 183.1 Area = 21 S/N = 355.70
181.0 -> 145.0 Area = 3 S/N = 38.22
216.9 -> 181.1 Area = S/N =
0.5 ppb
218.9 -> 183.1 Area = S/N =
181.0 -> 145.0 Area = S/N =
216.9 -> 181.0 Area = S/N =
1 ppb
Not detected
248.8 -> 213.8 Area = S/N =
176.9 -> 141.9 Area = S/N =
141.9 -> 106.9 Area = S/N =
5 ppb, quant not detected
Sensitivity loss resulting in low or undetectable signal
High Efficiency Source (HES) 7010C
Helium
HES
218.9 -> 183.1 Area = 36,534 S/N = 37.84
181.0 -> 145.0 Area = 43,165 S/N = 34.68
216.9 -> 181.1 Area = 37,673 S/N = 76.05
0.1 ppb
218.9 -> 183.1 Area = 32,481 S/N = 17.35
181.0 -> 145.0 Area = 47,065 S/N = 18.84
216.9 -> 181.0 Area = 36,086 S/N = 35.96
0.1 ppb
248.8 -> 213.8 Area = 29,250 S/N = 34.11
176.9 -> 141.9 Area = 19,466 S/N = 8.25
141.9 -> 106.9 Area = 25,342 S/N = 63.35
0.5 ppb
Hydrogen
HES
218.9 -> 183.1 Area = 11,737 S/N = 66.21
181.0 -> 145.0 Area = 11,496 S/N = 41.93
216.9 -> 181.1 Area = 12,406 S/N = 18.30
0.1 ppb
218.9 -> 183.1 Area = 3,923 S/N = 77.31
181.0 -> 145.0 Area = 5,040 S/N = 62.93
216.9 -> 181.0 Area = 4,000 S/N = 39.10
0.1 ppb
248.8 -> 213.8 Area = 5,883 S/N = 12.02
176.9 -> 141.9 Area = 3,743 S/N = 4.33
141.9 -> 106.9 Area = 5,470 S/N = 33.54
0.5 ppb
Translating to H2 yields a 2 to 5-fold sensitivity decrease
HES is the most sensitive source with H2


BHC-delta
Malathion
Bromophos-ethyl
Extractor-type (XTR) 7000E
Helium
Standard EI
Hydrogen
HydroInert
Hydrogen
Standard EI
Not recommended with H2
High Efficiency Source (HES) 7010C
Helium
HES
Hydrogen
HES
5 ppb
0.5 ppb
0.1 ppb
5 ppb Not detected
Translating to H2 yields a 2 to 5-fold sensitivity decrease
Sensitivity loss resulting in low or undetectable signal
Translating to H2 yields a 2 to 5-fold sensitivity decrease
HES is the most sensitive source with H2


Prothiofos
Tebuconazole
Piperonyl butoxide
Extractor-type (XTR) 7000E
Helium
Standard EI
Hydrogen
HydroInert
Hydrogen
Standard EI
Not recommended with H2
High Efficiency Source (HES) 7010C
Helium
HES
Hydrogen
HES
5 ppb
0.5 ppb
0.1 ppb
Translating to H2 yields a 2 to 5-fold sensitivity decrease
Sensitivity loss resulting in low or undetectable signal
Translating to H2 yields a 2 to 5-fold sensitivity decrease
HES is the most sensitive source with H2

Appendix Table 1. Calibration performance for 203 pesticides in spinach with hydrogen carrier gas using the Agilent 7000E GC/TQ equipped with HydroInert.

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Allidochlor	4.992	138.0 → 96.0	1	5,000	Quadratic	0.9997	10.6
Dichlorobenzonitrile, 2,6-	5.320	171.0 → 100.0	0.1	5,000	Quadratic	0.9992	17.1
Biphenyl	5.481	154.1 → 153.1	0.1	5,000	Quadratic	0.9992	12.8
Mevinphos, E-	5.671	127.0 → 109.0	1	1,000	Linear	0.9971	19.7
3,4-Dichloroaniline	5.781	160.9 → 99.0	0.1	5,000	Quadratic	0.9995	19.3
Pebulate	5.842	128.0 → 57.1	5	5,000	Quadratic	0.9985	6.2
Etridiazole	5.871	211.1 → 183.0	5	5,000	Quadratic	0.9994	19.2
N-(2,4-dimethylphenyl)formamide	6.073	120.0 → 77.0	10	1,000	Quadratic	0.9978	10.9
cis-1,2,3,6-Tetrahydrophthalimide	6.076	79.0 → 77.0	10	5,000	Quadratic	0.9957	17.9
Methacrifos	6.096	124.9 → 47.1	1	5,000	Linear	0.9997	13.1
Chloroneb	6.179	191.0 → 113.0	0.1	1,000	Quadratic	0.9991	7.6
2-Phenylphenol	6.299	169.1 → 115.1	0.1	1,000	Quadratic	0.9984	18.0
Pentachlorobenzene	6.378	249.9 → 215.0	0.1	5,000	Quadratic	0.9988	16.8
Tecnazene	6.915	214.9 → 179.0	0.5	5,000	Linear	0.9994	12.8
Propachlor	6.925	120.0 → 77.1	5	5,000	Quadratic	0.9995	14.6
Diphenylamine	6.991	169.0 → 168.2	0.1	1,000	Quadratic	0.9992	6.1
Cycloate	7.067	154.1 → 72.1	0.5	1,000	Quadratic	0.9989	19.8
2,3,5,6-Tetrachloroaniline	7.096	230.9 → 159.9	0.5	5,000	Quadratic	0.9939	16.7
Chlorpropham	7.142	127.0 → 65.1	0.5	1,000	Quadratic	0.9987	17.3
Trifluralin	7.261	264.0 → 160.1	0.5	5,000	Quadratic	0.9990	17.1
Ethalfluralin	7.293	275.9 → 202.1	1	1,000	Linear	0.9940	16.3
Benfluralin	7.295	292.0 → 264.0	0.5	5,000	Quadratic	0.9984	17.1
Sulfotep	7.394	237.8 → 145.9	0.5	5,000	Linear	0.9996	15.3
Phorate	7.396	121.0 → 47.0	1	5,000	Linear	0.9997	16.8
Diallate I	7.499	234.1 → 150.0	0.5	1,000	Quadratic	0.9993	14.2
BHC-alpha (Benzene Hexachloride)	7.662	216.9 → 181.0	1	5,000	Quadratic	0.9997	12.4
Hexachlorobenzene	7.789	283.8 → 248.8	0.1	1,000	Quadratic	0.9989	14.3
Dichloran	7.836	124.1 → 73.0	5	5,000	Quadratic	0.9978	11.7
Pentachloroanisole	7.844	264.8 → 236.8	0.1	5,000	Quadratic	0.9985	15.8
Atrazine	7.943	214.9 → 58.1	1	5,000	Quadratic	0.9995	10.0
Clomazone	8.010	125.0 → 89.0	0.5	1,000	Quadratic	0.9994	15.5
BHC-beta	8.099	218.9 → 183.1	0.5	1,000	Quadratic	0.9995	17.4
Profluralin	8.123	318.1 → 199.1	5	5,000	Quadratic	0.9972	15.7
BHC-gamma (Lindane, gamma-HCH)	8.169	218.9 → 183.1	1	1,000	Quadratic	0.9997	13.1
Terbufos	8.172	230.9 → 129.0	1	1,000	Quadratic	0.9999	11.2
Terbuthylazine	8.173	172.9 → 138.1	1	5,000	Quadratic	0.9993	12.9
Propyzamide	8.218	173.0 → 109.0	0.1	1,000	Quadratic	0.9997	16.0
Pentachloronitrobenzene	8.240	248.8 → 213.8	1	5,000	Quadratic	0.9987	13.6
Fonofos	8.267	246.1 → 137.0	1	1,000	Quadratic	0.9995	10.0
Pentachlorobenzonitrile	8.285	274.9 → 239.9	0.5	5,000	Quadratic	0.9977	13.1
Diazinon	8.298	137.1 → 84.0	1	1,000	Quadratic	0.9995	11.0
Pyrimethanil	8.320	198.0 → 118.1	0.5	1,000	Quadratic	0.9994	10.0
Fluchloralin	8.337	264.0 → 160.0	10	1,000	Quadratic	0.9929	17.9
Tefluthrin	8.428	177.1 → 87.0	0.5	1,000	Quadratic	0.9997	15.3
Disulfoton	8.440	88.0 → 60.0	0.5	1,000	Linear	0.9990	13.0

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Isazofos	8.545	256.9 → 162.0	5	5,000	Linear	0.9997	5.6
BHC-delta	8.571	217.0 → 181.1	5	1,000	Quadratic	0.9963	16.2
Triallate	8.576	142.9 → 83.0	0.5	5,000	Quadratic	0.9966	14.6
Terbacil	8.579	160.0 → 76.0	50	1,000	Quadratic	0.9985	14.6
Chlorothalonil	8.628	265.9 -> 230.9	N/A				
Endosulfan Ether	8.865	240.9 → 205.9	0.1	5,000	Quadratic	0.9932	16.2
Acetochlor	9.023	222.9 → 132.2	5	5,000	Linear	0.9994	7.4
Dimethachlor	9.023	196.9 → 148.2	1	5,000	Quadratic	0.9997	11.7
Propanil	9.026	161.0 → 99.0	0.1	5,000	Quadratic	0.9963	15.9
Pentachloroaniline	9.026	191.9 → 82.9	10	1,000	Quadratic	0.9959	14.8
Transfluthrin	9.131	163.1 → 143.1	0.1	5,000	Quadratic	0.9971	13.6
Vinclozolin	9.145	187.0 → 124.0	0.5	5,000	Quadratic	0.9980	13.8
Parathion-methyl	9.163	262.9 → 109.0	5	5,000	Quadratic	0.9999	11.2
Tolclofos-methyl	9.163	267.0 → 93.0	1	5,000	Quadratic	0.9991	12.7
Chlorpyrifos-methyl	9.165	124.9 → 47.0	1	5,000	Quadratic	0.9998	12.2
Alachlor	9.281	188.1 → 160.1	5	5,000	Linear	0.9989	6.7
Heptachlor	9.342	271.7 → 236.9	0.1	1,000	Linear	0.9983	16.3
Metalaxyl	9.367	234.0 → 146.1	1	1,000	Linear	0.9990	10.7
Propisochlor	9.368	162.0 → 120.1	5	5,000	Linear	0.9991	5.1
Ronnel	9.402	125.0 → 47.1	1	5,000	Quadratic	0.9987	12.8
Prodiamine	9.581	275.1 → 255.1	5	5,000	Quadratic	0.9976	11.9
Pirimiphos-methyl	9.604	290.0 → 125.0	0.5	1,000	Quadratic	0.9999	15.0
Fenitrothion	9.609	277.0 → 260.1	5	5,000	Quadratic	0.9999	8.3
Linuron	9.680	187.1 → 124.1	5	500	Quadratic	0.9931	12.0
Malathion	9.763	157.8 → 125.0	5	5,000	Quadratic	0.9999	16.0
Pentachlorothioanisole	9.768	295.8 → 245.8	1	5,000	Quadratic	0.9961	10.0
Dichlofluanid	9.784	123.0 → 77.0	N/A				
Metolachlor	9.927	238.0 → 162.2	0.1	1,000	Linear	0.9979	16.8
Aldrin	9.940	254.9 → 220.0	1	1,000	Linear	0.9972	6.2
Fenthion	9.950	278.0 → 109.0	1	1,000	Linear	0.9980	9.5
Anthraquinone	9.958	208.0 → 152.2	0.5	1,000	Quadratic	0.9987	14.1
Chlorpyrifos	9.975	196.9 → 169.0	5	5,000	Quadratic	0.9987	8.7
Parathion	10.005	291.0 → 109.0	5	5,000	Linear	0.9997	7.6
Triadimefon	10.047	208.0 → 111.0	0.5	1,000	Quadratic	0.9991	6.2
Dichlorobenzophenone, 4,4'-	10.065	139.0 → 111.0	0.5	1,000	Quadratic	0.9986	9.2
DCPA (Dacthal, Chlorthal-dimethyl)	10.076	298.9 → 221.0	1	1,000	Linear	0.9996	4.3
Fenson	10.232	141.0 → 77.1	0.5	1,000	Linear	0.9988	8.8
MGK-264	10.254	164.2 → 67.1	10	1,000	Linear	0.9949	12.4
Bromophos	10.304	330.9 → 315.9	1	5,000	Quadratic	0.9996	15.9
Pirimiphos-ethyl	10.312	318.1 → 166.1	1	1,000	Quadratic	0.9996	4.4
Diphenamid	10.334	239.0 → 167.1	1	1,000	Linear	0.9979	7.9
Isopropalin	10.363	280.1 → 238.1	5	1,000	Linear	0.9993	7.7
Isodrin	10.461	193.0 → 157.0	0.1	1,000	Linear	0.9977	14.7
Cyprodinil	10.464	225.2 → 224.3	1	1,000	Linear	0.9972	5.9
Pendimethalin	10.546	251.8 → 161.1	5	5,000	Quadratic	0.9997	8.2
Metazachlor	10.572	209.0 → 132.2	0.5	5,000	Quadratic	0.9996	15.0
Fipronil	10.591	350.8 → 254.8	10	500	Linear	0.9902	16.2

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Penconazole	10.610	248.0 → 157.1	1	1,000	Linear	0.9967	7.9
Chlozolinate	10.613	186.0 → 109.0	1	5,000	Quadratic	0.9992	12.7
Heptachlor Exo-Epoxide	10.633	352.8 → 262.9	1	1,000	Linear	0.9988	10.1
Tolylfluanid	10.662	238.0 → 137.0	N/A				
Allethrin	10.670	91.0 → 65.0	N/A				
Chlorfenvinphos	10.719	266.9 → 159.0	0.5	5,000	Quadratic	0.9997	14.5
Bromfenvinfos-methyl	10.733	295.0 → 108.9	10	1,000	Quadratic	0.9995	6.6
Quinalphos	10.768	146.0 → 118.0	5	1,000	Linear	0.9995	4.0
Captan	10.772	149.0 → 70.0	N/A				
Triflumizole	10.774	91.0 → 65.0	N/A				
Triadimenol	10.806	168.0 → 70.0	1	1,000	Linear	0.9991	9.1
Folpet	10.891	261.8 → 130.1	N/A				
Procymidone	10.894	282.8 → 96.0	1	1,000	Linear	0.9988	13.7
Chlorbenside	10.941	125.0 → 89.0	1	1,000	Linear	0.9981	10.0
Tetrachlorvinphos	10.945	78.9 → 47.0	10	5,000	Quadratic	0.9973	16.2
Bromophos-ethyl	11.051	358.7 → 302.8	1	1,000	Linear	0.9980	9.2
Chlordane-*trans*	11.055	271.7 → 236.9	0.1	5,000	Quadratic	0.9990	11.2
DDE-*o,p'*	11.100	246.0 → 176.2	0.5	1,000	Quadratic	0.9993	9.6
Paclobutrazol	11.155	125.1 → 89.0	0.1	1,000	Linear	0.9983	14.2
Endosulfan I (Alpha Isomer)	11.285	194.9 → 125.0	5	5,000	Quadratic	0.9989	10.9
Chlordane-*cis*	11.287	372.8 → 265.9	1	5,000	Quadratic	0.9992	8.6
Flutriafol	11.386	123.1 → 75.1	0.1	5,000	Quadratic	0.9997	12.0
Nonachlor, *trans*-	11.400	271.8 → 236.9	0.5	5,000	Quadratic	0.9988	10.4
Chlorfenson	11.416	175.0 → 111.0	0.1	5,000	Quadratic	0.9997	16.0
Fenamiphos	11.457	154.0 → 139.0	5	5,000	Quadratic	0.9991	16.3
Bromfenvinfos	11.459	266.9 → 159.1	1	1,000	Linear	0.9944	17.7
Flutolanil	11.475	173.0 → 95.0	0.1	5,000	Quadratic	0.9987	16.5
Iodofenphos	11.496	376.8 → 361.8	5	5,000	Quadratic	0.9997	14.2
Prothiofos	11.524	308.9 → 238.9	1	1,000	Linear	0.9996	11.8
Profenofos	11.603	338.8 → 268.7	5	1,000	Quadratic	0.9947	15.7
Pretilachlor	11.630	262.0 → 202.2	1	5,000	Quadratic	0.9997	6.9
DDE-*p,p'*	11.653	246.1 → 176.2	1	1,000	Quadratic	0.9991	10.5
Oxadiazon	11.685	174.9 → 112.0	0.5	1,000	Quadratic	0.9996	11.7
Fludioxonil	11.704	248.0 → 127.1	0.5	5,000	Quadratic	0.9982	18.8
Tricyclazole	11.750	189.0 → 161.1	5	500	Quadratic	0.9963	18.1
Dieldrin	11.751	262.9 → 193.0	1	5,000	Quadratic	0.9996	13.5
Oxyfluorfen	11.773	252.0 → 146.0	1	5,000	Quadratic	0.9957	18.6
DDD-*o,p'*	11.825	235.0 → 165.1	0.1	1,000	Linear	0.9983	12.0
Myclobutanil	11.853	179.0 → 125.1	0.1	1,000	Linear	0.9991	11.1
Flusilazole	11.886	233.0 → 165.1	0.5	500	Quadratic	0.9990	16.1
Bupirimate	11.902	272.9 → 193.1	1	1,000	Linear	0.9992	8.0
Fluazifop-*p*-butyl	12.035	281.9 → 91.0	0.1	1,000	Quadratic	0.9985	7.9
Nitrofen	12.060	202.0 → 139.1	1	5,000	Linear	0.9987	7.8
Ethylan	12.080	223.1 → 167.1	1	5,000	Quadratic	0.9995	12.5
Chlorfenapyr	12.105	247.1 → 227.1	5	5,000	Quadratic	0.9943	13.3
Endrin	12.150	262.8 → 193.0	1	5,000	Quadratic	0.9997	10.7
Chlorobenzilate	12.230	139.1 → 111.0	0.1	1,000	Linear	0.9987	9.6

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Endosulfan II (Beta Isomer)	12.321	206.9 → 172.0	1	5,000	Quadratic	0.9999	15.9
DDD-*p,p'*	12.419	237.0 → 165.1	0.5	5,000	Quadratic	0.9988	12.7
Ethion	12.471	230.9 → 175.0	0.5	1,000	Linear	0.9974	15.1
DDT-*o,p'*	12.473	237.0 → 165.2	1	5,000	Quadratic	0.9998	14.5
Chlorthiophos	12.520	324.8 → 268.9	0.5	5,000	Quadratic	0.9996	15.5
Nonachlor, *cis-*	12.529	408.8 → 299.8	1	5,000	Quadratic	0.9996	11.1
Endrin Aldehyde	12.598	344.9 → 244.9	5	250	Quadratic	0.9961	19.3
Sulprofos	12.685	140.0 → 125.1	0.5	5,000	Quadratic	0.9997	10.7
Triazophos	12.722	161.2 → 134.2	10	5,000	Quadratic	0.9995	12.0
Carbophenothion	12.872	153.0 → 96.9	5	5,000	Quadratic	0.9995	7.2
Carfentrazone-ethyl	12.876	329.9 → 309.9	0.5	1,000	Linear	0.9981	16.2
Methoxychlor Olefin	12.881	238.0 → 195.1	0.5	5,000	Quadratic	0.9995	20.0
Edifenphos	12.966	172.9 → 109.0	10	500	Linear	0.9959	9.4
Norflurazon	13.039	145.0 → 75.0	1	1,000	Quadratic	0.9964	12.1
DDT-*p,p'*	13.074	235.0 → 165.2	5	5,000	Linear	0.9992	6.6
Endosulfan Sulfate	13.080	271.9 → 237.0	5	1,000	Quadratic	0.9992	11.2
Lenacil	13.092	153.1 → 136.1	0.5	500	Linear	0.9903	14.3
Methoxychlor, *o,p'-*	13.247	227.1 → 121.1	0.1	5,000	Quadratic	0.9987	17.6
Hexazinone	13.309	171.0 → 71.1	1	500	Quadratic	0.9970	10.0
Tebuconazole	13.352	250.0 → 125.0	0.5	1,000	Quadratic	0.9986	9.6
Piperonyl Butoxide	13.424	176.1 → 103.1	0.5	1,000	Quadratic	0.9989	12.2
Propargite	13.425	135.0 → 77.1	10	5,000	Quadratic	0.9986	17.4
Captafol	13.428	150.0 → 79.0	N/A				
Resmethrin	13.448	171.0 → 128.0	5	1,000	Linear	0.9912	18.6
Nitralin	13.606	315.9 → 274.0	100	5,000	Quadratic	0.9992	69.8
Iprodione	13.772	313.8 → 55.9	N/A				
Tetramethrin I	13.860	164.0 → 107.1	5	1,000	Quadratic	0.9992	12.3
Pyridaphenthion	13.874	340.0 → 199.0	5	5,000	Quadratic	0.9999	10.1
Endrin Ketone	13.928	147.0 → 111.0	5	5,000	Quadratic	0.9970	23.7
Bifenthrin	13.957	181.2 → 165.2	0.5	5,000	Quadratic	0.9978	18.0
Phosmet	13.958	160.0 → 133.1	100	5,000	Quadratic	0.9987	16.3
Bromopropylate	13.977	338.8 → 182.9	0.5	5,000	Quadratic	0.9986	14.8
EPN	13.981	169.0 → 141.1	10	5,000	Quadratic	0.9997	10.9
Methoxychlor, *p,p'-*	14.082	227.0 → 169.1	1	5,000	Quadratic	0.9993	13.2
Fenpropathrin	14.098	207.9 → 181.0	0.5	5,000	Quadratic	0.9946	14.4
Tebufenpyrad	14.163	332.9 → 171.0	0.5	1,000	Quadratic	0.9980	10.3
Azinphos-methyl	14.438	160.0 → 132.1	50	1,000	Linear	0.9968	6.1
Phenothrin I	14.438	122.9 → 81.1	5	1,000	Linear	0.9948	9.3
Tetradifon	14.481	158.9 → 111.0	0.5	5,000	Quadratic	0.9988	14.3
Phosalone	14.641	182.0 → 111.0	5	5,000	Quadratic	0.9991	19.7
Pyriproxyfen	14.675	136.1 → 78.1	0.5	1,000	Linear	0.9974	15.8
Leptophos	14.685	171.0 → 51.0	5	5,000	Quadratic	0.9997	8.0
Cyhalothrin (Lambda)	14.734	181.1 → 152.1	10	500	Linear	0.9844	12.9
Mirex	14.906	271.8 → 236.8	1	5,000	Quadratic	0.9996	6.2
Acrinathrin	14.928	207.8 → 181.1	10	500	Quadratic	0.9938	13.9
Fenarimol	15.154	139.0 → 75.0	1	1,000	Quadratic	0.9940	15.0
Pyrazophos	15.183	221.0 → 193.1	10	5,000	Quadratic	0.9998	8.0

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Azinphos-ethyl	15.273	132.0 → 77.1	50	5,000	Quadratic	0.9994	12.2
Pyraclofos	15.311	194.0 → 138.0	50	1,000	Quadratic	0.9973	17.3
Permethrin, (1R)-*cis*-	15.663	183.1 → 168.1	5	1,000	Quadratic	0.9961	13.0
Permethrin, (1R)-*trans*-	15.790	163.0 → 127.0	1	5,000	Quadratic	0.9904	18.4
Pyridaben	15.831	147.2 → 117.1	1	1,000	Quadratic	0.9949	14.0
Fluquinconazole	15.909	108.0 → 57.0	0.5	1,000	Quadratic	0.9990	17.2
Coumaphos	15.934	225.9 → 163.1	10	500	Linear	0.9858	18.3
Prochloraz	15.982	180.0 → 138.0	10	1,000	Quadratic	0.9993	11.2
Cyfluthrin I	16.232	162.9 → 127.0	10	1,000	Quadratic	0.9943	18.4
Cypermethrin I	16.539	163.0 → 127.0	10	1,000	Quadratic	0.9966	17.5
Acequinocyl	16.575	187.9 → 160.0	N/A				
Flucythrinate I	16.763	156.9 → 107.1	1	1,000	Quadratic	0.9998	11.1
Ethofenprox	16.840	163.0 → 107.1	1	1,000	Quadratic	0.9956	13.7
Fluridone	17.241	328.9 → 328.1	1	1,000	Quadratic	0.9999	16.2
Fenvalerate I	17.470	167.0 → 125.1	5	1,000	Quadratic	0.9998	16.0
Fluvalinate-tau I	17.663	250.0 → 200.0	N/A				
Deltamethrin	17.984	250.7 → 172.0	10	5,000	Quadratic	1.0000	11.7

Appendix Table 2. Calibration performance for 203 pesticides in spinach with hydrogen carrier gas using the Agilent 7010C GC/TQ.

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Allidochlor	4.992	132.0 → 56.1	1	1,000	Quadratic	0.9995	16.3
Dichlorobenzonitrile, 2,6-	5.320	171.0 → 100.0	0.1	1,000	Quadratic	0.9996	14.6
Biphenyl	5.481	154.1 → 153.1	0.1	500	Quadratic	0.9991	19.1
Mevinphos, E-	5.671	127.0 → 109.0	0.1	500	Quadratic	0.9984	18.4
3,4-Dichloroaniline	5.781	160.9 → 99.0	0.1	1,000	Quadratic	0.9983	15.8
Pebulate	5.842	128.0 → 57.1	1	1,000	Quadratic	0.9999	10.4
Etridiazole	5.871	211.1 → 183.0	0.5	500	Quadratic	0.9997	16.5
N-(2,4-dimethylphenyl)formamide	6.073	120.0 → 77.0	5	500	Quadratic	0.9987	8.3
cis-1,2,3,6-Tetrahydrophthalimide	6.076	151.1 → 80.0	1	1,000	Quadratic	0.9996	6.6
Methacrifos	6.096	124.9 → 47.1	0.1	500	Quadratic	0.9990	19.8
Chloroneb	6.179	191.0 → 113.0	0.1	1,000	Linear	0.9995	11.7
2-Phenylphenol	6.299	169.1 → 115.1	1	1,000	Linear	0.9995	14.7
Pentachlorobenzene	6.378	249.9 → 215.0	0.1	1,000	Quadratic	0.9992	16.3
Tecnazene	6.915	214.9 → 179.0	0.1	1,000	Quadratic	0.9997	14.4
Propachlor	6.925	176.1 → 57.1	0.1	500	Quadratic	0.9964	15.7
Diphenylamine	6.991	169.0 → 168.2	1	1,000	Quadratic	0.9988	12.4
Cycloate	7.067	154.1 → 72.1	0.1	500	Quadratic	0.9972	18.0
2,3,5,6-Tetrachloroaniline	7.096	230.9 → 159.9	0.1	1,000	Quadratic	0.9990	14.4
Chlorpropham	7.142	127.0 → 65.1	0.1	1,000	Quadratic	0.9990	16.7
Trifluralin	7.261	306.1 → 264.0	0.1	500	Quadratic	0.9994	17.0
Ethalfluralin	7.293	275.9 → 202.1	0.5	500	Quadratic	0.9994	16.8
Benfluralin	7.295	292.0 → 264.0	0.1	500	Quadratic	0.9995	17.0
Sulfotep	7.394	237.8 → 145.9	0.1	500	Quadratic	0.9987	15.7
Phorate	7.396	121.0 → 47.0	0.5	500	Quadratic	0.9988	11.1
Diallate I	7.499	234.1 → 150.0	0.1	500	Quadratic	0.9985	17.8

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
BHC-alpha (Benzene Hexachloride)	7.662	216.9 → 181.0	0.1	500	Quadratic	0.9997	18.8
Hexachlorobenzene	7.789	283.8 → 248.8	0.1	1,000	Linear	0.9988	16.2
Dichloran	7.836	124.1 → 73.0	0.1	500	Quadratic	0.9993	18.2
Pentachloroanisole	7.844	264.8 → 236.8	0.1	1,000	Linear	0.9988	16.9
Atrazine	7.943	214.9 → 58.1	0.1	1,000	Quadratic	0.9998	19.8
Clomazone	8.010	125.0 → 89.0	0.1	1,000	Quadratic	0.9997	14.1
BHC-beta	8.099	218.9 → 183.1	0.1	1,000	Quadratic	0.9996	16.9
Profluralin	8.123	318.1 → 199.1	5	1,000	Quadratic	0.9995	8.7
BHC-gamma (Lindane, gamma-HCH)	8.169	218.9 → 183.1	1	500	Quadratic	0.9999	3.0
Terbufos	8.172	230.9 → 129.0	1	1,000	Quadratic	0.9997	13.1
Terbuthylazine	8.173	228.9 → 173.1	0.1	1,000	Quadratic	0.9998	9.1
Propyzamide	8.218	173.0 → 109.0	1	1,000	Quadratic	0.9996	17.2
Pentachloronitrobenzene	8.240	248.8 → 213.8	0.1	1,000	Quadratic	0.9992	13.7
Fonofos	8.267	246.1 → 137.0	0.5	500	Quadratic	0.9994	19.8
Pentachlorobenzonitrile	8.285	274.9 → 239.9	0.1	1,000	Linear	0.9995	16.6
Diazinon	8.298	137.1 → 84.0	0.5	1,000	Quadratic	0.9999	12.7
Pyrimethanil	8.320	198.0 → 118.1	0.1	1,000	Quadratic	0.9997	18.6
Fluchloralin	8.337	325.8 → 62.9	0.5	1,000	Quadratic	0.9998	16.9
Tefluthrin	8.428	177.1 → 87.0	0.1	500	Linear	0.9974	16.1
Disulfoton	8.440	88.0 → 60.0	0.5	1,000	Quadratic	0.9996	7.4
Isazofos	8.545	256.9 → 162.0	1	500	Quadratic	0.9981	13.9
BHC-delta	8.571	217.0 → 181.1	1	500	Quadratic	0.9992	8.2
Triallate	8.576	268.0 → 184.1	0.5	500	Linear	0.9993	13.2
Terbacil	8.579	160.0 → 76.0	50	1,000	Quadratic	0.9935	13.0
Chlorothalonil	8.628	265.9 → 230.9	10	500	Quadratic	0.9955	17.4
Endosulfan Ether	8.865	240.9 → 205.9	0.5	500	Quadratic	0.9975	18.5
Acetochlor	9.023	222.9 → 132.2	0.1	1,000	Quadratic	0.9986	15.4
Dimethachlor	9.023	196.9 → 148.2	0.1	500	Quadratic	0.9981	18.1
Propanil	9.026	161.0 → 99.0	0.5	1,000	Linear	0.9991	6.1
Pentachloroaniline	9.026	191.9 → 82.9	5	1,000	Quadratic	0.9965	11.6
Transfluthrin	9.131	163.1 → 143.1	5	1,000	Linear	0.9975	12.5
Vinclozolin	9.145	187.0 → 124.0	0.5	250	Quadratic	0.9973	18.5
Parathion-methyl	9.163	125.0 → 47.0	0.5	1,000	Quadratic	0.9984	18.3
Tolclofos-methyl	9.163	267.0 → 93.0	0.5	1,000	Linear	0.9983	17.1
Chlorpyrifos-methyl	9.165	124.9 → 47.0	0.5	1,000	Quadratic	0.9983	16.8
Alachlor	9.281	188.1 → 160.1	5	1,000	Linear	0.9946	19.0
Heptachlor	9.342	271.7 → 236.9	5	1,000	Linear	0.9981	8.2
Metalaxyl	9.367	234.0 → 146.1	0.1	1,000	Quadratic	0.9995	17.4
Propisochlor	9.368	162.0 → 120.1	1	1,000	Linear	0.9956	12.7
Ronnel	9.402	125.0 → 47.1	0.5	1,000	Quadratic	0.9987	18.6
Prodiamine	9.581	321.0 → 203.0	0.5	500	Quadratic	0.9997	15.5
Pirimiphos-methyl	9.604	290.0 → 125.0	0.5	1,000	Quadratic	0.9996	19.4
Fenitrothion	9.609	125.1 → 47.0	0.5	1,000	Quadratic	0.9996	15.4
Linuron	9.680	187.1 → 124.1	1	500	Linear	0.9990	8.1
Malathion	9.763	157.8 → 125.0	0.1	1,000	Quadratic	0.9953	13.9
Pentachlorothioanisole	9.768	295.8 → 245.8	5	1,000	Quadratic	0.9960	12.4
Dichlofluanid	9.784	123.0 → 77.0	N/A				

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Metolachlor	9.927	238.0 → 162.2	0.1	1,000	Linear	0.9992	12.2
Aldrin	9.940	254.9 → 220.0	0.5	250	Quadratic	0.9917	17.9
Fenthion	9.950	278.0 → 109.0	0.1	1,000	Quadratic	0.9999	3.6
Anthraquinone	9.958	208.0 → 152.2	0.1	1,000	Linear	0.9991	8.4
Chlorpyrifos	9.975	313.8 → 257.8	0.1	1,000	Linear	0.9998	4.3
Parathion	10.005	291.0 → 109.0	1	1,000	Quadratic	0.9998	14.5
Triadimefon	10.047	208.0 → 111.0	1	1,000	Linear	0.9971	13.0
Dichlorobenzophenone, 4,4'-	10.065	139.0 → 111.0	1	1,000	Quadratic	0.9994	9.2
DCPA (Dacthal, Chlorthal-dimethyl)	10.076	298.9 → 221.0	0.1	1,000	Quadratic	0.9988	19.9
Fenson	10.232	141.0 → 77.1	1	1,000	Quadratic	0.9984	8.0
MGK-264	10.254	164.2 → 67.1	10	1,000	Linear	0.9947	10.8
Bromophos	10.304	330.9 → 315.9	0.5	1,000	Quadratic	0.9985	14.6
Pirimiphos-ethyl	10.312	318.1 → 166.1	1	1,000	Linear	0.9982	8.1
Diphenamid	10.334	239.0 → 167.1	5	1,000	Linear	0.9990	12.1
Isopropalin	10.363	280.1 → 238.1	1	1,000	Linear	0.9991	18.4
Isodrin	10.461	193.0 → 157.0	0.5	500	Quadratic	0.9943	17.5
Cyprodinil	10.464	225.2 → 224.3	0.1	1,000	Linear	0.9971	14.5
Pendimethalin	10.546	251.8 → 161.1	0.1	100	Quadratic	0.9999	10.9
Metazachlor	10.572	209.0 → 132.2	5	1,000	Quadratic	0.9982	9.8
Fipronil	10.591	350.8 → 254.8	10	1,000	Quadratic	0.9932	18.3
Penconazole	10.610	248.0 → 157.1	5	1,000	Linear	0.9992	8.8
Chlozolinate	10.613	186.0 → 109.0	0.5	1,000	Quadratic	0.9994	19.1
Heptachlor Exo-Epoxide	10.633	352.8 → 262.9	0.5	500	Quadratic	0.9942	19.0
Tolylfluanid	10.662	238.0 → 137.0	10	500	Quadratic	0.9988	18.1
Allethrin	10.670	91.0 → 65.0	N/A				
Chlorfenvinphos	10.719	266.9 → 159.0	5	1,000	Quadratic	0.9983	12.5
Bromfenvinfos-methyl	10.733	169.9 → 99.0	10	500	Quadratic	0.9998	3.8
Quinalphos	10.768	146.0 → 118.0	5	1,000	Quadratic	0.9998	6.8
Captan	10.772	149.0 → 70.0	N/A				
Triflumizole	10.774	91.0 → 65.0	N/A				
Triadimenol	10.806	128.0 → 100.0	0.5	500	Quadratic	0.9922	14.3
Folpet	10.891	261.8 → 130.1	N/A				
Procymidone	10.894	282.8 → 96.0	1	500	Quadratic	0.9951	18.0
Chlorbenside	10.941	125.0 → 89.0	5	1,000	Quadratic	0.9964	12.8
Tetrachlorvinphos	10.945	78.9 → 47.0	5	500	Quadratic	0.9948	13.8
Bromophos-ethyl	11.051	358.7 → 302.8	5	1,000	Linear	0.9951	14.4
Chlordane-*trans*	11.055	271.7 → 236.9	5	1,000	Linear	0.9935	16.5
DDE-*o,p'*	11.100	246.0 → 176.2	5	1,000	Quadratic	0.9926	20.0
Paclobutrazol	11.155	125.1 → 89.0	0.5	500	Quadratic	0.9959	19.7
Endosulfan I (Alpha Isomer)	11.285	194.9 → 125.0	5	1,000	Linear	0.9932	18.1
Chlordane-*cis*	11.287	372.8 → 265.9	5	1,000	Quadratic	0.9948	17.9
Flutriafol	11.386	123.1 → 75.1	10	1,000	Quadratic	0.9969	19.7
Nonachlor, *trans*-	11.400	406.8 → 299.8	10	1,000	Quadratic	0.9988	18.5
Chlorfenson	11.416	175.0 → 111.0	0.1	10	Quadratic	0.9949	17.0
Fenamiphos	11.457	154.0 → 139.0	N/A				
Bromfenvinfos	11.459	266.9 → 159.1	1	1,000	Quadratic	0.9979	10.9
Flutolanil	11.475	173.0 → 95.0	0.5	1,000	Linear	0.9955	15.9

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Iodofenphos	11.496	376.8 → 361.8	10	1,000	Quadratic	0.9957	19.6
Prothiofos	11.524	308.9 → 238.9	10	1,000	Quadratic	0.9996	7.4
Profenofos	11.603	207.9 → 63.0	1	500	Quadratic	0.9979	12.7
Pretilachlor	11.630	262.0 → 202.2	0.5	1,000	Quadratic	0.9986	14.7
DDE-*p,p'*	11.653	246.1 → 176.2	10	1,000	Linear	0.9922	19.9
Oxadiazon	11.685	174.9 → 112.0	1	250	Quadratic	0.9902	15.9
Fludioxonil	11.704	248.0 → 127.1	0.5	1,000	Linear	0.9984	10.1
Tricyclazole	11.750	189.0 → 161.1	10	500	Quadratic	0.9988	15.1
Dieldrin	11.751	277.0 → 241.0	5	1,000	Linear	0.9950	15.4
Oxyfluorfen	11.773	252.0 → 146.0	5	250	Linear	0.9956	15.6
DDD-*o,p'*	11.825	235.0 → 165.1	5	500	Linear	0.9974	17.7
Myclobutanil	11.853	179.0 → 125.1	0.5	1,000	Linear	0.9977	12.4
Flusilazole	11.886	233.0 → 165.1	0.5	500	Quadratic	0.9974	16.7
Bupirimate	11.902	272.9 → 193.1	0.1	500	Quadratic	0.9934	17.9
Fluazifop-*p*-butyl	12.035	281.9 → 91.0	0.1	500	Quadratic	0.9966	17.3
Nitrofen	12.060	202.0 → 139.1	0.5	500	Linear	0.9940	17.6
Ethylan	12.080	223.1 → 167.1	5	1,000	Quadratic	0.9947	15.4
Chlorfenapyr	12.105	247.1 → 227.1	0.5	1,000	Quadratic	0.9976	15.0
Endrin	12.150	262.8 → 193.0	5	1,000	Quadratic	0.9963	11.2
Chlorobenzilate	12.230	139.1 → 111.0	5	1,000	Quadratic	0.9964	11.3
Endosulfan II (Beta Isomer)	12.321	206.9 → 172.0	1	1,000	Quadratic	0.9987	10.2
DDD-*p,p'*	12.378	237.0 → 165.1	5	1,000	Quadratic	0.9917	19.1
Ethion	12.471	230.9 → 175.0	5	1,000	Linear	0.9971	12.2
DDT-*o,p'*	12.473	237.0 → 165.2	0.1	1,000	Quadratic	0.9990	14.1
Chlorthiophos	12.520	324.8 → 268.9	5	1,000	Linear	0.9966	13.6
Nonachlor, *cis*-	12.529	408.8 → 299.8	0.1	50	Quadratic	0.9968	15.7
Endrin Aldehyde	12.598	249.9 → 214.9	10	1,000	Quadratic	0.9992	7.6
Sulprofos	12.685	140.0 → 125.1	0.1	1,000	Linear	0.9974	16.0
Triazophos	12.722	161.2 → 134.2	5	1,000	Quadratic	0.9976	9.0
Carbophenothion	12.872	342.0 → 157.0	0.1	1,000	Linear	0.9973	9.2
Carfentrazone-ethyl	12.876	329.9 → 309.9	0.1	1,000	Quadratic	0.9987	16.9
Methoxychlor Olefin	12.881	238.0 → 195.1	5	1,000	Linear	0.9966	12.5
Edifenphos	12.966	172.9 → 109.0	5	500	Quadratic	0.9998	16.3
Norflurazon	13.039	145.0 → 75.0	5	1,000	Linear	0.9988	7.3
DDT-*p,p'*	13.074	235.0 → 165.2	0.1	1,000	Quadratic	0.9983	19.1
Endosulfan Sulfate	13.080	271.9 → 237.0	0.1	1,000	Quadratic	0.9980	18.5
Lenacil	13.092	153.1 → 136.1	5	500	Quadratic	0.9980	14.2
Methoxychlor, *o,p'*-	13.247	227.1 → 121.1	0.5	1,000	Quadratic	0.9989	15.6
Hexazinone	13.309	171.0 → 71.1	0.5	1,000	Quadratic	0.9996	11.0
Tebuconazole	13.352	250.0 → 125.0	1	1,000	Quadratic	0.9997	3.1
Piperonyl Butoxide	13.424	176.1 → 103.1	5	1,000	Quadratic	0.9957	14.3
Propargite	13.425	135.0 → 107.1	5	1,000	Quadratic	0.9991	9.2
Captafol	13.428	150.0 → 79.0	N/A				
Resmethrin	13.448	171.0 → 128.0	5	1,000	Quadratic	0.9993	6.5
Nitralin	13.606	315.9 → 274.0	100	1,000	Quadratic	0.9962	11.8
Iprodione	13.772	313.8 → 55.9	N/A				
Tetramethrin I	13.860	164.0 → 107.1	5	1,000	Quadratic	0.9994	9.6

Name	RT	Transition	CF Limit Low	CF Limit High	CF	CF R^2	Relative Standard Error
Pyridaphenthion	13.874	340.0 → 199.0	5	1,000	Quadratic	0.9968	7.6
Endrin Ketone	13.928	316.9 → 280.9	5	1,000	Quadratic	0.9994	9.3
Bifenthrin	13.957	181.2 → 165.2	5	1,000	Quadratic	0.9978	8.9
Phosmet	13.958	160.0 → 133.1	100	1,000	Quadratic	0.9994	16.5
Bromopropylate	13.977	338.8 → 182.9	0.1	1,000	Linear	0.9960	12.6
EPN	13.981	169.0 → 77.1	5	1,000	Quadratic	0.9974	8.0
Methoxychlor, *p,p'*-	14.082	227.0 → 169.1	1	1,000	Quadratic	0.9986	6.9
Fenpropathrin	14.098	207.9 → 181.0	5	1,000	Linear	0.9971	16.7
Tebufenpyrad	14.163	332.9 → 171.0	1	500	Linear	0.9986	14.5
Azinphos-methyl	14.438	160.0 → 132.1	50	1,000	Quadratic	0.9982	9.5
Phenothrin I	14.438	122.9 → 81.1	50	1,000	Linear	0.9967	13.0
Tetradifon	14.481	158.9 → 111.0	0.5	1,000	Quadratic	0.9995	18.2
Phosalone	14.641	182.0 → 111.0	1	1,000	Linear	0.9933	18.4
Pyriproxyfen	14.675	136.1 → 78.1	5	1,000	Linear	0.9993	8.9
Leptophos	14.685	171.0 → 51.0	5	1,000	Quadratic	0.9977	14.4
Cyhalothrin (Lambda)	14.734	208.1 → 181.1	10	1,000	Linear	0.9983	12.0
Mirex	14.906	271.8 → 236.8	5	1,000	Linear	0.9974	9.8
Acrinathrin	14.928	207.8 → 181.1	0.5	1,000	Linear	0.9971	9.6
Fenarimol	15.154	139.0 → 75.0	0.5	1,000	Linear	0.9952	9.5
Pyrazophos	15.183	221.0 → 193.1	5	1,000	Quadratic	0.9968	19.0
Azinphos-ethyl	15.273	132.0 → 77.1	10	1,000	Quadratic	0.9959	12.1
Pyraclofos	15.311	194.0 → 138.0	10	500	Quadratic	0.9988	12.0
Permethrin, (1R)-*cis*-	15.663	183.1 → 168.1	5	500	Quadratic	0.9974	8.8
Permethrin, (1R)-*trans*-	15.790	163.0 → 127.0	1	1,000	Quadratic	0.9994	12.9
Pyridaben	15.831	147.2 → 117.1	1	1,000	Quadratic	0.9996	5.9
Fluquinconazole	15.909	108.0 → 57.0	0.5	1,000	Linear	0.9980	15.2
Coumaphos	15.934	361.9 → 109.0	10	500	Quadratic	0.9961	14.1
Prochloraz	15.982	310.0 → 69.8	1	1,000	Quadratic	0.9975	13.0
Cyfluthrin I	16.232	162.9 → 127.0	5	1,000	Linear	0.9938	14.8
Cypermethrin I	16.539	163.0 → 127.0	5	1,000	Linear	0.9959	12.6
Acequinocyl	16.575	187.9 → 160.0	N/A				
Flucythrinate I	16.763	156.9 → 107.1	1	250	Quadratic	0.9962	18.1
Ethofenprox	16.840	163.0 → 107.1	0.5	500	Quadratic	0.9992	19.4
Fluridone	17.241	328.0 → 258.9	5	1,000	Quadratic	0.9987	18.9
Fenvalerate I	17.470	167.0 → 125.1	0.5	1,000	Linear	0.9961	15.3
Fluvalinate-tau I	17.663	181.0 → 152.0	50	1,000	Linear	0.9937	8.2
Deltamethrin	18.141	250.7 → 172.0	10	1,000	Quadratic	0.9904	18.6

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