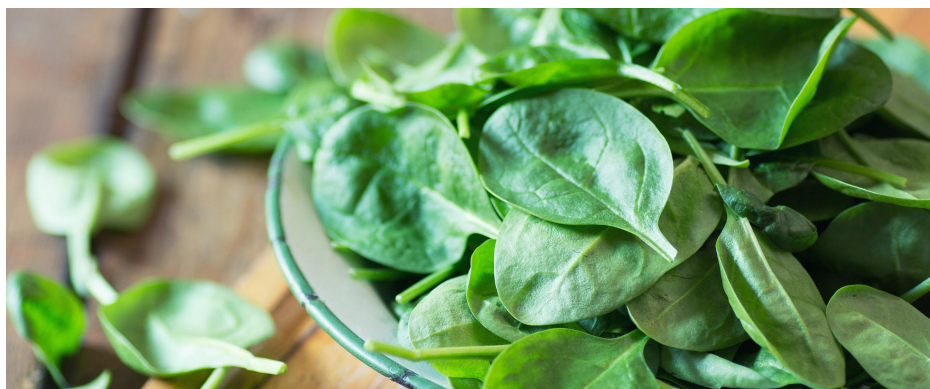


# Enhanced Longevity and Revolutionized Robustness for the Sensitive Detection of 190 Pesticides over 800 Injections



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## Abstract

Multiresidue pesticide analysis has become one of the most difficult but important analytical challenges for those using gas chromatography and mass spectrometry. The Agilent 8890 gas chromatograph (GC) coupled with the Agilent 7010 triple quadrupole mass spectrometer (GC/TQ) with a high efficiency source 2.0 (HES 2.0) upgrade is an analytically accurate, robust, and reproducible instrument for multiresidue pesticide analysis of complex samples. The analysis of 190 pesticides in a spinach extract was conducted using an Agilent QuEChERS extraction kit across 800 injections. Only GC inlet maintenance was required over the duration of the injections. The instrument configuration that enabled robust performance included a multimode inlet, a mid-column backflushing configuration, and the HES 2.0. No degradation of the analytical method, sensitivity, or instrument performance occurred, allowing for the high-throughput, accurate, robust, and sensitive detection of pesticides in spinach.

## Introduction

Multiresidue pesticide analysis remains an important analytical challenge for food safety.<sup>1-7</sup> Pesticides used to improve crop yield can end up in the final product, raising concerns for consumer safety. As a result, multiple governing bodies worldwide have published requirements for the maximum legal residue limit (MRL) or tolerance for pesticides allowed in a product. However, the number of pesticides used in food products continues to grow as novel chemicals are introduced, which in turn increases the complexity of the multiresidue pesticide analysis.

For especially difficult matrices, QuEChERS, which stands for quick, easy, cheap, effective, rugged, and safe, has become widely accepted as a sample preparation technique for multiresidue pesticide analysis.<sup>1</sup> Agilent QuEChERS extraction kits provide prepackaged dispersive and extraction products, extraction salts, and ceramic homogenizers in easy-to-use kits. The kits are ready-made for various methods, including methods of the Association of Official Agricultural Chemists (AOAC)<sup>2</sup> and European Standard (EN).<sup>3</sup>

QuEChERS extracts of food commodities can be analyzed by either GC or high performance liquid chromatography (HPLC) combined with a mass spectrometer (MS) or tandem mass spectrometers (MS/MS).<sup>4,5</sup> Depending on the extent of sample cleanup and the food commodity being analyzed, QuEChERS extracts can cause contamination of the instrument, resulting in poor data quality.<sup>6</sup> This contamination can exhibit as loss

of sensitivity, retention time shifting, poor peak shape, and more. Regular maintenance of the instrument, including GC inlet maintenance, GC column trimming, and ion source cleaning, is required to ensure the robustness and accuracy of the method results.

Backflushing is one of the key practices in which GC/MS/MS analyses of complex matrices can be improved.<sup>7</sup> Backflushing refers to the reversing of flows in the capillary column so that unwanted matrix components are flushed out of the GC split vent instead of proceeding to the detector. Backflushing can provide improved method robustness and help minimize the required maintenance of the mass spectrometer.

Agilent has introduced the new HES 2.0 ion source as part of the 7010D triple quadrupole mass spectrometer (TQ), and it is also available as an upgrade to 7010A/B/C GC/TQ instruments. The HES 2.0 ion source provides improved system robustness, allowing the analysis of hundreds of injections of pesticides in food matrices with only GC maintenance and ion source cleaning necessary. The

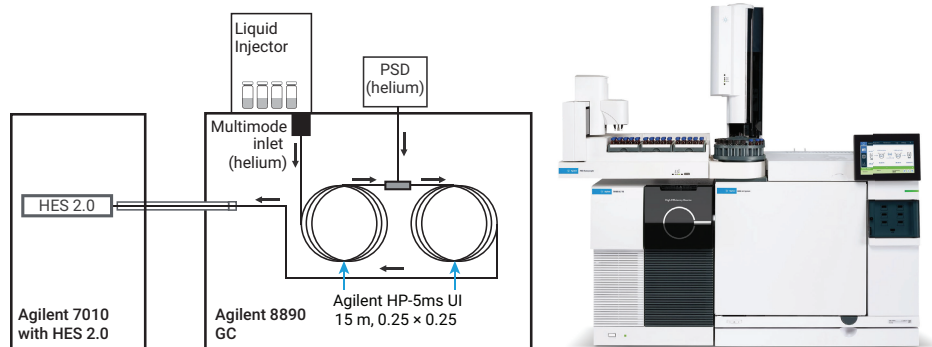
HES 2.0 delivers the same unparalleled analytical sensitivity for ultratrace-level analysis as the original HES.

Multiresidue pesticide analysis in spinach extract was carried out using a 7010B GC/TQ upgraded with the HES 2.0. Matrix-matched standards were used to analyze and quantify over 400 injections of baby spinach extract spiked with 50 ppb of multiresidue standards, demonstrating both method and instrument robustness. The multimode inlet (MMI) and backflushing between two 15 m columns allowed for minimal downtime for GC inlet maintenance. Sensitivity and quantitative accuracy were maintained without any maintenance performed on the mass spectrometer.

## Experimental

### GC/TQ analysis

An 8890 GC with a 7010B TQ system upgraded with the HES 2.0 was used for analysis. The instrument and method were configured as outlined in a previous application note<sup>7</sup>, as shown in Figure 1.



**Figure 1.** The Agilent 8890/7010B GC/TQ system upgraded with the HES 2.0 and system configuration.

The GC was equipped with an Agilent 7650A automatic liquid sampler (ALS) and 50-position tray. The GC used an MMI to achieve a temperature-programmed splitless injection. Mid-column backflush was carried out using an Agilent Purged

Ultimate Union (PUU) installed between two identical 15 m columns; the 8890 GC pneumatic switching device (PSD) module allowed for fewer occurrences of regular maintenance. The method parameters are listed in Table 1.

**Table 1.** Agilent 8890 GC and Agilent 7010B upgraded with the HES 2.0 ion source conditions for pesticide analysis.

GC	
Instrument	Agilent 8890 with Fast Oven, Auto Injector and Tray
Inlet	Multimode Inlet (MMI)
Mode	Splitless
Purge Flow to Split Vent	15 mL/min at 0.75 min
Septum Purge Flow	3 mL/min
Septum Purge Flow Mode	Switched
Injection Volume	1.0 µL
Injection Type	Standard
L1 Air Gap	0.1 µL
Gas Saver	Off
Inlet Temperature	60 °C for 0.1 min, then to 280 °C at 600 °C/min
Postrun Inlet Temperature	310 °C
Postrun Total Flow	25 mL/min
Carrier Gas	Helium
Inlet Liner	Agilent Ultra Inert 2 mm dimpled liner (p/n 5190-2297)
Oven	
Initial Oven Temperature	60 °C
Initial Oven Hold	1 min
Ramp Rate 1	40 °C/min
Final Temperature 1	170 °C
Final Hold 1	0 min
Ramp Rate 2	10 °C/min
Final Temperature 2	310 °C
Final Hold 2	3 min
Total Run Time	20.75 min
Postrun Time (Backflushing)	1.5 min
Equilibration Time	3 min

Column 1	
Type	Agilent HP-5ms UI (p/n 19091S-431UI)
Length	15 m
Diameter	0.25 mm
Film Thickness	0.25 µm
Control Mode	Constant flow
Flow	1.00 mL/min
Inlet Connection	Multimode inlet (MMI)
Outlet Connection	PSD (PUU)
PSD Purge Flow	5 mL/min
Postrun Flow (Backflushing)	-7.873 mL/min
Column 2	
Type	Agilent HP-5ms UI (p/n 19091S-431UI)
Length	15 m
Diameter	0.25 mm
Film Thickness	0.25 µm
Control Mode	Constant flow
Flow	1.200 mL/min
Inlet Connection	PSD (PUU)
Outlet Connection	MSD
Postrun Flow (Backflushing)	8.202 mL/min
MSD	
Model	Agilent 7010B
Source	Agilent HES 2.0
Vacuum Pump	Performance turbo
Tune File	Atunes.eihs.tune.xml
Solvent Delay	3 min
Quad Temp (MS1 and MS2)	150 °C
Source Temperature	280 °C
Mode	dMRM or Scan
He Quench Gas	4 mL/min
N <sub>2</sub> Collision Gas	1.5 mL/min
MRM Statistics	
Total MRMs (dMRM mode)	552
Minimum Dwell Time (ms)	2.63
Minimum Cycle Time (ms)	82.42
Maximum Concurrent MRMs	48
EM Voltage Gain Mode	10

The Agilent Pesticide and Environmental Pollutant (P&EP) database (P&EP 4, part number G9250AA) was used to easily and rapidly create the dynamic multiple reaction monitoring (dMRM) method. This method, which enabled the analysis of 190 pesticides with a total of 552 MRMs, resulted in a maximum of 48 concurrent MRMs, as shown in Figure 2.

### QuEChERS sample preparation

The sample preparation procedure is summarized in Figure 3. A bag of frozen organic baby spinach was homogenized using a spice grinder. Then, eight replicates were prepared. For each replicate, 15 g of the homogenized spinach were weighed into a 50 mL test tube. Then, two of the replicates were designated as samples, while the remaining six were designated for pooled matrix-matched standards. Fifteen microliters of the internal standard mixture (part number 5190-0502) diluted to 50 ng/μL was added to the two spinach samples. To all eight replicates, 15 mL of 1% acetic acid in acetonitrile was added and the mixture was vortexed until well mixed. To each

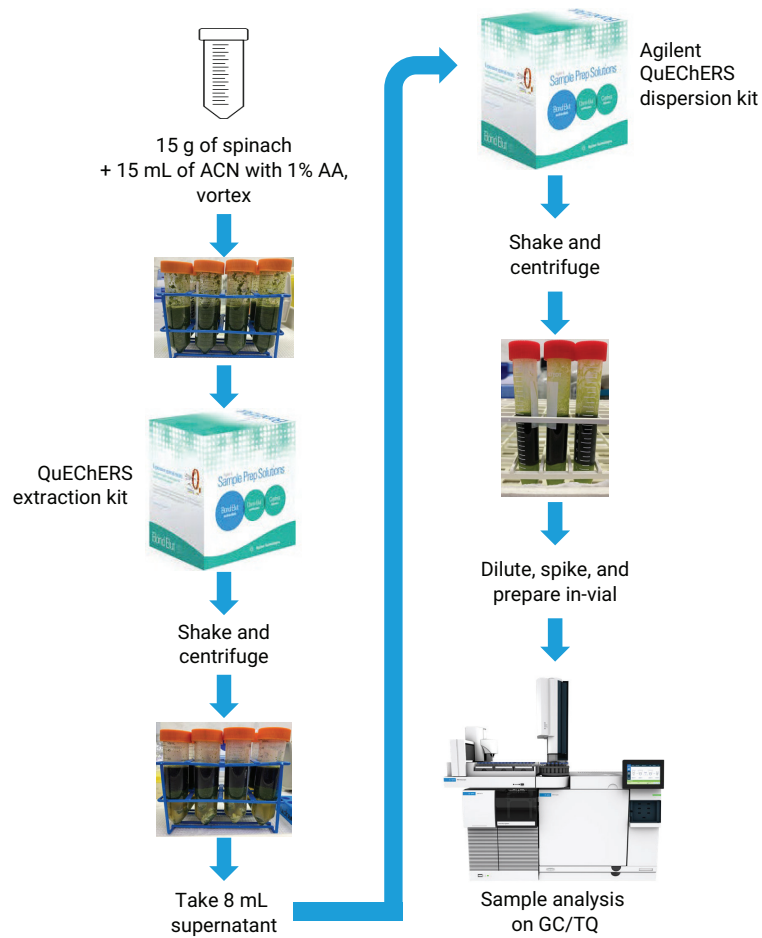


Figure 3. Sample preparation workflow.

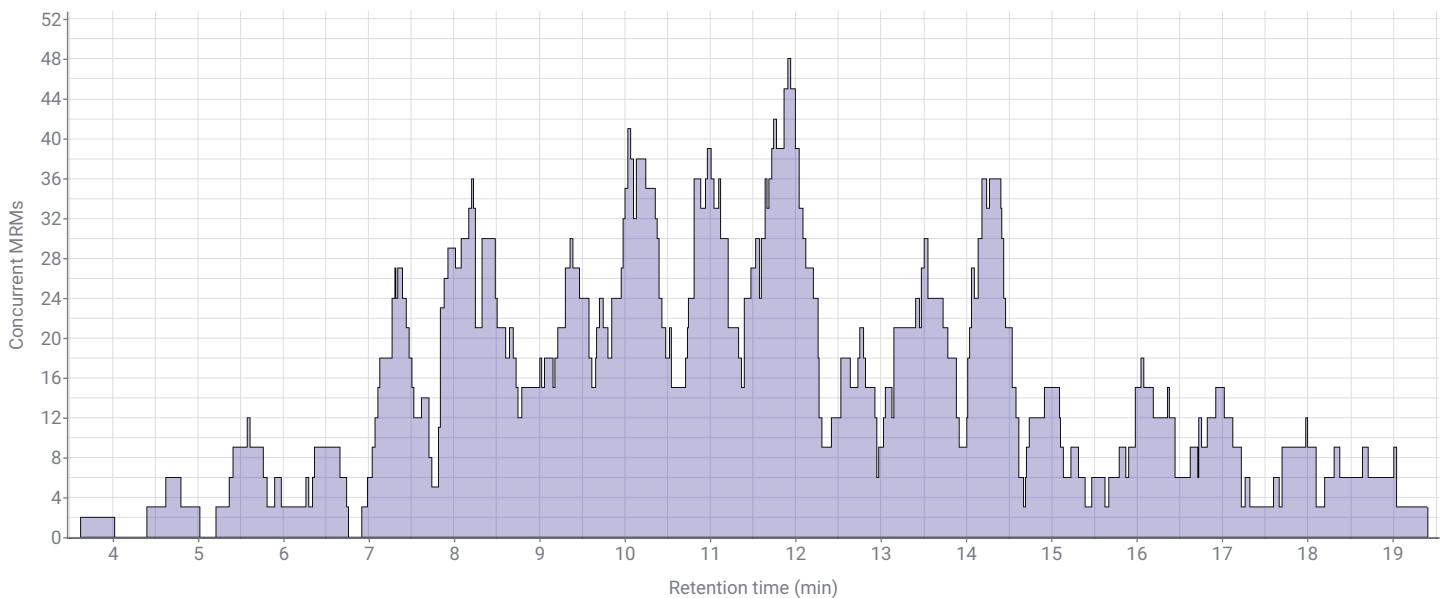


Figure 2. Concurrent MRMs versus retention time.

50 mL tube, the salt packet and two homogenizers from the QuEChERS kit (part number 5982-5755) were added for extraction. These were shaken for 1 minute, then centrifuged at 4,000 rpm with a maximum radius of 17.4 cm for 5 minutes. For the samples and the pooled standards, 8 mL of the supernatant was transferred to a tube with salt for dispersion using the QuEChERS kit (part number 5982-5058). These were shaken for 30 seconds then centrifuged as before for 5 minutes. The supernatant for each of the samples was removed and placed in an amber glass vial. For the pooled standards, the supernatant of all replicates was removed and mixed in a large amber jar for standard preparation.

### Standard preparation

The multiresidue matrix-matched standards were created from the FDA analytical reference standards kit (part number PSM-101). Mixes A, B, C, D, E, L, M, N, O, and P from the PSM-101 pesticides mix were combined to create a 10 ppm stock standard of 190 pesticide residues. The stock solution was then diluted in acetonitrile down to the following nominal concentrations: 1,000, 100, 10, and 1 ppb. In a GC vial, the standards were combined with the spinach extract. The internal standard mixture of parathion- $d_{10}$  and alpha-BHC- $d_6$ , and acetonitrile were combined until the nominal concentration of the internal standard was 50 ppb and the nominal concentrations of the matrix-matched standards in a total volume of 1,500  $\mu$ L were as follows: 0.1, 0.5, 1, 5, 10, 50, 100, 253.3, 500, and 1,000 ppb. Extra vials of the 50-ppb matrix-matched standard were made for quantification to test robustness. The samples were diluted by a factor of three in the vials to match the matrix concentration in the standards. This 3x dilution factor was determined by analyzing the matrix alone in full scan mode as described in a

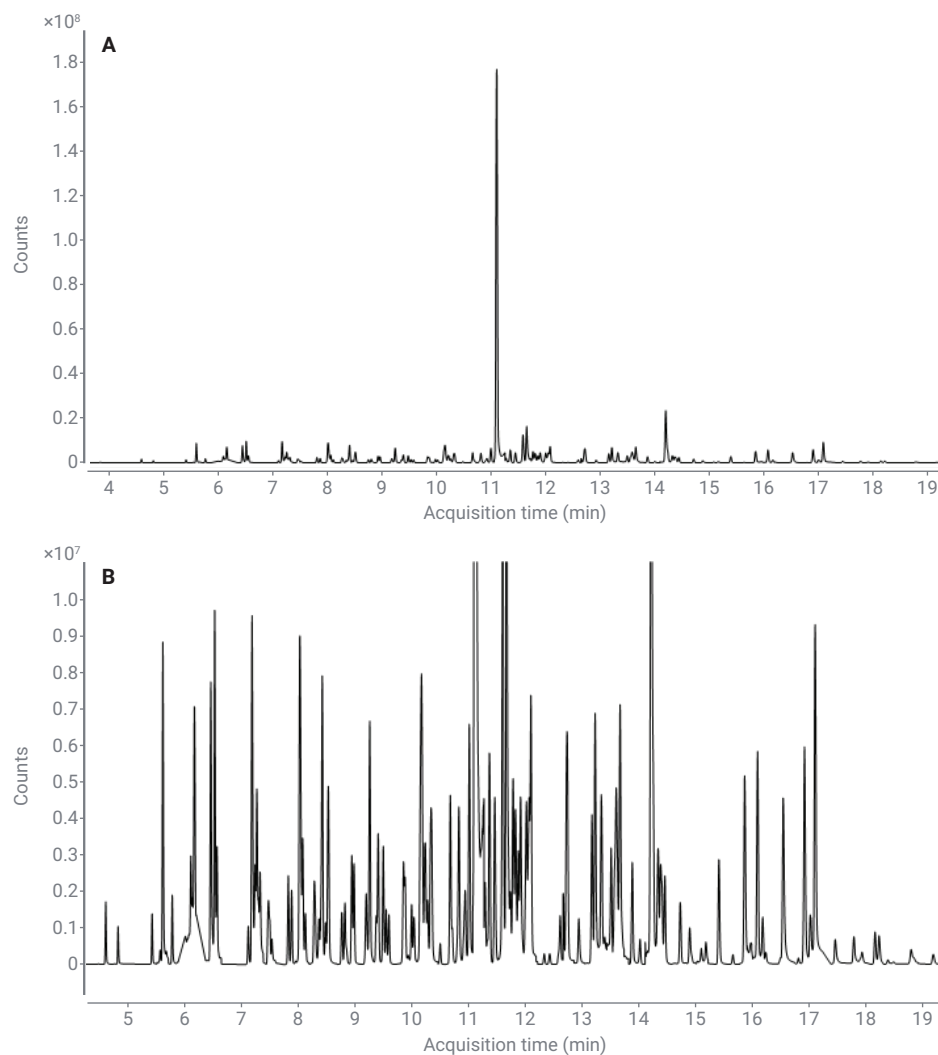
previous application note<sup>7</sup> to ensure that the instrument was not overloaded or saturated by the matrix. Vials with 250  $\mu$ L glass inserts were used with 100  $\mu$ L of each standard or sample in-vial for GC analysis.

### Sequence

Each sequence included 102 injections of spinach extract, either as a sample or matrix-matched standard. Additional injections of blank acetonitrile were used to evaluate system cleanliness by ensuring no analyte carryover or additional background contamination. A representative MRM chromatogram of

the 50-ppb matrix-matched standards in spinach extract is shown in Figure 4A with a zoomed in portion shown in Figure 4B. The sequence included:

- Matrix-matched calibration curve (10 pts)
- Two spinach samples
- Matrix-matched calibration curve (10 pts)
- Matrix-matched standards (50 ppb)  $\times$  60 times
- Matrix-matched calibration curve (10 pts)  $\times$  2 times, each standard in duplicate



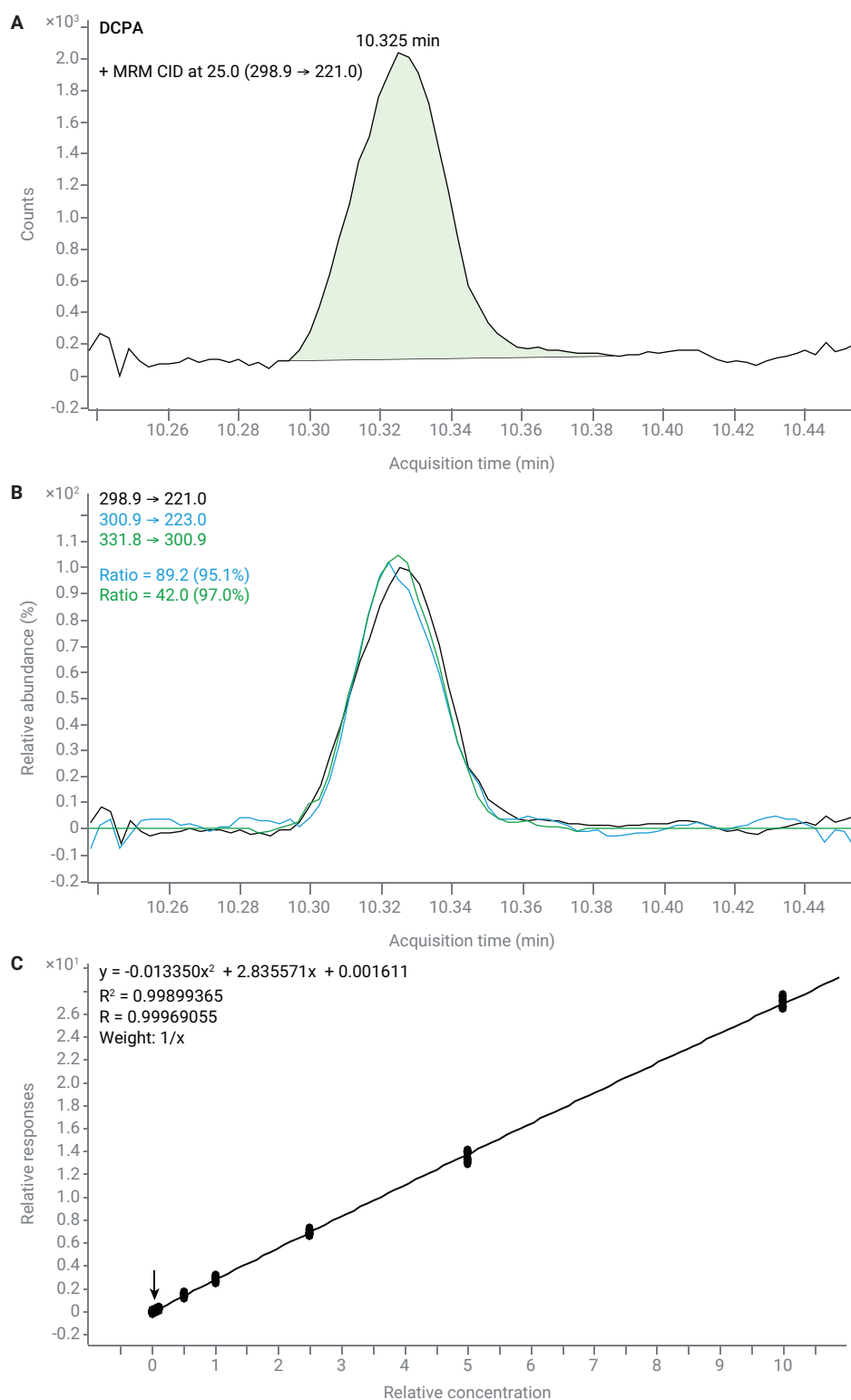
**Figure 4.** A representative chromatogram (A) and a zoomed in portion of the chromatogram (B).

To achieve more than 400 injections of the 50 ppb matrix-matched standard, seven sequences were run for a total of 819 injections, of which 714 were spinach matrix injections. After each sequence, the GC inlet liner and septum were changed, and the 5  $\mu$ L syringe was changed as necessary. Also, the GC vials were refreshed with samples and standards that had been stored in the freezer. No additional instrument maintenance was performed.

## Results and discussion

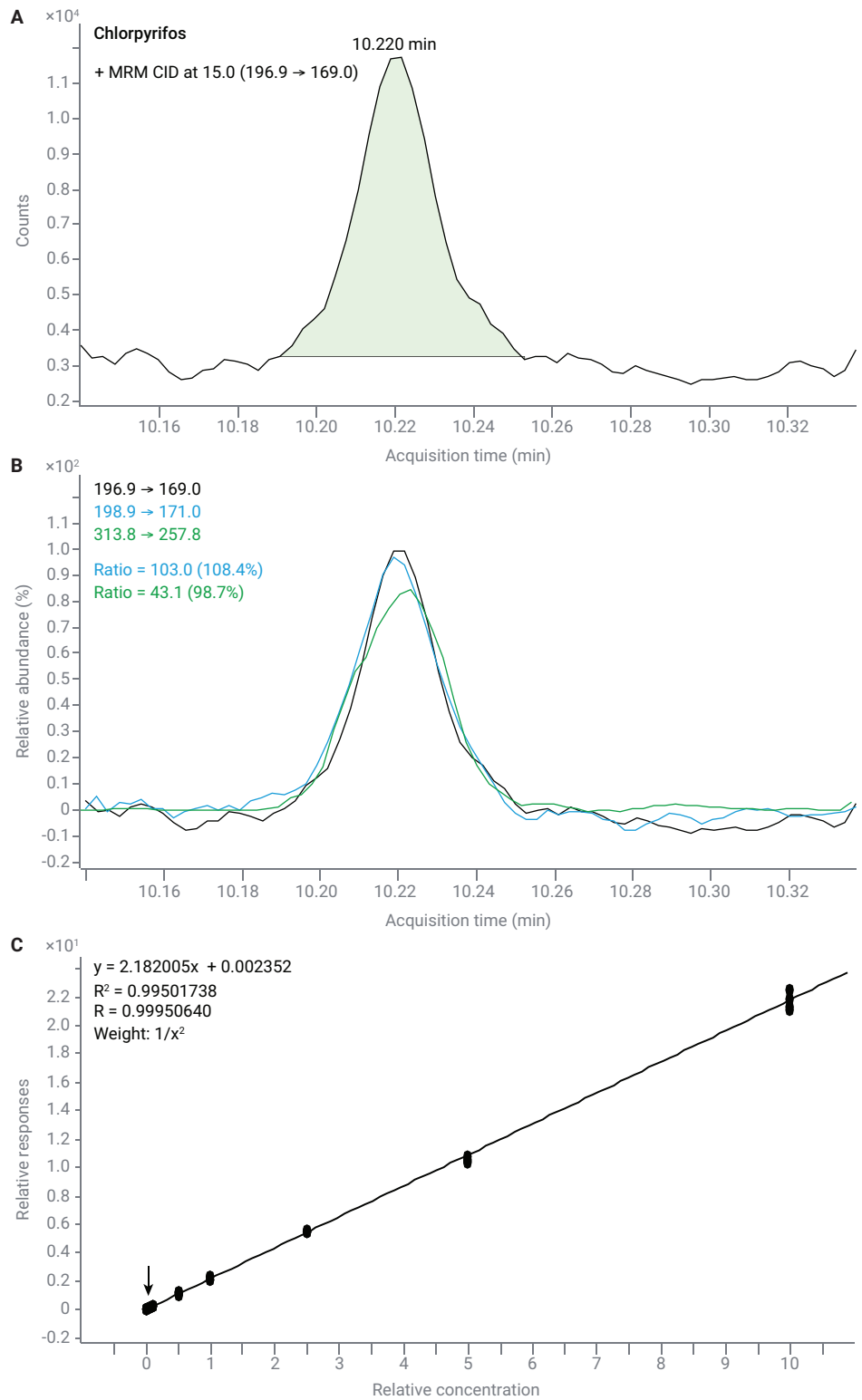
Of the 190 pesticide residues analyzed by GC/TQ, 114 were selected for further study based on their analytical response and performance. These 114 residues were chosen because their calibration curves were either linear or quadratic throughout the seven sequences. These curves did not require extensive analyst intervention, such as manual integration, and had calibration curves that encompassed the 50 ppb point so that the 50 ppb matrix-matched standards for robustness could be calculated as samples. Any points on the calibration curve that had signal-to-noise (S/N) < 3, were interfered with by contaminants, or had accuracy greater than or equal to  $\pm 25\%$  were excluded ( $\geq \pm 25\%$ ). A table summarizing these residues can be found at the end of the application note in Table 2.

Many of the pesticide residues could accurately be quantified down to 0.5 or 0.1 ppb while maintaining S/N > 10 and quantification accuracy of < 25%. For example, Figures 5A, 5B, and 5C show the 0.1 ppb peak, corresponding qualifiers, and calibration curve of DCPA, respectively. The data are defined well by a quadratic calibration curve over the calibration range 0.1 to 1,000 ppb through four orders of magnitude. DCPA has many MRLs as defined by the US FDA down to 50 ppb in various fruits and vegetables.



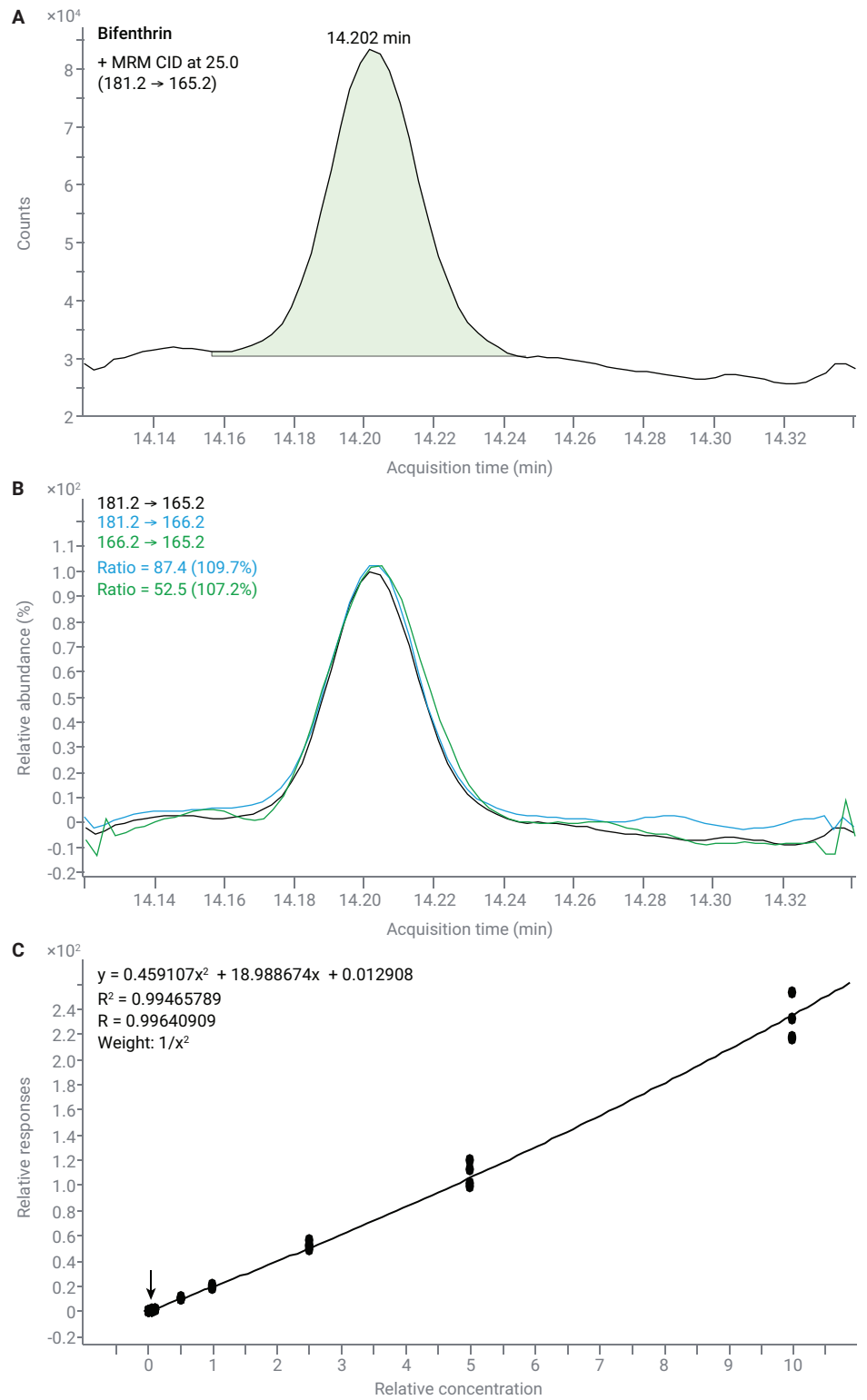
**Figure 5.** Integrated peak (A) and qualifiers (B) of the 0.1 ppb peak of DCPA as well as the full calibration curve (C).

Figures 6A and 6B show the chlorpyrifos 0.5 ppb peak and qualifiers (respectively), while Figure 6C shows the corresponding calibration curve. The curve is linear through 3.5 orders of magnitude and chlorpyrifos has MRLs in various food commodities, the lowest of which is 0.01 ppm in food items such as egg, fig, grape, and apple.

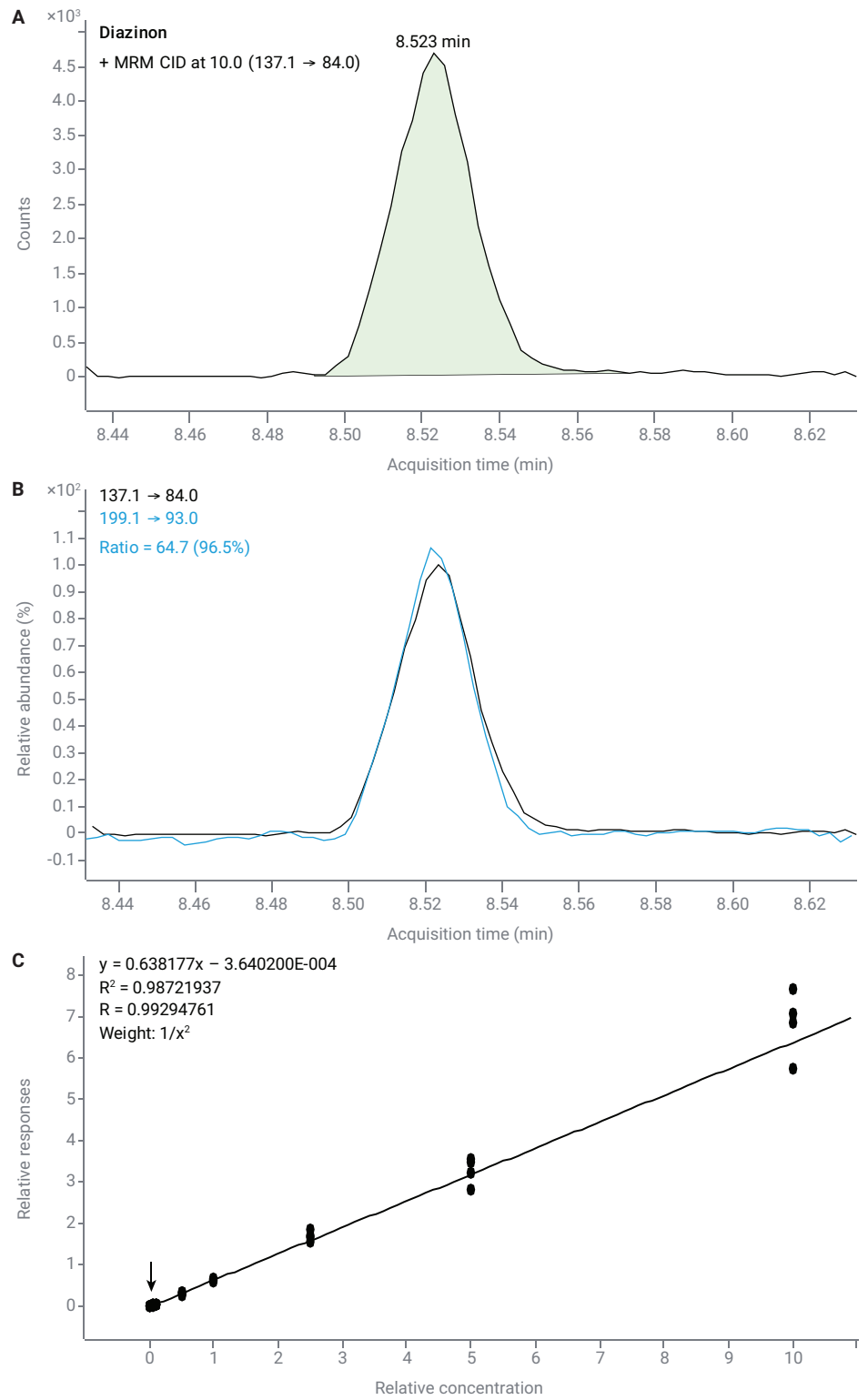


**Figure 6.** Integrated peak (A), qualifiers (B) of the 0.5 ppb peak of chlorpyrifos as well as the full calibration curve (C).

In terms of spinach MRLs, Figures 7, 8, and 9 provide three examples. Figure 7 shows the results for bifenthrin, which is quadratic through 3.5 orders of magnitude down to 0.5 ppb and has an MRL of 0.2 ppm in spinach. Diazinon, linear through 3.5 orders of magnitude down to 0.5 ppb, is shown in Figure 8, with an MRL in spinach of 0.7 ppm.

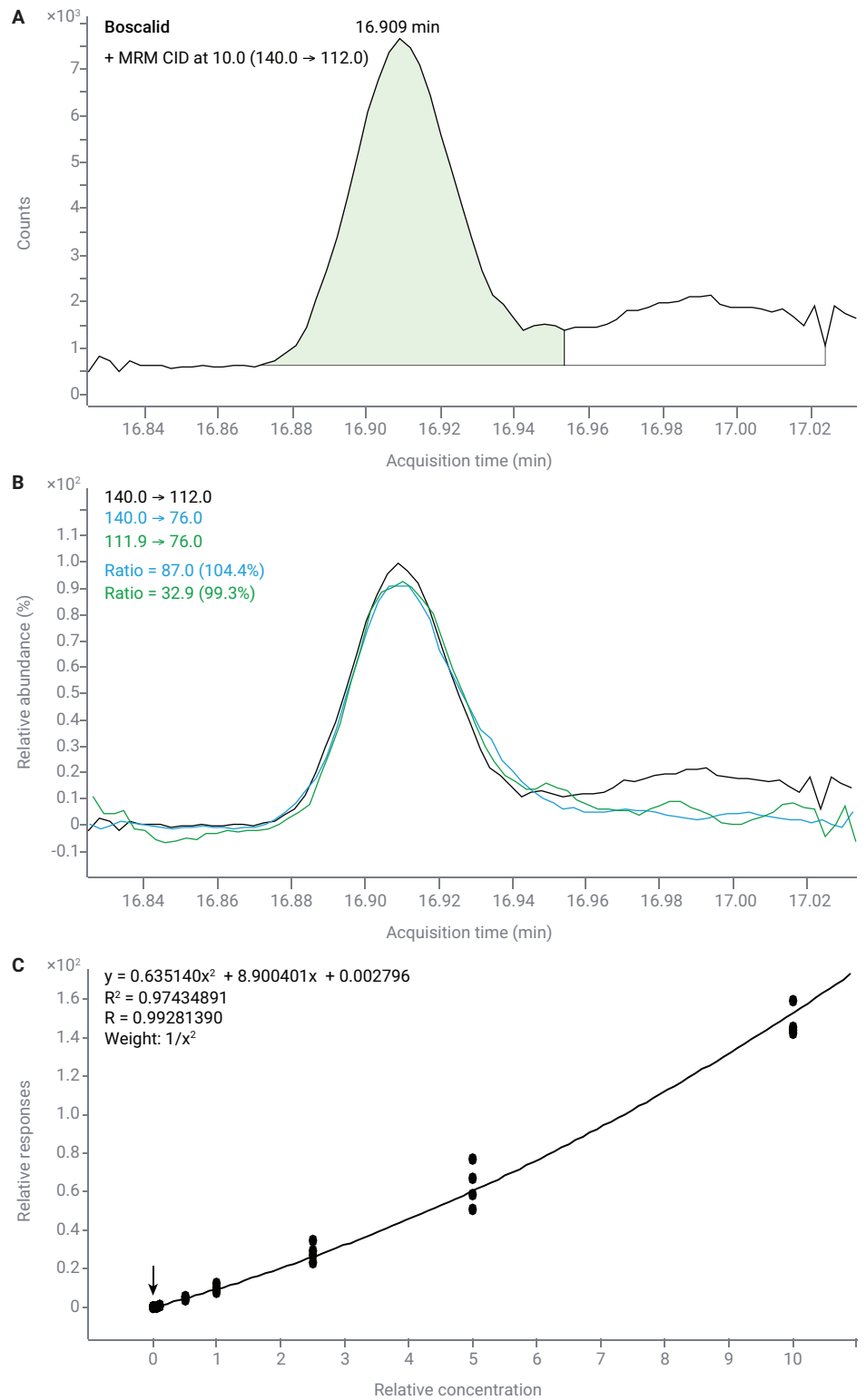


**Figure 7.** Integrated peak (A), qualifiers (B) of the 0.5 ppb peak of bifenthrin as well as the full calibration curve (C).



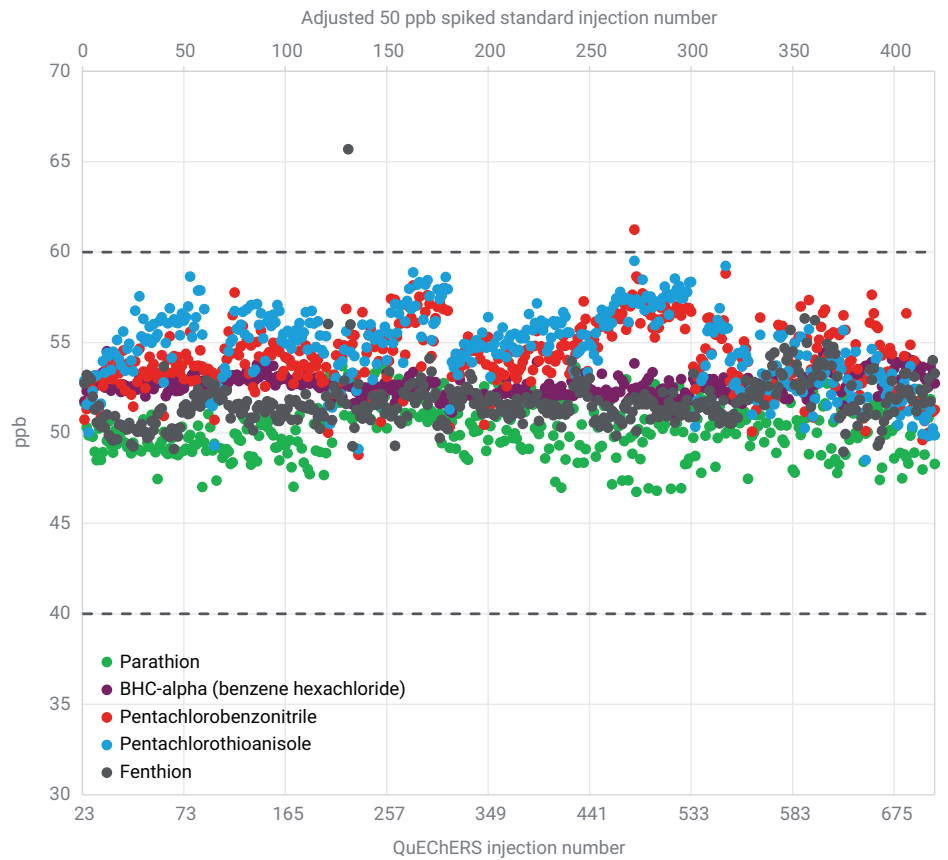
**Figure 8.** Integrated peak (A), qualifiers (B) of the 0.5 ppb peak for diazinon as well as the full calibration curve (C).

Lastly, boscalid is shown in Figure 9 with an MRL of 1 ppb; it is easily defined by a quadratic curve with four orders of magnitude down to 0.1 ppb. In the spinach sample, all three residues fell below the limit of quantification (LOQ) of the analytical method, and below their respective spinach MRLs. In the spinach samples, both boscalid and bifenthrin fell below the limit of detection (LOD) as no peak was detected for either residue. However, a small amount of diazinon was detected that was not present in the solvent blank. However, the area of the peak fell well below the LOQ and had an S/N very close to 3, and therefore approached or fell below the LOD.



**Figure 9.** Integrated peak (A), qualifiers (B) of 0.1 ppb peak of boscalid as well as the full calibration curve (C).

The innovative HES 2.0 source enabled enhanced response stability for the analyzed pesticides over 400 replicate injections of the matrix-matched calibration standard at 50 ppb analyzed within a sequence with over 800 total injections. Figure 10 shows the 400 replicates of the 50 ppb matrix-matched standard, calculated as samples from the corresponding calibration curves across six sequences. The X-axis on the top corresponds to the number of injections of just the 50 ppb matrix-matched standard for robustness. The lower X-axis corresponds to the total injection number of spinach QuEChERS matrix, and therefore excludes blank injections. The concentration in ppb versus injection number plot shows how robust and accurate the analysis was. The results showed all but one point falling within  $\pm 20\%$  error, the usual % error given by GC/TQ data, and most points well within  $\pm 10\%$  of the actual. The %RSD for 400 replicates of all 114 residues are summarized in Table 2, with nearly 80% of the 114 residues having %RSD < 10%, and only five having %RSD above 20%. The robustness of the analysis and the instrument is clearly shown, with only inlet maintenance required between sequences and no further maintenance of the instrument needed.



**Figure 10.** Calculated concentration of pesticides in 50 ppb matrix-matched standard over the course of 714 injections of spinach QuEChERS extract.

**Table 2.** Summary of 114 residues, including calibration range, calibration curve fit, and %RSD over the 400 injections of 50 ppb matrix-matched standard injections for robustness. Those results with %RSD > 20% are highlighted in red.

Name	Retention Time (minutes)	Min Cal (ppb)	Max Cal (ppb)	Curve Fit	Curve Weight	%RSD
Ethiolate	4.609	0.5	1,000	Linear	1/x <sup>2</sup>	7.6
Dichlorvos	4.826	0.5	1,000	Quadratic	1/x	10.4
Nicotine	5.424	0.5	1,000	Linear	1/x <sup>2</sup>	11.9
Biphenyl	5.615	1	1,000	Linear	1/x <sup>2</sup>	6.2
2-Phenylphenol	6.457	5	1,000	Quadratic	1/x	7.5
Pentachlorobenzene	6.566	0.1	1,000	Linear	1/x <sup>2</sup>	4.8
Tecnazene	7.118	0.1	1,000	Linear	1/x <sup>2</sup>	3.9
Diphenylamine	7.186	0.1	1,000	Quadratic	1/x <sup>2</sup>	6.5
Ethoprophos	7.238	5	1,000	Quadratic	1/x	12.3
2,3,5,6-Tetrachloroaniline	7.297	0.5	1,000	Linear	1/x <sup>2</sup>	4.9
Chlorpropham	7.325	0.5	1,000	Quadratic	1/x	7.5
Trifluralin	7.462	1	1,000	Quadratic	1/x <sup>2</sup>	6.6
Benfluralin	7.496	0.1	1,000	Quadratic	1/x <sup>2</sup>	7.2
BHC-alpha (Benzene Hexachloride)	7.881	1	1,000	Linear	1/x <sup>2</sup>	1.0
2,6-Diisopropyl-naphthalene	8.02	5	1,000	Quadratic	1/x	5.5
Hexachlorobenzene	8.024	0.5	1,000	Quadratic	1/x	4.5
Ethoxyquin	8.034	0.1	1,000	Quadratic	1/x <sup>2</sup>	25.3
Dichloran	8.04	1	250	Linear	1/x <sup>2</sup>	7.7
Simazine	8.043	5	1,000	Linear	1/x <sup>2</sup>	7.0
Pentachloroanisole	8.073	0.1	1,000	Linear	1/x <sup>2</sup>	3.3
Atrazine	8.124	1	1,000	Linear	1/x <sup>2</sup>	5.5
Beta-BHC	8.278	1	1,000	Linear	1/x <sup>2</sup>	4.9
Terbutylazine	8.363	1	1,000	Linear	1/x <sup>2</sup>	14.6
BHC-gamma (Lindane, Gamma HCH)	8.398	1	1,000	Linear	1/x <sup>2</sup>	4.5
Pentachloronitrobenzene	8.478	0.5	1,000	Quadratic	1/x <sup>2</sup>	33.7
Pentachlorobenzonitrile	8.515	0.1	1,000	Quadratic	1/x <sup>2</sup>	3.1
Diazinon	8.526	0.5	1,000	Linear	1/x <sup>2</sup>	5.8
Pyrimethanil	8.53	0.1	1,000	Linear	1/x <sup>2</sup>	5.0
BHC-delta	8.763	1	1,000	Quadratic	1/x	11.4
Triallate	8.817	1	1,000	Quadratic	1/x <sup>2</sup>	4.4
Iprobenfos	8.942	0.5	1,000	Quadratic	1/x <sup>2</sup>	17.3
Pirimicarb	8.976	1	1,000	Linear	1/x <sup>2</sup>	8.9
Pentachloroaniline	9.178	0.1	1,000	Linear	1/x <sup>2</sup>	4.6
Propanil	9.193	0.5	1,000	Quadratic	1/x <sup>2</sup>	11.4
Metribuzin	9.256	0.5	1,000	Quadratic	1/x <sup>2</sup>	5.8
Dimethachlor	9.255	0.5	1,000	Linear	1/x <sup>2</sup>	6.0
Vinclozolin	9.372	0.1	1,000	Linear	1/x <sup>2</sup>	9.5
Chlorpyrifos-methyl	9.404	0.1	1,000	Quadratic	1/x <sup>2</sup>	8.4
Parathion-methyl	9.403	5	1,000	Quadratic	1/x	9.3
Ametryn	9.495	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.5
Tolclofos-methyl	9.496	5	1,000	Linear	1/x <sup>2</sup>	5.8
Prometryn	9.541	0.1	1,000	Quadratic	1/x <sup>2</sup>	6.9
Pirimiphos-methyl	9.85	0.5	1,000	Quadratic	1/x <sup>2</sup>	8.9
Fenitrothion	9.855	0.1	1,000	Quadratic	1/x <sup>2</sup>	10.2

Name	Retention Time (minutes)	Min Cal (ppb)	Max Cal (ppb)	Curve Fit	Curve Weight	%RSD
Ethofumesate	9.877	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.5
Malathion	9.995	10	1,000	Quadratic	1/x	20.0
Pentachlorothioanisole	10.032	0.1	1,000	Linear	1/x <sup>2</sup>	3.5
Metolachlor	10.166	5	1,000	Linear	1/x <sup>2</sup>	6.2
Fenthion	10.187	0.5	1,000	Linear	1/x <sup>2</sup>	2.4
Chlorpyrifos	10.224	0.5	1,000	Linear	1/x <sup>2</sup>	4.5
Parathion	10.242	1	1,000	Linear	1/x <sup>2</sup>	2.7
Triadimefon	10.275	0.5	1,000	Quadratic	1/x	11.6
Tetraconazole	10.319	0.5	1,000	Quadratic	1/x <sup>2</sup>	7.5
DCPA (Dacthal, Chlorthal-dimethyl)	10.328	0.1	1,000	Quadratic	1/x	7.3
Isocarbophos	10.346	0.1	1,000	Linear	1/x <sup>2</sup>	4.7
Butralin	10.496	0.5	1,000	Linear	1/x <sup>2</sup>	5.7
Cyprodinil	10.672	0.5	1,000	Linear	1/x <sup>2</sup>	7.8
MGK-264	10.709	0.1	1,000	Linear	1/x <sup>2</sup>	7.3
Pendimethalin	10.797	0.5	1,000	Linear	1/x <sup>2</sup>	4.6
Penconazole	10.826	0.5	1,000	Quadratic	1/x <sup>2</sup>	9.8
Heptachlor Exo-epoxide	10.904	10	1,000	Quadratic	1/x	14.1
Fipronil	10.915	0.5	1,000	Quadratic	1/x	10.7
Triadimenol	11.008	0.5	1,000	Quadratic	1/x <sup>2</sup>	7.1
Quinalphos	11.01	1	1,000	Linear	1/x <sup>2</sup>	3.3
Chlordane-trans	11.326	100	1,000	Quadratic	1/x	13.6
DDE-o,p'	11.363	0.1	500	Quadratic	1/x <sup>2</sup>	11.8
Mepaniprim	11.458	0.5	1,000	Linear	1/x <sup>2</sup>	7.1
Flutriafol	11.596	0.5	1,000	Quadratic	1/x	6.6
Flutolanil	11.664	0.5	1,000	Quadratic	1/x <sup>2</sup>	4.6
Napropamide	11.697	0.5	1,000	Linear	1/x <sup>2</sup>	8.5
Hexaconazole	11.73	0.5	1,000	Linear	1/x <sup>2</sup>	8.6
Isoprothiolane	11.776	0.1	1,000	Linear	1/x <sup>2</sup>	4.8
Prothiofos	11.782	0.5	1,000	Linear	1/x <sup>2</sup>	5.2
Fludioxonil	11.819	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.9
DEF	11.871	0.5	1,000	Linear	1/x <sup>2</sup>	7.4
DDE-p,p'	11.91	0.1	500	Quadratic	1/x <sup>2</sup>	9.8
Oxyfluorfen	11.988	0.5	1,000	Linear	1/x <sup>2</sup>	5.2
Myclobutanil	12.013	0.5	1,000	Quadratic	1/x <sup>2</sup>	8.2
Buprofezin	12.066	1	1,000	Quadratic	1/x <sup>2</sup>	6.2
Bupirimate	12.089	0.5	1,000	Linear	1/x <sup>2</sup>	6.7
Kresoxim-methyl	12.093	0.5	1,000	Quadratic	1/x	5.9
Chlorfenapyr	12.326	0.5	1,000	Quadratic	1/x <sup>2</sup>	4.8
Endrin	12.425	5	1,000	Quadratic	1/x	10.3
Ethion	12.718	5	1,000	Linear	1/x <sup>2</sup>	7.5
Benalaxyl	13.167	0.5	1,000	Quadratic	1/x <sup>2</sup>	7.7
Trifloxystrobin	13.223	0.5	1,000	Linear	1/x <sup>2</sup>	5.3
Quinoxifen	13.222	0.1	1,000	Linear	1/x <sup>2</sup>	7.7
Endosulfan Sulfate	13.328	1	1,000	Quadratic	1/x <sup>2</sup>	13.2
Tebuconazole	13.565	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.6
Nuarimol	13.595	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.4
Triphenyl Phosphate	13.659	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.1

Name	Retention Time (minutes)	Min Cal (ppb)	Max Cal (ppb)	Curve Fit	Curve Weight	%RSD
Piperonyl butoxide	13.662	0.5	1,000	Quadratic	1/x <sup>2</sup>	5.9
Epoxiconazole	13.876	0.5	1,000	Quadratic	1/x <sup>2</sup>	8.5
Spiromesifen	14.014	1	1,000	Quadratic	1/x	15.5
Tetramethrin I	14.207	0.5	1,000	Quadratic	1/x	7.4
Bifenthrin	14.179	0.5	1,000	Quadratic	1/x <sup>2</sup>	4.4
EPN	14.226	10	1,000	Quadratic	1/x <sup>2</sup>	5.8
Bromopropylate	14.221	0.5	1,000	Quadratic	1/x <sup>2</sup>	5.2
Etoazole	14.375	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.3
Tebufenpyrad	14.398	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.9
Fenamidone	14.449	0.5	1,000	Quadratic	1/x <sup>2</sup>	7.4
Tetradifon	14.72	5	1,000	Quadratic	1/x <sup>2</sup>	9.2
Metrafenone	15.648	0.5	1,000	Quadratic	1/x <sup>2</sup>	6.4
Bitertanol I	15.857	0.5	1,000	Quadratic	1/x <sup>2</sup>	9.7
Spirodiclofen	15.976	5	1,000	Quadratic	1/x <sup>2</sup>	49.3
Pyridaben	16.081	0.5	1,000	Quadratic	1/x <sup>2</sup>	5.8
Cyfluthrin I	16.484	5	1,000	Quadratic	1/x <sup>2</sup>	22.2
Fenbuconazole	16.535	5	1,000	Quadratic	1/x <sup>2</sup>	9.5
Cypermethrin I	16.8	5	1,000	Quadratic	1/x	23.8
Boscalid	16.909	0.1	1,000	Quadratic	1/x <sup>2</sup>	8.4
Ethofenprox	17.096	0.5	1,000	Quadratic	1/x <sup>2</sup>	5.9
Difenoconazole I	18.148	1	1,000	Quadratic	1/x	12.4
Azoxystrobin	18.787	10	1,000	Quadratic	1/x <sup>2</sup>	11.2
Dimethomorph I	19.175	5	1,000	Quadratic	1/x	15.3

## Conclusion

The analytical performance of the Agilent 7010 Series triple quadrupole mass spectrometer (GC/TQ) upgraded with the HES 2.0 electron ionization (EI) source was demonstrated for multiresidue pesticide analysis. The system demonstrates analytical sensitivity as the same or better than the original HES as well as excellent accuracy and robustness. The 7010 GC/TQ with HES 2.0, coupled with an Agilent 8890 GC with an MMI inlet and 15 m × 15 m mid-column backflush configuration minimizes instrument downtime by allowing for inlet maintenance without requiring the cooling of the heated zones. With no impact to the analytical method or degradation of the instrument performance, this application demonstrates the ability of the instrument to provide robust and reliable analytical results, including for challenging matrices.

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