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Enhanced Longevity and Revolutionized Robustness for Sensitive Detection of 190 Pesticides over 800 Injections with Novel HES 2.0 Source

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Introduction

Multi-residue pesticide analysis is a difficult but important analytical challenge for food safety[1-5]. As the number and type of pesticides continues to grow, so do the maximum legal residue limits (MRLs) for pesticides allowed in a product. For especially difficult matrices, QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) is widely used for sample preparation prior to analysis by chromatography coupled with mass spectrometry.[1] Depending on the extent of sample clean-up and the food commodity being analyzed, QuEChERS extracts can cause contamination of the instrument, resulting in poor data quality. The novel HES 2.0 ion source for Agilent's GC/TQ provides improved system robustness, allowing for the analysis of hundreds of injections of food matrix with only GC maintenance.

Novel HES 2.0

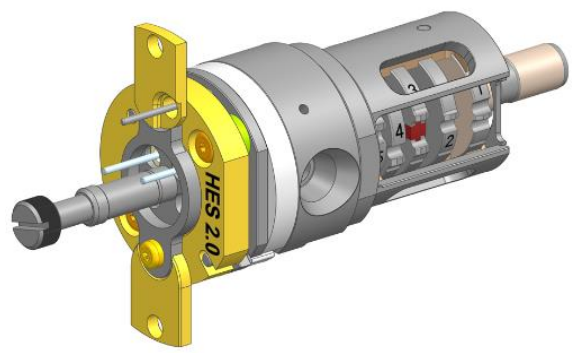

Figure 1: Model of the Agilent HES 2.0

The HES 2.0, as seen in Figure 1, is a new EI source equipped with a novel dipolar RF lens that redirects carrier gas and low mass ions by >95%. The deflected ions land on adjacent lenses and are pumped out prior to entering the mass analyzer, providing reduced noise and extended instrument robustness while maintaining sensitivity. A ramped RF amplitude vs. mass is implemented to avoid spectral tilt (Figure 2).

The HES 2.0 will be available in Agilent's 7010D GC/TQ or as part of an upgrade kit to an existing 7010 or 7000 GC/TQ system.

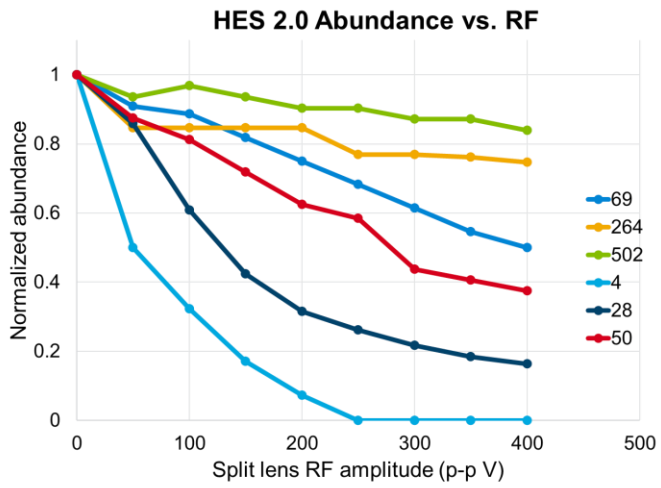

Figure 2: Split lens RF profile

Instrumentation

An Agilent 8890 GC with a 7010B TQ system upgraded with the HES 2.0 was used for analysis, as seen in Figure 3. A multimode inlet (MMI) was used to achieve a temperature-programmed splitless injection. Mid-column backflush using the Agilent Purged Ultimate Union (PUU) installed between two identical 15 meter columns and the 8890 GC pneumatic switching device (PSD) module allowed for fewer occurrences of regular maintenance

The Agilent Pesticide & Environmental Pollutant (P&EP) database (Part #G9250AA) was used to easily and rapidly create the dynamic multiple reaction monitoring (dMRM) method, which allowed for the analysis of 190 pesticides with a total of 552 MRMs, resulting in a maximum of 48 concurrent MRMs and a minimum dwell time of 2.63 ms.

Parameter	Setting
MMI Mode	Splitless
Liner	UI 2mm dimpled (5190-2297)
Inlet Temp	60 °C for 0.1 min, then to 280 °C at 600 °C/min. Post Run 310 °C.
Oven	60 °C for 1.0 min, then 170 °C at 40 °C/min, then 310 °C at 10 °C/min and hold 3 min. Post Run time 1.5 min.
Carrier Gas	Helium
Column 1 Run/Postrun flow (mL/min)	HP-5MS UI (19091S-431UI) 1.00 / -7.873
Column 2 Run/Postrun flow (mL/min	HP-5MS UI (19091S-431UI) 1.2 / 8.202
PSD Purge Flow (PUU)	5 mL/min
Solvent Delay	3 min
Quad Temp (Q1 and Q2)	150 °C
Source Temp	280 °C
He Quench Gas	4 mL/min
N2 Collision Gas	1.5 mL/min

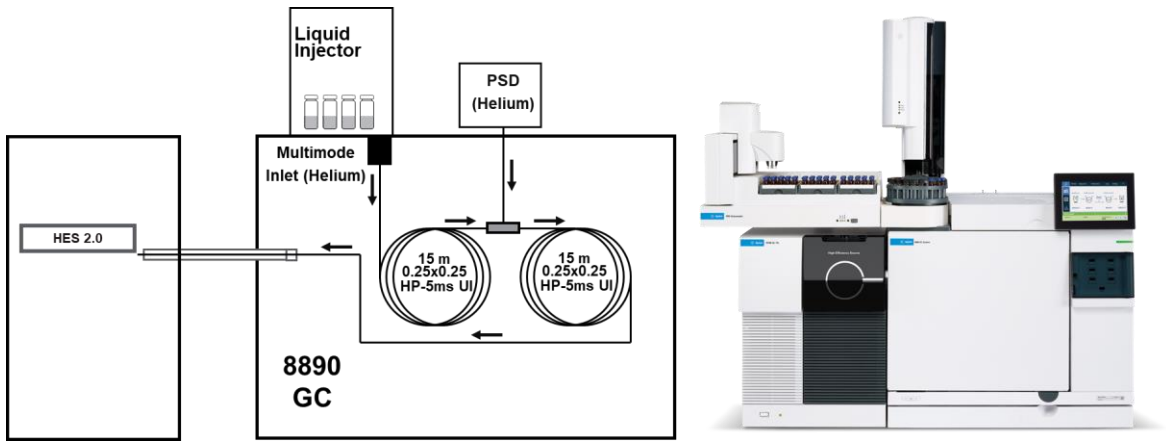

Figure 3: System configuration for the Agilent 8890/7010B GC/TQ upgraded with the HES 2.0 ion source.

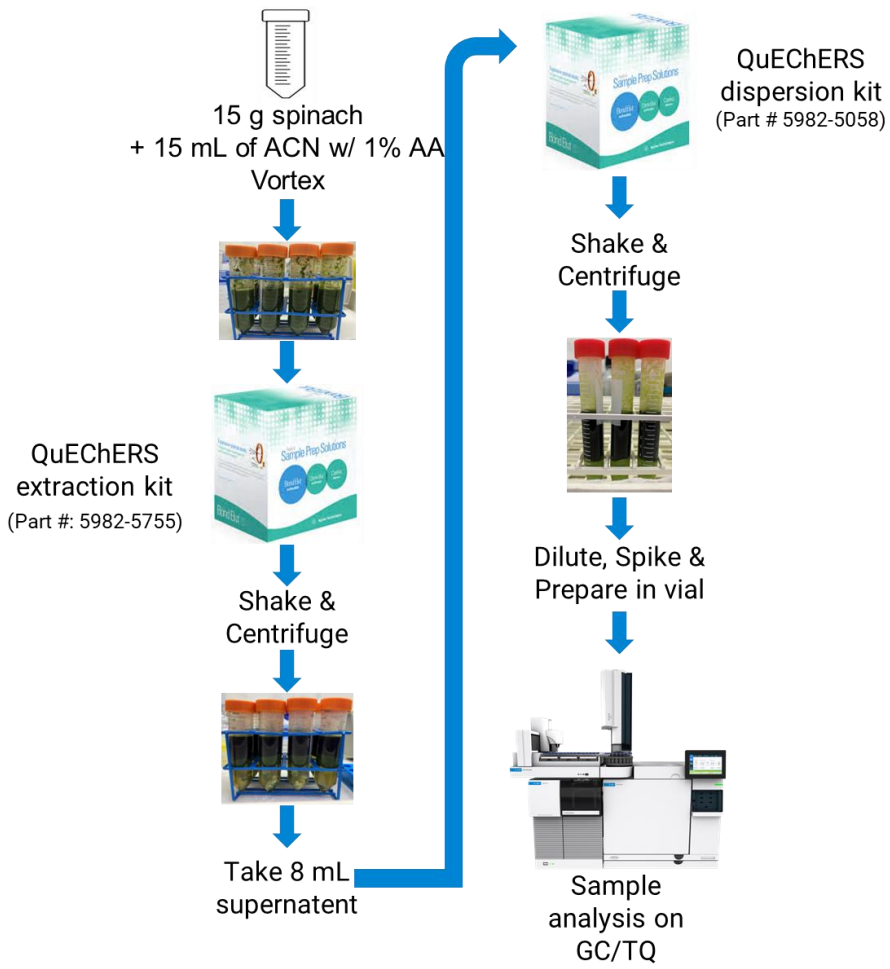

Figure 4: Sample preparation workflow

Spinach Sample Preparation

Frozen organic baby spinach was homogenized with a spice grinder, and 8 replicates were prepared as in Figure 4. Two replicates were designated as samples and 15 µL of the internal standard mixture (P/N 5190-0502; parathion-d10 and alpha-BHC-d6) diluted to 50 ng/µL concentration was added prior to the extraction step. The other six replicates were pooled to create matrix-matched standards.

Standard Preparation

Mixes A-E and L-P from the PSM-101 pesticides mix were combined to create a 10-ppm stock standard of 190 pesticide residues. Standards were prepared at the following nominal concentrations: 0.1, 0.5, 1, 5, 10, 50, 100, 253.3, 500, 1000 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 3 in vial to match the matrix concentration in the standards and to ensure the system was not overloaded or saturated by matrix.

Sequences

Each sequence included 102 injections of spinach extract either as sample or matrix-matched standard. Seven sequences were run for a total of 819 injections, 714 of which were spinach matrix and more than 400 of which were the 50-ppb matrix-matched standard for robustness. After each sequence, GC inlet maintenance was performed. No MS maintenance was required.

Analytical Results

A representative chromatogram is shown in Figure 6, right. Of the 190 pesticide residues analyzed by GC/TQ, 114 were selected for further study because their calibration curves were either linear or quadratic throughout the seven sequences. These curves did not require manual integration and had calibration curves that encompassed the 50 ppb point for the robustness evaluation. Any points on the calibration curve that had signal-to-noise (S/N) < 10, were interfered with by contaminants, or had accuracy ≥ ±25% were excluded.

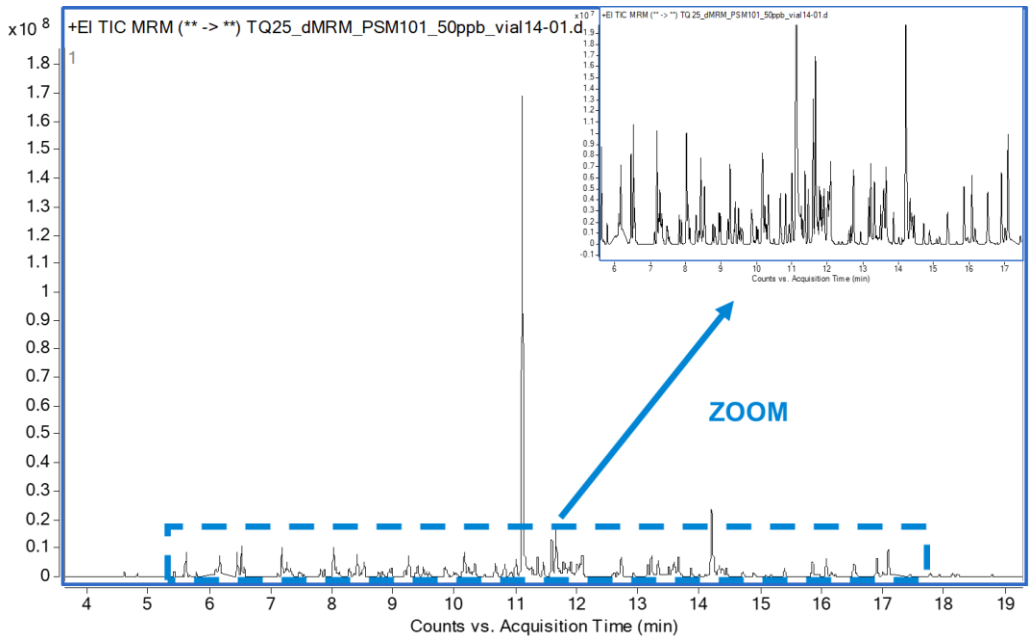

Figure 6: Chromatogram of 50 ppb matrix-matched standard in spinach extract.

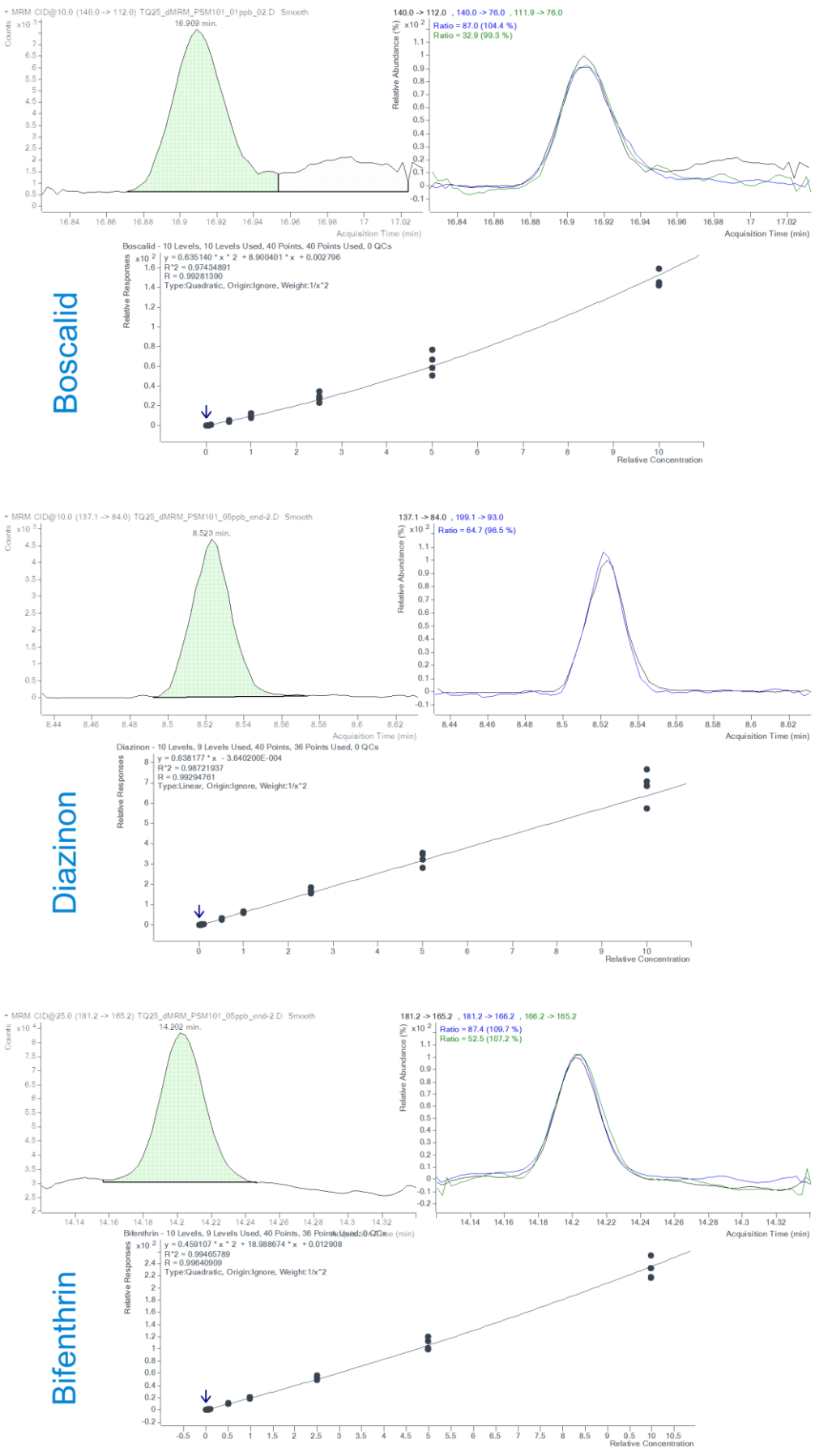

Figure 5: Integrated peaks, qualifiers, and calibration curves of 3 pesticide residues with MRLs in spinach.

Sensitivity and Linearity

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%. Shown in Figure 5, left, are 3 examples of pesticide residues, all of which have MRLs in spinach as defined by the U.S. FDA, and all of which fell below the LOQ of the method:

- Boscalid (upper left): MRL of 1 ppm in spinach, quadratic over 4 orders of magnitude down to 0.1 ppb
- Diazinon (middle left): MRL of 0.7 ppm in spinach, linear over 3.5 orders of magnitude down to 0.5 ppb
- Bifenthrin (bottom left): MRL of 0.2 ppm in spinach, quadratic over 3.5 orders of magnitude down to 0.5 ppb.

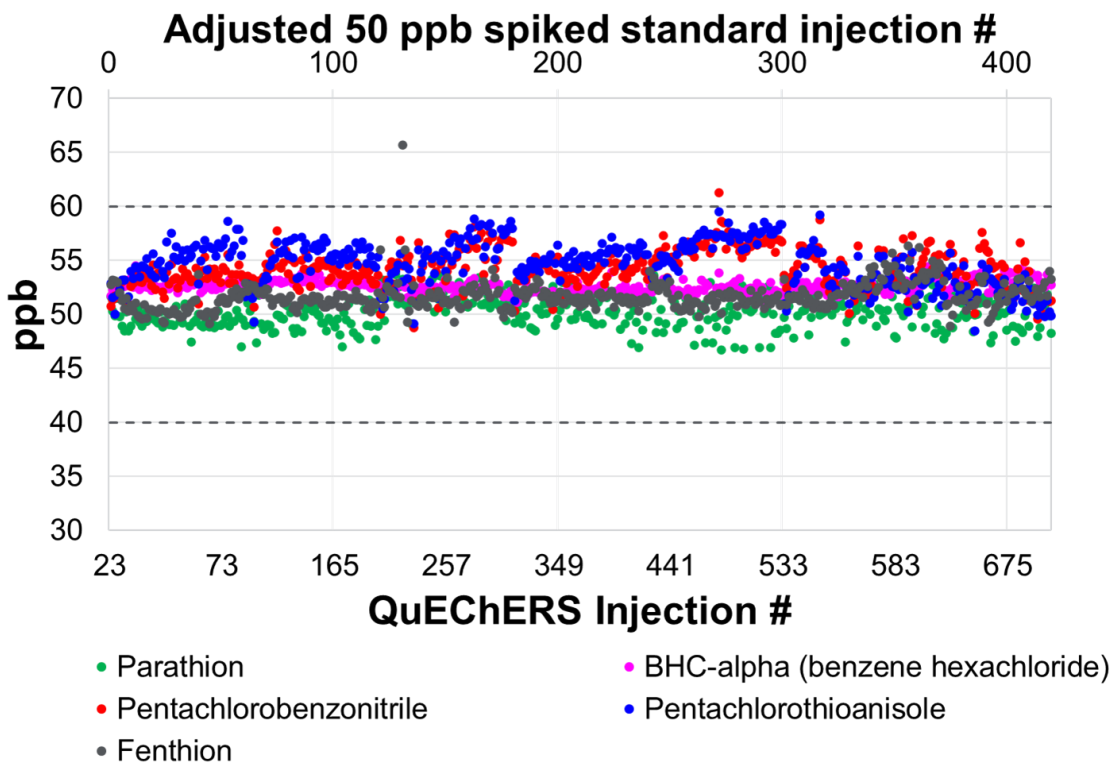

Figure 7: Robustness results for 50-ppb matrix matched standard

Conclusions

Robustness

Figure 7 shows 400 replicates of the 50 ppb matrix-matched standard, calculated as samples across six sequences. The results showed all but one point falling within ±20% error, and most well within ±10% of the actual. The %RSD for these 400 replicates of all 114 residues were calculated, with nearly 80% of the 114 residues having %RSD < 10%, and only 5 having %RSD above 20% as summarized in Figure 8.

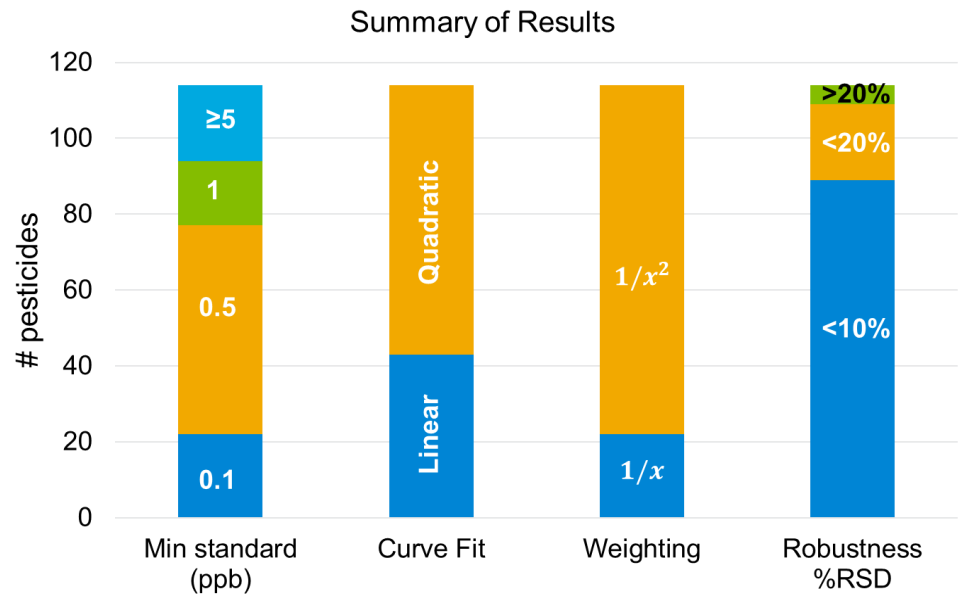

Figure 8: Summary of analytical and robustness results of 114 pesticide residues.

Conclusions

The analytical performance of the Agilent 7010 GC/TQ with the novel HES 2.0 ion source was demonstrated for multiresidue pesticide analysis:

- Robust, reliable analytical results, including for challenging matrices
- Same unparalleled analytical sensitivity as the original HES
- Only inlet maintenance required with no degradation of performance over >800 injections.

References

[1]Anastassiades, M., et. al. J. AOAC Int. 2003, 86, 412-431.

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