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Achieving the MRLs with Hydrogen Carrier Gas: GC/MS/MS Analysis of 200 Pesticides in Produce

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Introduction

Arising Need for Analyzing Pesticides with Hydrogen

Recurring helium shortages and increased prices drive the demand for performing GC/MS analysis with alternative carrier gasses. While helium is the best carrier gas for GC/MS, hydrogen is the second-best alternative. However, unlike helium, hydrogen is not an inert gas. Hence, it could react with target analytes resulting in compound degradation, chromatographic problems such as peak tailing, distorted ion ratios in the mass spectrum, poor library matching, and sensitivity loss.

Pesticides analysis can be challenging even with He carrier gas given the diverse and labile nature of many pesticides and complex matrices, in which they are analyzed. This presentation discusses the key strategies for analyzing pesticides with H_2 carrier gas while delivering high-quality uncompromised results.

Experimental

Key Considerations for Successful Transitioning GC/MS/MS Analysis from Helium to Hydrogen

It is important to recognize the differences with using hydrogen carrier. The EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion Guide [1] provides detailed instructions for method conversion from He to H_2 carrier. The user guide outlines considerations and procedures for H_2 safety necessary to make the transition to H_2 carrier gas successful.

Additional factors complicating pesticide residue analysis include low tolerance limits that require high sensitivity of the analysis, thermal lability, chemical diversity, and interreferences arising from complex matrices. This work leveraged the key practices that enhance pesticide residue analysis with GC/MS/MS applicable to both He and H_2 carrier gas outlined elsewhere [2]. Among those best practices were effective sample extraction and matrix cleanup, midcolumn backflushing, and the use of the temperature-programmed injection in solvent vent mode with a 2 mm dimpled liner (without glass wool).

The instrument conditions are summarized below:

- Solvent vent injection, 2 µL, 2 mm dimpled liner, 60 °C for 0.1 min, then to 280 °C at 600 °C/min
- Two HP-5ms UI 20m (0.18mm x 0.18µm) columns connected with the purged ultimate union (PUU)
- Oven program: 60 °C for 1 min, then to 170 °C at 40 °C/min, 0 min hold, then to 310 °C at 10 °C/min, hold for 2.25 min.
- Column flows: 1.1 and 1.3 mL/min; H_2 carrier gas.

Maintaining the Retention Times and Chromatographic Resolution with Hydrogen Carrier Gas

The combination of method translation followed by retention time locking allowed for transferring the conventional 20-minute analysis of 203 pesticides with He to H_2 carrier gas, while maintaining the relative elution order and precisely matching the retention times (Fig. 1). The same techniques were also used to translate the 20-minute analysis to 10 minutes with hydrogen carrier gas (Fig. 1, bottom). Chromatographic resolution achieved with H_2 and the 20-min analysis surpassed that with He enabling better separation between the targets and the coeluting interferences from the complex spinach matrix. The resolution with a 10-min analysis and H_2 was comparable to that with He and 20-min analysis.

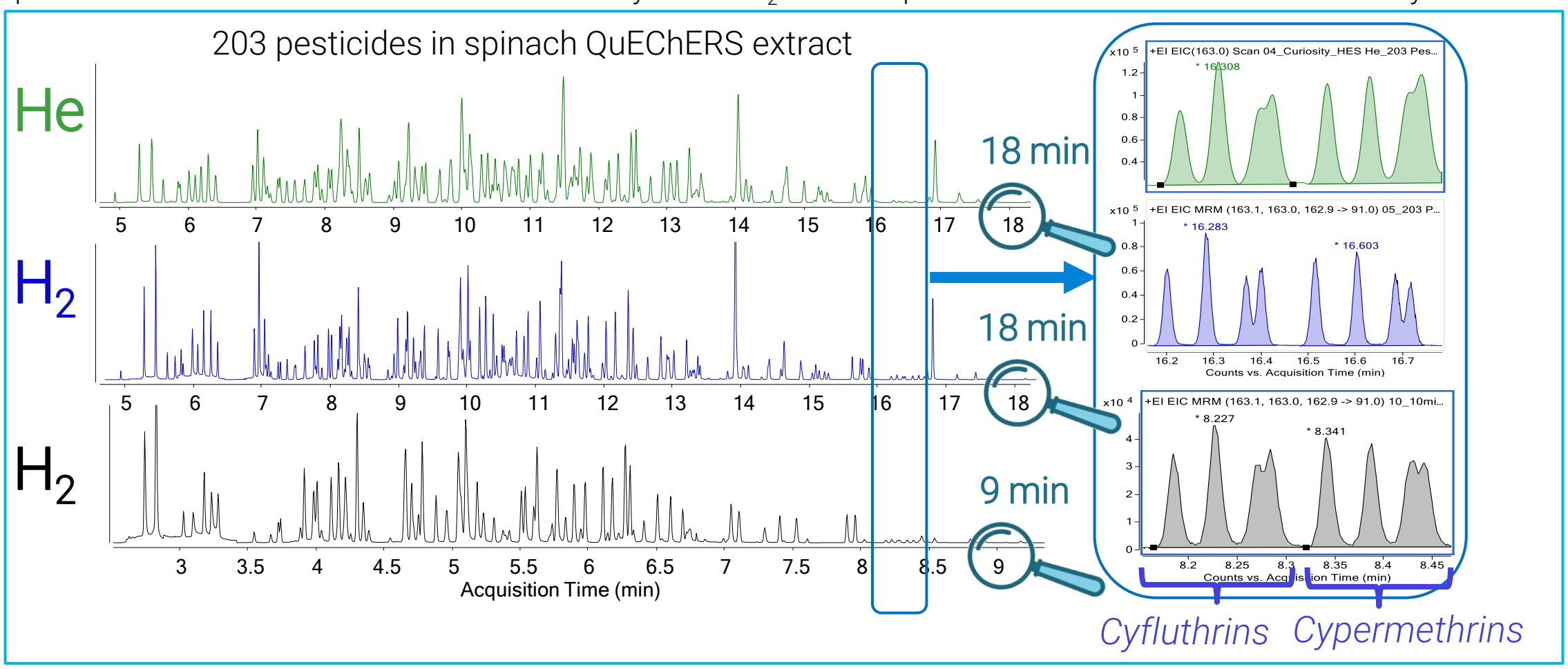


Figure 1. MRM Chromatograms od 203 pesticides in spinach QuEChERS extract analyses with He and H_2 carrier gasses.

Does Spectrum Distortion Happen with Hydrogen? No, if Using the Hydrogen-Optimized EI Source Hardware

H_2 carrier gas provides advantages for chromatographic separation. However, it could present a challenge for detection with a mass spectrometer. Due to its reactivity, H_2 carrier gas can alter the spectrum for compounds susceptible to reacting with hydrogen. Fig. 3A shows the distorted mass spectrum for tecnazene, a fungicide used to control dry rot, acquired with the conventional EI source. Using the hydrogen-optimized HydroInert source and the HES source allows for maintaining the same ion ratios as observed with helium carrier gas (Fig. 3B, C). Minimizing in-source reactions with H_2,allows for using the existing spectral libraries for identity confirmation and the MRM transitions developed with He for reliable quantitation.

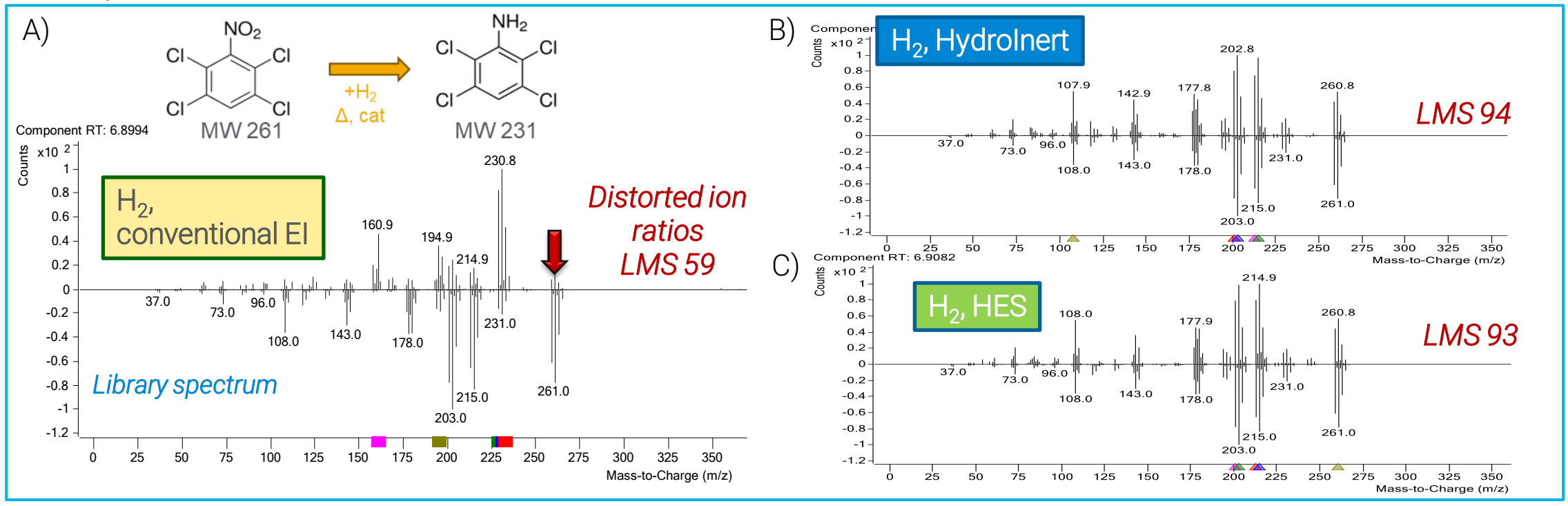


Figure 2. Spectra acquired for tecnazene with H_2 and Conventional EI, HydroInert, and HES compared to the NIST library.

Results and Discussion

Distorted Ion Ratios Lead to Decreased Sensitivity

The extent of GC/MS/MS sensitivity reduction with H_2 compared to He varies if the target is susceptible to reacting with H_2. Compounds that do not interact with H_2, show 2-5 times higher detection limits with H_2 than with He. For compounds susceptible to reacting with H_2 (as can be confirmed by the distorted spectrum), sensitivity can be reduced over 100 times.

For example, tecnazene, which spectra were shown in Fig. 2, demonstrates sensitivity reduction over 100 times when using the conventional EI source with H_2 (Fig. 3B vs. Fig. 3A). This can be attributed to the reduction of the molecular ion and the MRM precursor m/z 261 with the conventional source.

By using the HydroInert or the HES EI sources and minimizing the in-source reactions, the sensitivity of analysis is restored to the levels comparable to those with He. Fig. 3C,D show that tecnazene can be reliably quantitated below the default MRL of 10 ppb with both the HydroInert and the HES source. Such sensitivity cannot be achieved when using the conventional EI source with H_2.

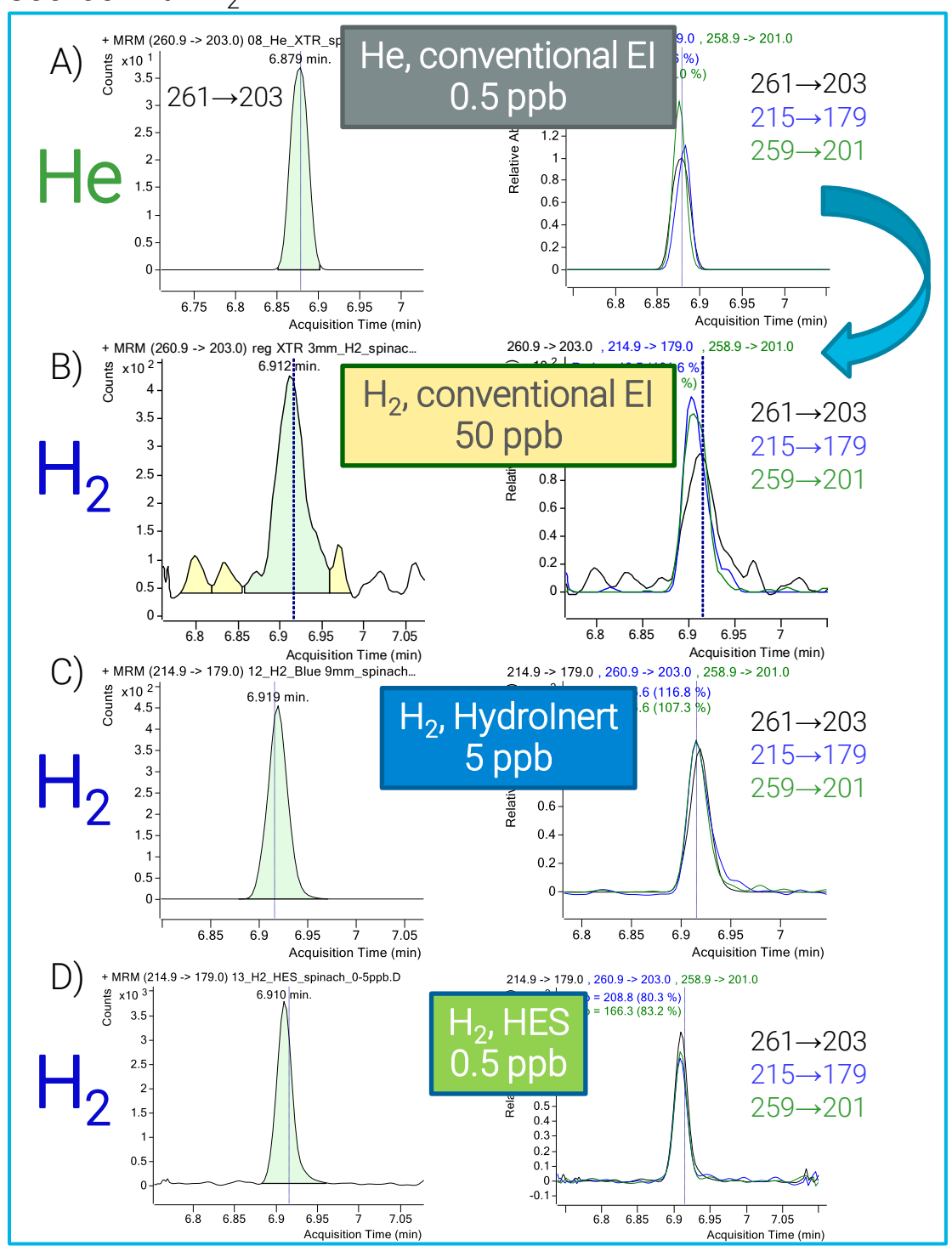


Figure 3. MRM chromatograms for tecnazene acquired with He and H_2.

Results and Discussion

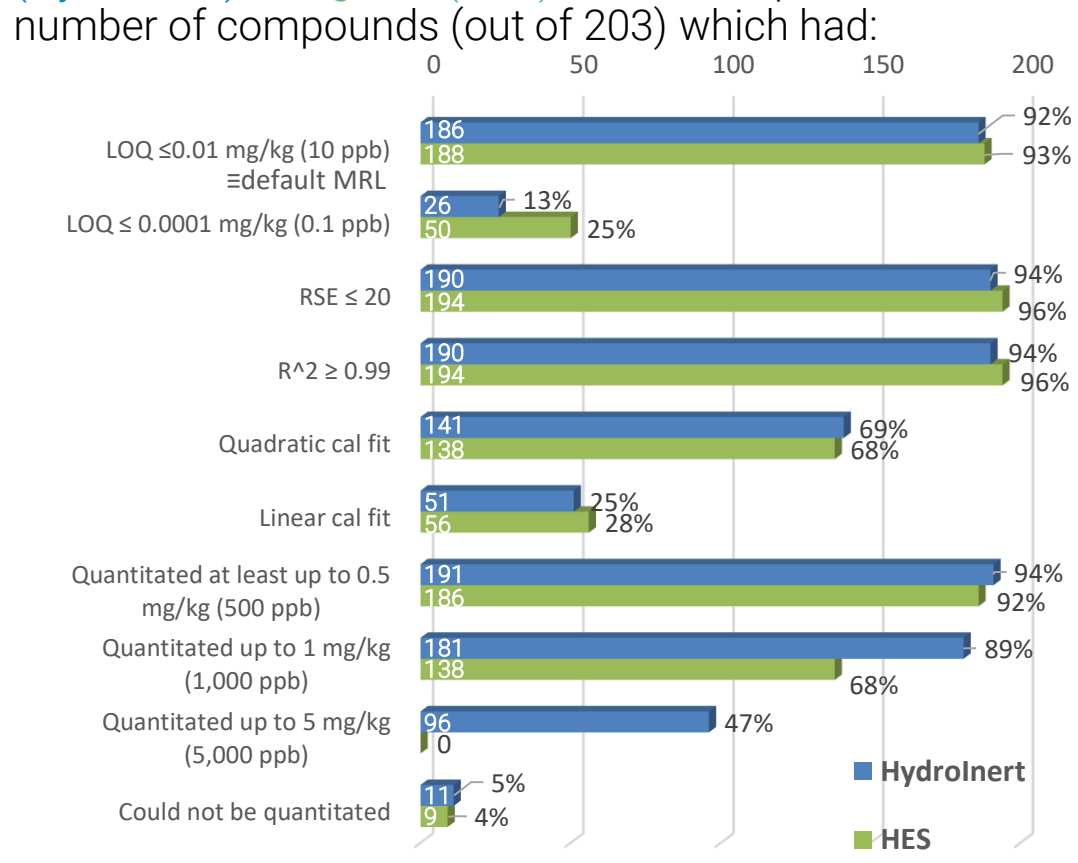
Compounds with Diverse Chemical Structures React with H_2 Resulting in Spectral Distortion

Evaluating analyte's mass spectrum with H_2 is the simplest way to determine if the target undergoes undesirable chemical transformation in the EI source. If the spectrum appears distorted, then difficulties with compound quantitation are expected. In this case, the MRMs would need to be re-optimized, and quantitation accuracy may still suffer due to the uncontrolled and nonreproducible chemical transformations in the source. The table below shows library match scores for 15 pesticides that demonstrated in-source reactivity with hydrogen when a conventional EI source was used. The library match scores and ion ratios were restored with the HydroInert source and mostly restored with the HES source.

Pesticide/EI Source Type	RT, min	Helium Carrier Gas		Hydrogen Carrier Gas		
		Conventional EI Source	High Efficiency Source	Conventional EI Source	HydroInert EI Source	High Efficiency Source
Tecnazene	6.915	82	84	59	94	93
BHC alpha isomer	7.623	98	98	81	93	96
Dichloran	7.783	89	93	67	90	89
BHC beta isomer	8.019	97	97	77	92	96
Pentachloronitrobenzene	8.212	91	93	67	91	95
BHC delta isomer	8.502	90	94	74	87	94
Heptachlor	9.328	91	88	74	87	93
Malathion	9.742	90	90	56	84	76
Bromophos-ethyl	11.037	93	90	62	87	92
Prothiofos	11.510	95	94	65	92	91
Profenofos	11.561	91	87	66	90	85
Sulprofos	12.666	98	88	61	87	91
Edifenphos	12.953	92	94	59	92	77
Tebuconazole	13.292	93	92	66	89	76
Piperonyl butoxide	13.402	92	94	68	92	79

Calibration Performance in Spinach QuEChERS Extract

The developed 20-min GC/MS/MS analysis method employing HydroInert and HES sources was applied to analyzing 203 pesticides in spinach QuEChERS extract. The calibration results are summarized below. The blue (HydroInert) and green (HES) bars correspond to the number of compounds (out of 203) which had:



Conclusions

Pesticides can be analyzed with H_2 at or below MRLs

However, just like with He, some pesticides may be more challenging to analyze at low concentrations.

- Over 90% of targets could be quantitated at or below 10 ppb (mg/kg) in spinach extract, which is the default MRL
- Using the optimized GC conditions (injection, column set) and suitable MS EI source is essential when using H_2
- HydroInert source provides improved sensitivity compared to the conventional EI source and best spectral fidelity
- HES provides best sensitivity and good spectral fidelity.

References

[1]Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion. User Guide. 5994-2312EN. 2022.

[2]Five Keys to Unlock Maximum Performance in the Analysis of Over 200 Pesticides in Challenging Food Matrices by GC/MS/MS. 5994-4965EN. 2022.

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