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A Robust High-Throughput GC/MS/MS Analysis of 203 Pesticides in Fresh Produce Under 10 Minutes with Helium and Hydrogen Carrier Gasses

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Introduction

Growing demand for more rapid methods for analysis of chemical residues

There is a growing demand for more rapid methods for the identification and quantitation of chemical residues in food analysis without scarifying any robustness and chromatographic performance.

This work focuses on achieving fast GC/Triple Quadrupole MS (GC/TQ) analysis of over 200 pesticides, while maintaining robust system performance in a highly pigmented spinach matrix.

Common challenges with fast methods addressed in this work:

- New retention times were accurately predicted using the chromatography theory (no need to re-analyze hundreds of compounds)
- Chromatographic resolution was maintained compared to the conventional method
- Method robustness was achieved with the mid-column backflushing technique
- Two presented GC column configurations enable flexibility
- Compatibility with helium and hydrogen carrier gases.

Experimental

Mid-column backflush configurations for fast and robust analysis

Two column configurations used with the Agilent 8890/7000E and 8890/7010C GC/TQ are shown in Fig. 1.

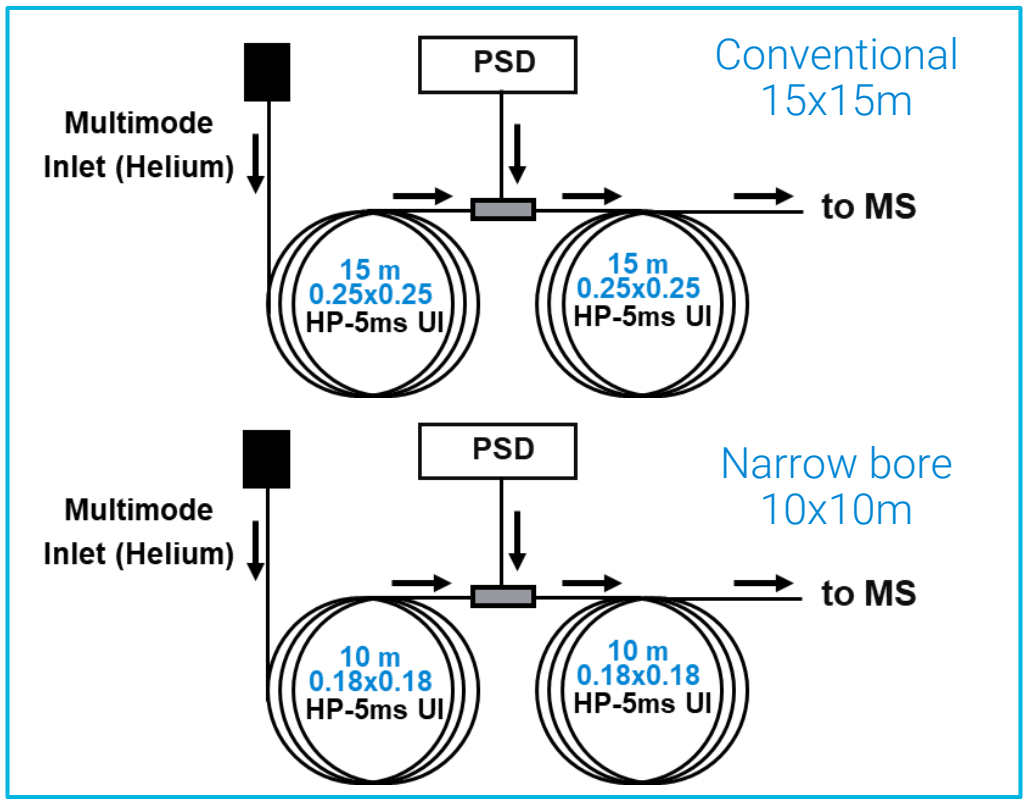


Figure 1. Two mid-column backflush configurations.

Results and Discussion

Maintaining chromatographic resolution of over 200 pesticides within 10 minutes

The presented 15x15m and 10x10m mid-column backflush configurations, enabled the 10-minute analysis for over 200 pesticides with three MRM transitions acquired per each compound.

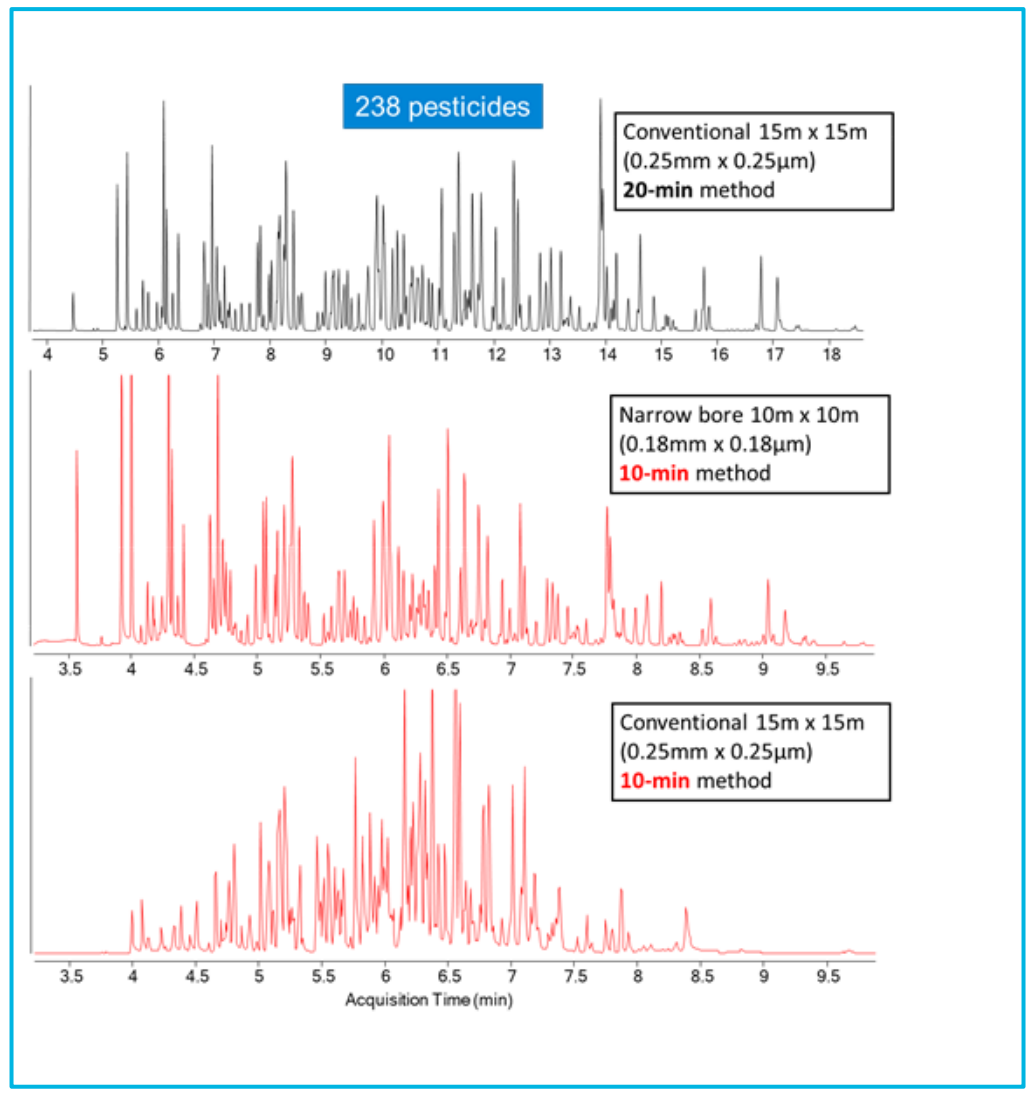


Figure 2. MRM total ion current chromatograms for a mixture of 238 pesticides acquired with the conventional 20-min method (top), fast 10-min method with the narrow bore configuration (middle), and fast 10-min method with the conventional 15x15m configuration (bottom).

Chromatographic resolution with the 10-min analysis:

- was completely preserved with the narrow bore 10x10m setup (Fig. 2, middle)
- largely maintained with the conventional 15x15m setup (Fig. 2, bottom)

The relative elution order of the compounds was preserved with the Agilent's GC Method Translation technique used for transferring the method to the 10x10m configuration

New retention times (RTs) were calculated using the following equation for the 10x10m configuration:

$RT_{new} = RT_{old} / 2 + 0.09$ minutes.

To update the RTs for the 10-min method with the conventional 15x15m configuration, a combination of pesticides and n-alkanes were used.

Sensitivity and calibration linearity with the fast 10-minute analysis

Sensitivity of the analysis achieved with the new 10-min method was comparable to that observed with the conventional 20-min analysis. Both new 10-minute methods with the 15x15m and the 10x10m column configurations allowed for detecting even the most challenging pesticides below their established MRLs. For example, deltamethrin, a challenging compound for GC/MS, was shown to be accurately quantitated in the highly pigmented spinach matrix down to 0.1 ppb.

The majority of 203 target compounds demonstrated linear calibration over a wide range of either 0.1-1,000 ppb or 0.5-1,000 ppb with the 10-minute method enabling their reliable quantitation at the varying MRLs.

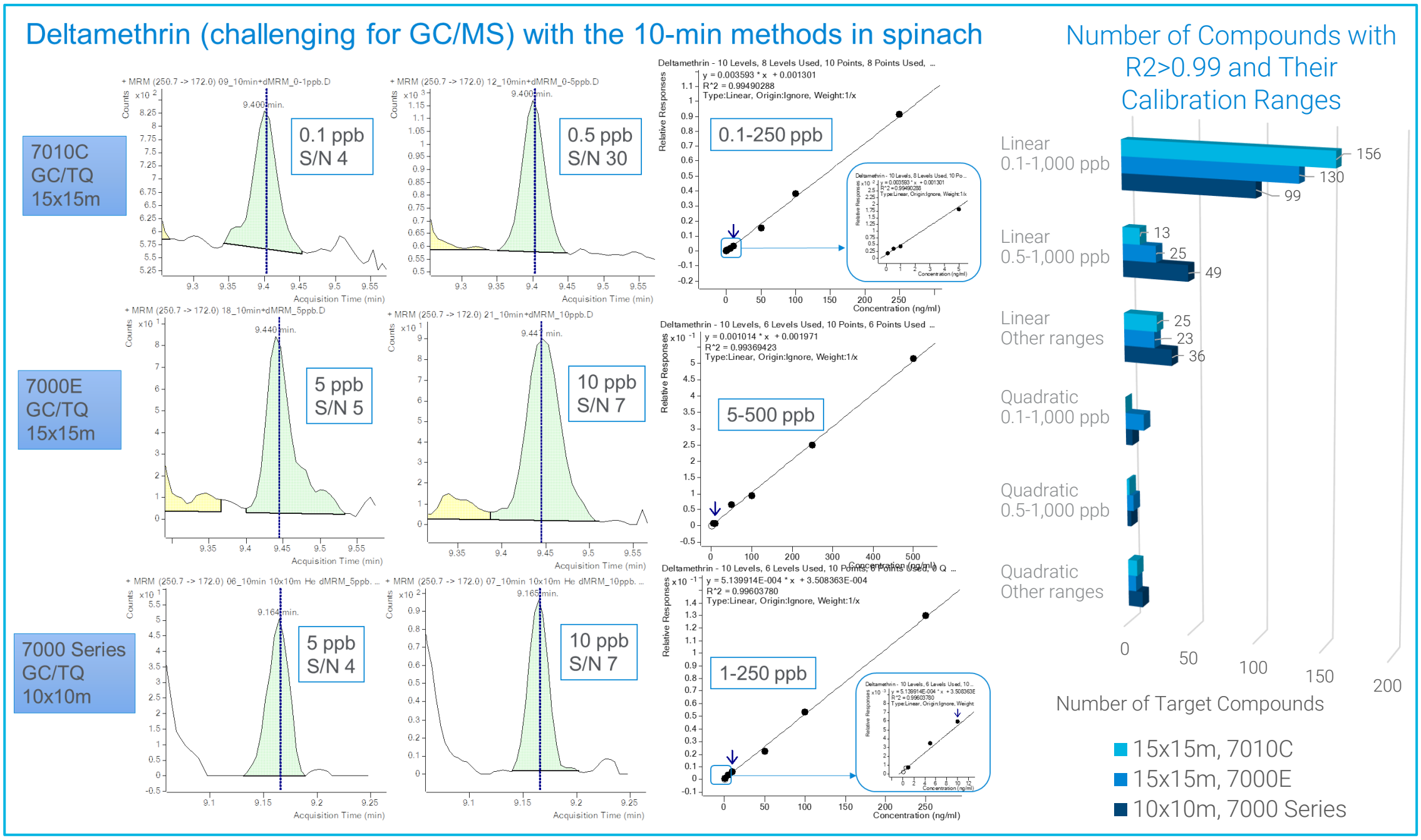


Figure 3. MRM chromatograms and matrix-matched calibration curves in spinach extract for deltamethrin (left) and the calibration performance for the 203 pesticides with the fast 10-minute methods in spinach (right).

Method robustness with 700 injections of a spinach extract

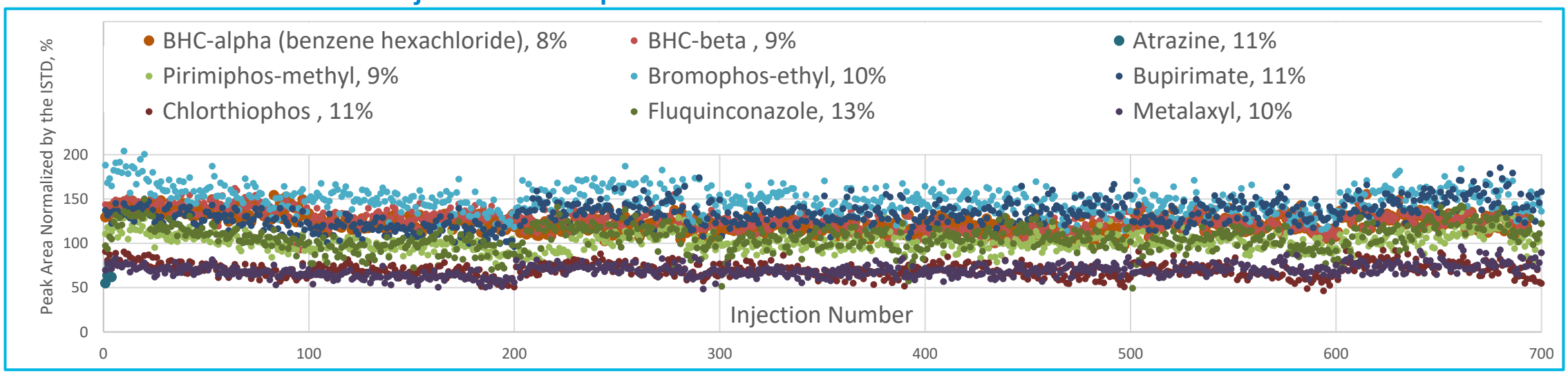


Figure 4. Stability of the peak area for pesticides spiked at 20 ppb into spinach extract normalized by the ISTD over 700 consecutive injections with the 10-min analysis using the conventional 15x15m column configuration.

Results and Discussion

Method robustness with 700 injections of a spinach extract

The robustness of the 10-minute analysis was demonstrated by:

- analyzing a challenging, highly pigmented spinach extract spiked with target pesticides at 20 ppb
- demonstrating the stability of the target compound responses normalized by the internal standards (ISTD) over 700 consecutive injections (Fig. 4)
- limiting maintenance procedure to septum and liner replacement every 100 injections.
  There was no need to perform inlet cleaning, GC column trimming or MS source cleaning or re-tuning.

Fast pesticide analysis with hydrogen carrier gas

- The analysis times of 8 and 10 minutes were achieved with the narrow bore 10x10m configuration when using hydrogen carrier gas.
- The RTs observed with the 10-min with hydrogen carrier gas were the same as the RTs observed with the 10-min method with helium.
- New RTs observed with the 8-min method with hydrogen were calculated based on the retention times for the conventional 20-minute method using the following equation:

  $RT_{new} = RT_{old} / 2.5 + 0.06$ minutes.

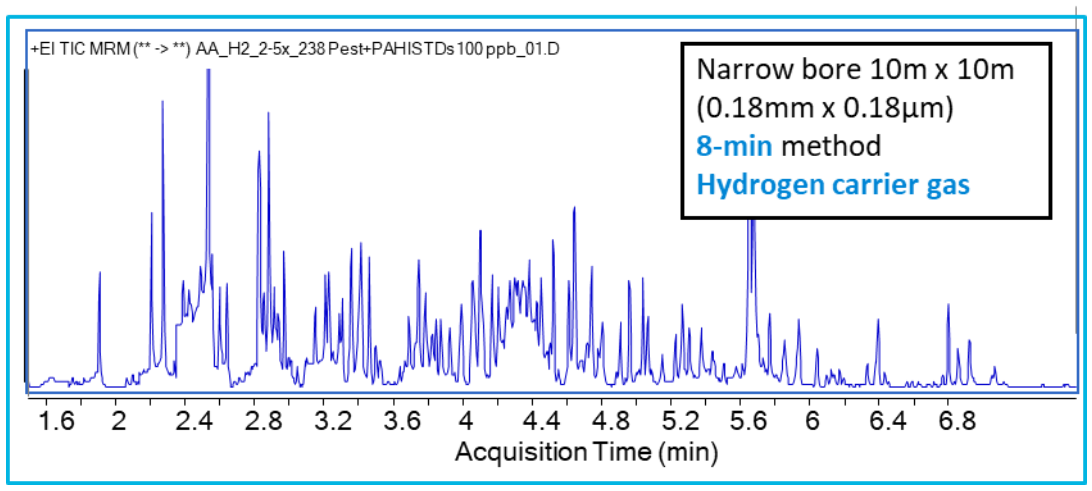


Figure 5. MRM TIC for a mixture of 238 pesticides acquired with the fast 8-min method with the 10x10m configuration using hydrogen carrier gas.

Maintaining spectral fidelity with the novel EI source with hydrogen carrier gas

A common problem when using hydrogen carrier gas in GC/MS is overcoming undesired in-source reactions between target analytes and reactive hydrogen gas.

The novel HydroInert EI source allows for maintaining spectral fidelity even for compounds highly susceptible to reacting with hydrogen

Pesticide analysis with hydrogen carrier gas with the novel HydroInert source

Figure 6 demonstrates that the novel HydroInert source prevented the undesired de-chlorination of heptachlor when compared to the conventional EI source.

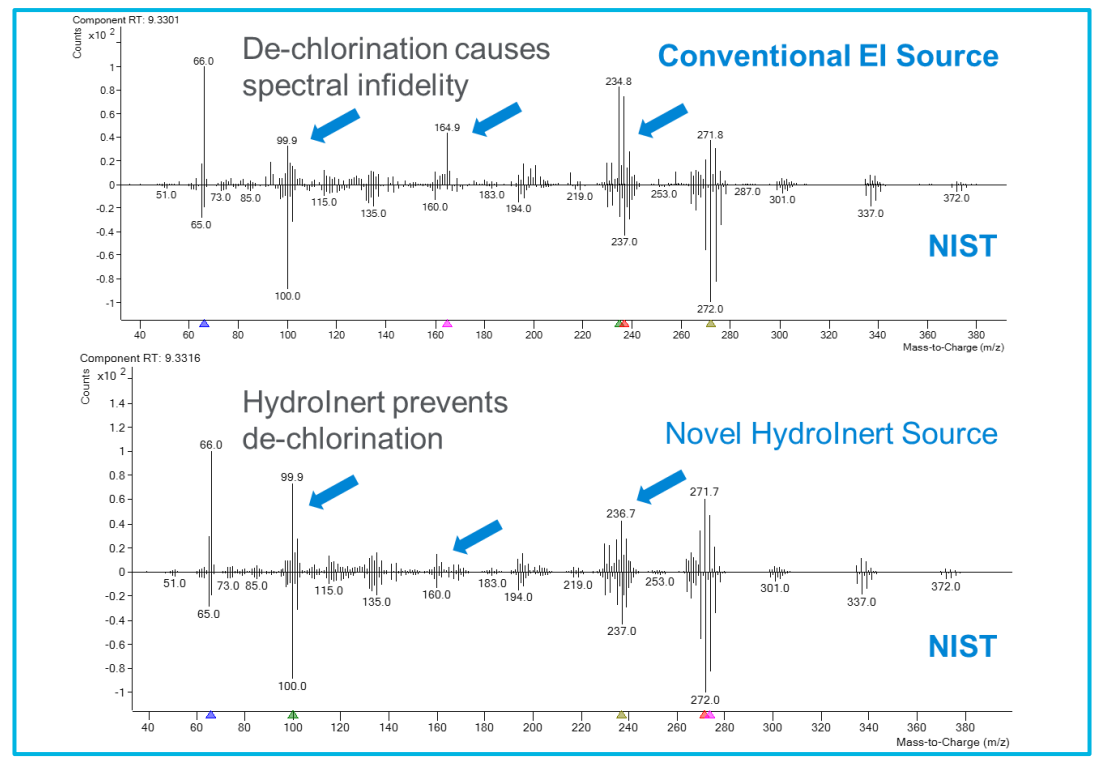
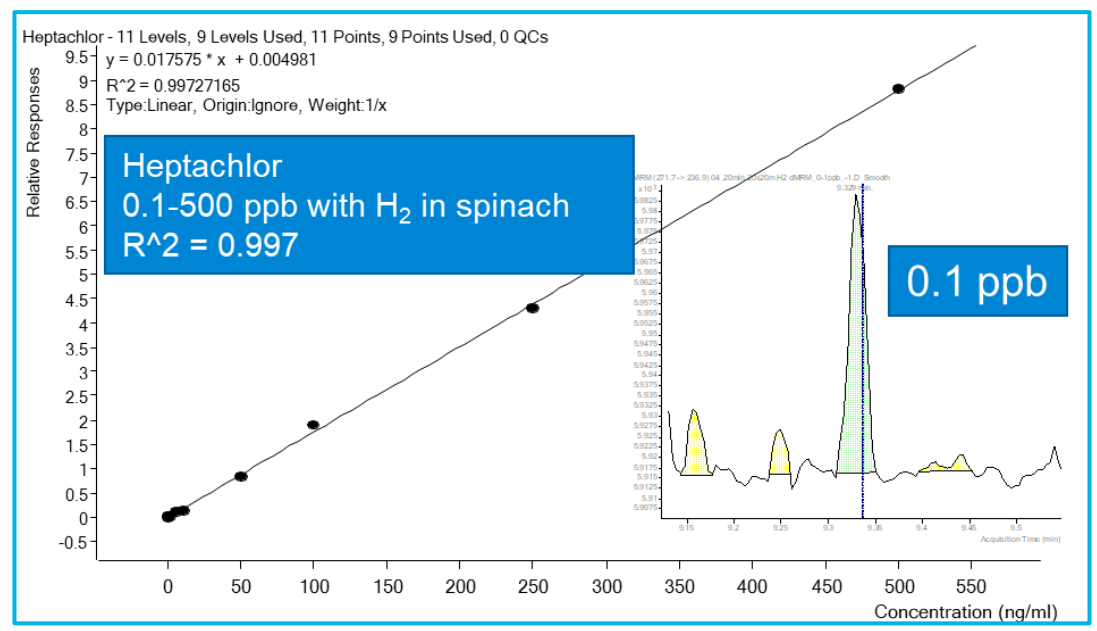


Figure 6. Mass spectra for heptachlor with hydrogen carrier gas

Heptachlor was accurately quantitated in spinach extract over a wide concentration range of 0.1-500 ppb with hydrogen carrier gas using the HydroInert source (Fig. 7).



Conclusions

- A fast and robust analysis of 203 pesticides in under 10 minutes was achieved with helium and hydrogen carrier gasses.
- Two mid-column backflush configurations enabled robust method performance without sacrificing chromatographic resolution, method sensitivity, and linearity.
- The novel HydroInert source enabled spectral fidelity and performance comparable to that observed with helium when using hydrogen carrier gas.

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