Optimized Strategies for Gas Chromatography and Mass Spectroscopy Analyses of Contaminants in Water, Soil, and Range of Food Samples to Ensure Safety and Sustainability

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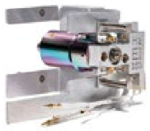

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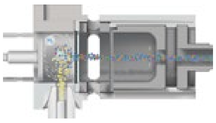

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Enable direct analysis of powders, tablets, food samples, and liquids with minimal-to-no sample preparation.

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Midcolumn backflushing extends the maintenance-free operation of the advanced GC/MS system.

Optimized Strategies for Gas Chromatography and Mass Spectroscopy Analyses of Contaminants in Water, Soil, and Range of Food Samples to Ensure Safety and Sustainability

Adapted from: Staying Ahead in a Rapidly Changing World with GC/MS Solutions: Application Compendium

Introduction

Increased scrutiny of the world's water, food, and soil resources leads to tighter regulation which warrants improved detection methods of potential contaminants to ensure safety and sustainability. Analytical labs detect contaminants using established gas chromatography/mass spectroscopy (GC/MS) methods. Challenges such as insufficient helium (He) supplies and challenging matrices coupled with higher analytical demand require new approaches.

This digest provides four sections on detailed GC/MS methods with instruments and parameter settings for substituting H_2 carrier gas with the HydroInert source for helium carrier gas. The analyses show mass spectral fidelity, a wide calibration range, and adherence to the US Environmental Protection Agency (EPA) method 8270 calibration criteria for the identification/measurement of over a hundred compounds in soil mixtures and water. The second four sections of the digest describe optimized methods for identifying and quantifying pesticides in challenging food matrices with several GC/MS configurations and extensive details on sample extraction and cleanup, comparison of dynamic multiple reaction monitoring (dMRM) data acquisition mode versus dual simultaneous dMRM/scan data acquisition modes, procedures for preventing leaks in GC/MS and GC/TQ systems, and documentation for reproducibility of recovery of spiked samples in challenging matrices. Table 1 summarizes the instruments, attachments, software, and run times (7–20 min).

Instrument/Compounds	**SVOCs**	**SVOCs**	**VOCs**	**SVOCs**	**Pesticides**	**Pesticides**	**Pesticides**	**Pesticides**
Matrix	Composite mixture of soils		Drinking water	Water, tap water	Spinach, walnuts, cayenne pepper	Spinach, walnuts, cayenne pepper	Spinach	Kale
Gas chromatography								
Agilent 5977 GC	✓		✓					
Agilent 8890 GC		✓	✓	✓	✓	✓	✓	✓
Split/splitless inlet	Pulsed split 10:1		Pulsed split 21:1	Pulsed split 5:1	Splitless	Splitless	Splitless	Splitless
Headspace sampler			Agilent 8697					
Liquid sampler		autosampler		7693A	7693A	7693A	7693A	7693A
Multimode inlet (MMI)		✓		Agilent 8890	✓	✓	✓	✓
Inset liner								
Ultra Inert inlet liner	✓	✓	✓	✓	✓	✓	✓	NR
Glass wool	✓	✓	NR	✓				
Midcolumn backflush with purged Ultimate union, & pneumatic switching device					✓	✓	✓	✓
Column	20 m × 0.18 mm, 0.36 µm	20 m × 0.18 mm, 0.18 µm	20 m × 0.18 mm, 1 µm	30 m × 0.25 mm, 0.25 µm	Two 15 m x 0.25mm x 0.25 µm	Two 15 m x 0.25mm x 0.25 µm	Two 15 m x 0.25mm x 0.25 µm	Two 15 m × 0.25 mm x 0.25 µm
Mass spectrometry								
Agilent 5977B Inert Plus GC/MS	✓		✓					
Agilent 5977C Inert Plus GC/MS			✓					
Agilent MS 7000E		✓		✓	✓	✓	✓	
Agilent MS 7010C					✓	✓	✓	✓
Quadrupole	Single	Triple	NR	Triple	Triple	Triple	Triple	Triple
Source								
Helium				✓	✓	✓	✓	✓
H_2 carrier gas & HydroInert **with 9mm HydroInert extraction lens**	✓	✓	✓					
Tuning criteria								
EPA methods 8270D/E	✓	✓	NR	✓	NR	NR	NR	NR
Initial calibration criteria (# levels)	13	15	8	11	11	11	10	NR
Software								
Multiple reaction monitoring (MRM) mode								✓
dynamic MRM (dMRM) mode		✓		✓	✓		✓	
dMRM/scan modes					✓	✓		
MassHunter workstation							✓	✓
MassHunter pesticides & environmental pollutants MRM database							✓	
Run time	NR	11.3 min	7 min		20 min	20 min	10 min	20 min

Table 1. Summary of instruments used for measuring/identifying the indicated compounds. NR, not reported; SVOCs, semivolatile organic compounds

H_2 Carrier Gas Usage With HydroInert in GC/MS

Adapted from an article by Henry, A.S.

The instruments (Table 1, column 1), conditions, and a list of consumables are described for the optimized method with GC/MS analyses of semivolatile organic compounds (SVOCs) in composite mixtures of soils using hydrogen (H_2) carrier gas with HydroInert. Comparison of GC/MSD (mass spectrometer detector) analyses of nitrobenzene with and without the HydroInert EI source showed that HydroInert prevents hydrogenation of target analytes (Fig.1). Methods with HydroInert for meeting the decafluorotriphenylphosphine (DFTPP) tuning criteria and the initial calibration of the concentration range are detailed. The optimized GC and MSD method for the Agilent 5977C and 5977B Inert Plus GC/MSD met the EPA method 8270D/E guidelines for various parameters including scan range (0.1 to 100 µg/mL) and scan rate. Of 96 previously tested SVOCs, 84% exhibited the full sensitivity range. Concentration ranges of six of 120 compounds required linear fits and ten compounds required quadratic fits. The resolution of three isomer pairs was greater than 50%. This optimized 12-min method using HydroInert met the criteria of EPA guidelines including the EPA method 8270 criteria and retained the mass spectral fidelity, which provided breakthroughs for the use of H_2 carrier gas.

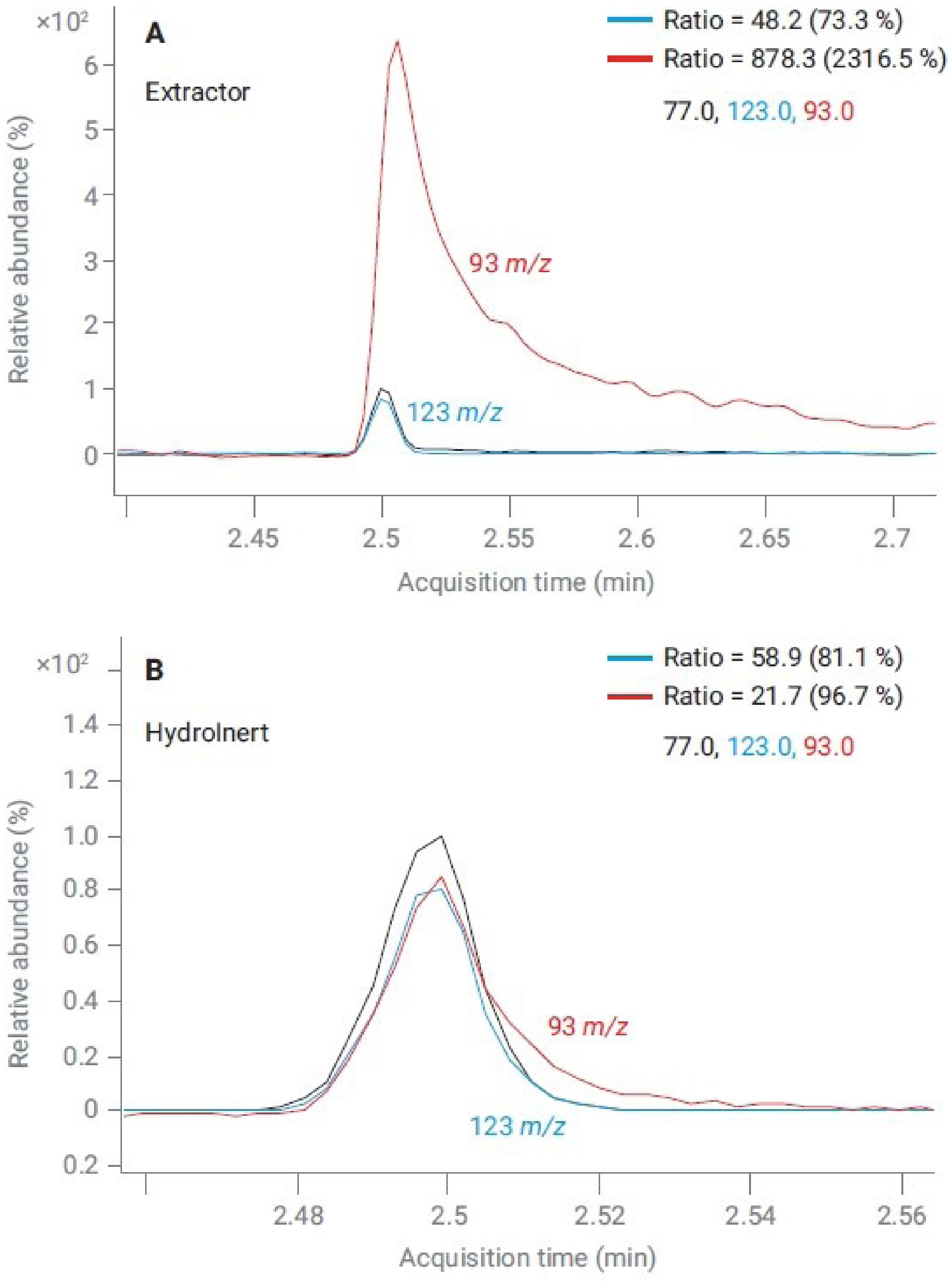

Figure 1. Extracted ion chromatographs (EICs) of nitrobenzene by GC/MS with H_2 carrier gas.
(A) InertPlus Extractor does not prevent hydrogenation of nitrobenzene to aniline (abundant 93m/z ion);
(B) HydroInert prevents nitrobenzene's efficient hydrogenation to aniline for reduced tailing and improvement to the ion ratios.

Analysis of Semivolatile Organic Compounds with H_2 Carrier Gas and HydroInert by Gas Chromatography–Triple Quadrupole Mass Spectroscopy (GC–MS/MS; GC/TQ)

Adapted from an article by Henry, A.S.

GC/MS/MS can often detect lower concentrations than GC/MS, extending the range to 0.2 µg/mL. The use of the Agilent HydroInert source reduces H_2 carrier-gas-induced dechlorination and hydrogenation reactions and supports the analysis of many target compounds across a wide calibration range (0.02 to 100 µg/mL). An optimized 12-min method using H_2 carrier gas using HydroInert with the GC/TQ system meets EPA method 8270 guidelines. The detailed methods include instrumentation, consumables, and instrument conditions (e.g., Table 1, column 2, temperature program for MMI and column; temperatures for transfer line, ion source, and quadrupole; nitrogen collision gas at 1.5 mL/min). The GC/TQ tuning process which used the DFTPP ion ratio criteria showed that the values of DDT breakdown and tailing factors were within the EPA method 8270 criteria. The calibration data of 120 compounds showed that 92.5% met the range of 0.1 to 100 µg/mL of the EPA method 8270. The calibration curves of ten compounds required quadratic fits and six compounds needed linear fits. Resolutions of three isomer pairs ranged from resolved at baseline to >50% resolved (Fig. 2). Usage of HydroInert source with H_2 carrier gas also allows users to retain MRM transitions used with He systems, thereby reducing development work. Mass spectral fidelity is retained.

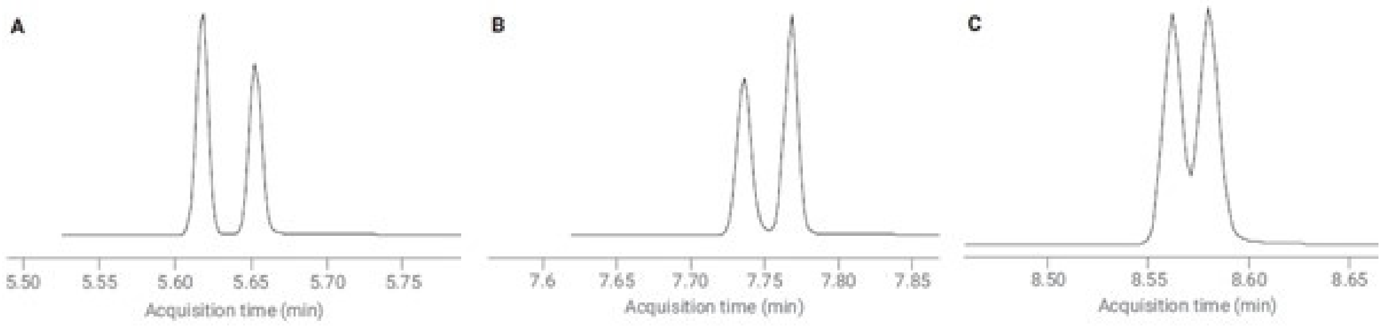

Figure 2. EICs for multiple reaction monitoring (MRM) transitions for critical isomer pairs. (A) phenanthrene and anthracene (178.1➛152.1 m/z); (B) benz[a]anthracene and chrysene (228.1➛226.1 m/z); (C) benzo(b)fluoranthene and benzo(k) fluoranthene (252.1➛250.1 m/z).

Volatile Organic Compounds Analysis in Drinking Water with Headspace GC/MSD using H_2 Carrier Gas and HydroInert

Adapted from an article by Quimby, B.D. and Andrianova, A.A.

In comparison to He in GC/MSD systems, H_2 as the carrier gas can provide faster chromatographic speed and improved resolution. However, H_2 as a reactive gas can disturb ion ratios within the mass spectrum, and induce peak tailing, spectral infidelity, and nonlinear calibration. The GC/MSD (Table 1, column 3) was used to develop, evaluate, and optimize the separation method for spiked 80 volatile organic compounds (VOC) in drinking water in H_2 carrier gas with the HydroInert source. The results of the scan mode method demonstrated excellent calibration linearity, an average range of 0.16 to 25 µg/L, and excellent spectral matching against the NIST20 library. The results of the evaluation of the selective ion monitoring (SIM) mode demonstrated excellent calibration linearity: the average method detection limit (MDL) for the 80 compounds was 0.026 µg/L. Their average range went from 0.07 to 25 µg/L. Two municipal tap water samples were analyzed with this 7-min method using HydroInert and H_2 carrier gas (Fig. 3). Note that a lower analyte concentration reduces the signal-to-noise ratio and 0.1 µg/L was listed as the lower limit. SIM data with its precise retention time (RT) matching can be used at lower concentrations.

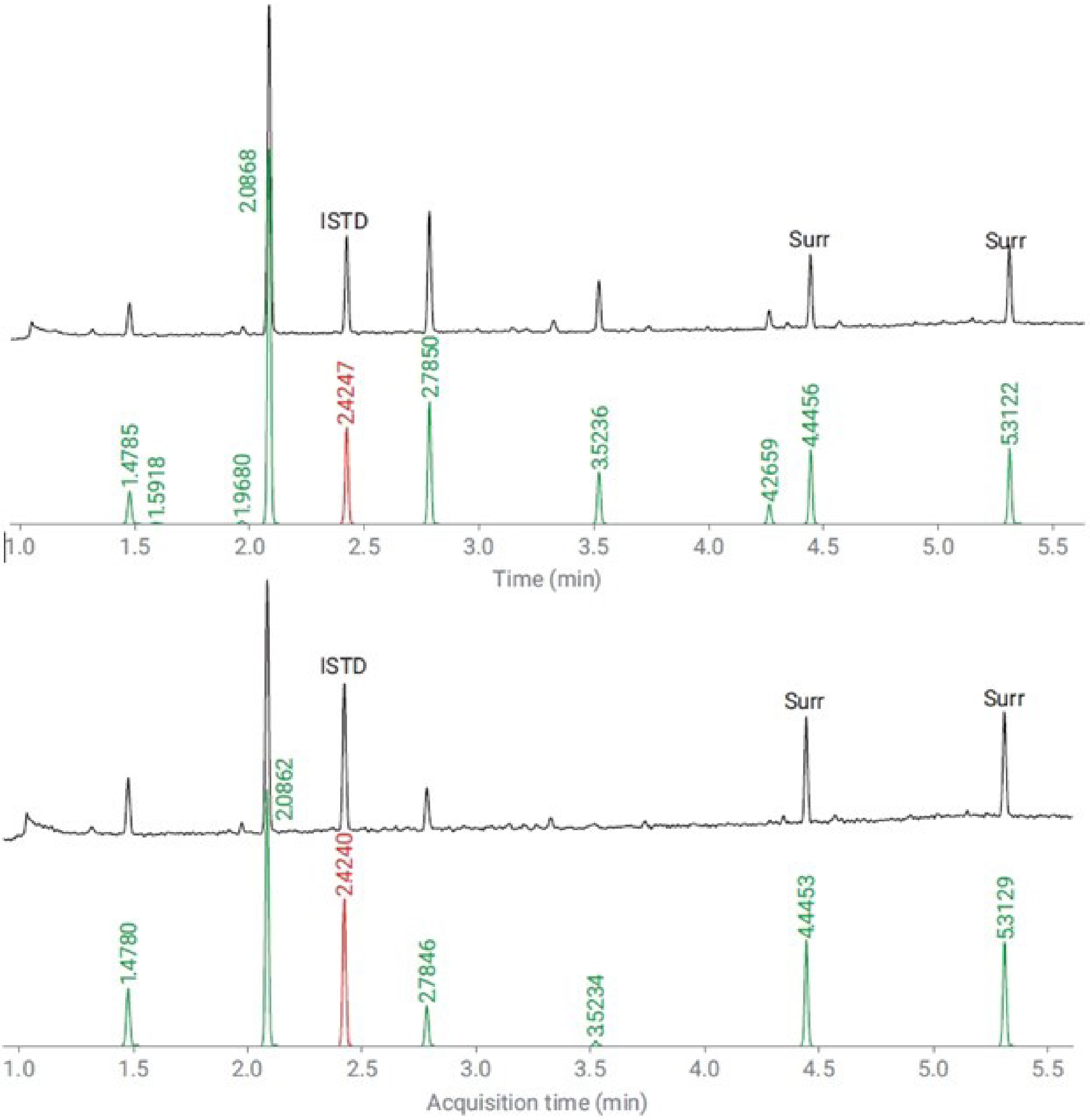

Figure 3. Total ion current (TIC) (black) and deconvolution (green) chromatographs of tap water samples. Top: Eastern Pennsylvania; Bottom: Eastern Pennsylvania tap water sample. Both samples showed evidence for trichloromethane (RT 2.087), bromodichloromethane (RT 2.785), and dibromochloromethane (RT 3.524).

Analysis of Semivolatile Organic Compounds with US EPA 8270E using the Agilent 7000E Triple Quadrupole GC/MS (GC/TQ)

Adapted from an article by Fausett, E., Ciotti, R., and Walker, D.

A sensitive method is described for analyzing SVOCs with a GC/TQ (Table 1, column 4). The MRM acquisition mode on GC/TQ offers excellent selectivity, leading to several benefits such as quicker batch reviews, fewer complications with matrix interferences, and improved sensitivity that allows for the use of smaller sample volumes. This GC/TQ system can detect low levels of SVOCs, maintain excellent dynamic range, and meet laboratory needs for analysis of solid samples, surface, and groundwater samples in 16.9 min (Fig. 4). The success of the method increased with the following techniques: (1) GC/TQ provided greater sensitivity and increased selectivity which simplified data reduction; (2) The pulsed split injection (5:1 ratio) improved sensitivity and maintained advantages of split injection; (3) The 9 mm extractor lens increased linearity and overall performance for difficult analytes; (4) RT locking maintained relevant peaks despite column trimming and drift from MRM analysis; (5) Dynamic MRM analysis mode simplified the process of removing and adding analytes and decreased the number of simultaneously monitored transitions. Calibration of 69 of 74 analytes used an average response factor (RF) fit with a relative standard deviation (RSD) ≤20%, in line with the EPA 8270E criteria. Regarding SVOC analysis, GC/TQ offers four significant advantages compared to the single quadrupole GC/MSD. First, higher selectivity reduces matrix interferences and data complexity, thereby supporting faster batch review. Second, increased sensitivity allows the use of smaller sample sizes and extraction volumes which in turn reduce waste, improve sustainability, and decrease costs for sample transport, solvent, and waste disposal. Third, dynamic MRM improves instrument performance by reducing the number of individual MRM transitions. Fourth, the tuning verification on the GC/TQ can follow the Manufacturer's Recommended Tune to replace any DFTPP tune checks for mass accuracy and resolution.

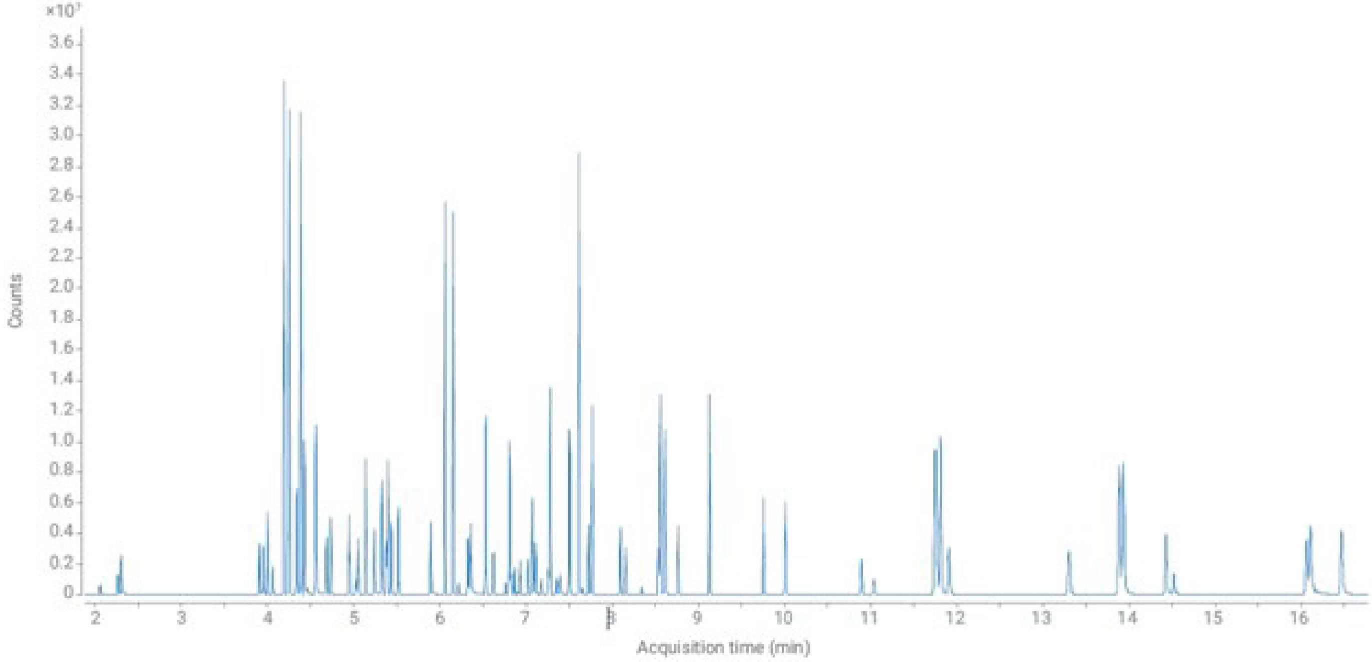

Figure 4. Separation of all dMRM transitions on TIC from composite in 16.9 minutes.

Five Keys to Unlock Maximum Performance in the Analysis of Over 200 Pesticides in Challenging Food Matrices by GC/MS/MS

Adapted from an article by Andrianova, A.A. and Zhao, L.

The US EPA sets tolerances for each pesticide for a given food. The GC/MS/MS (GC/TQ) systems (Table 1, column 5) can provide rapid and reliable identification and quantification of trace levels of chemical pollutants. The maximum residue limit (MRL) for specific pesticides on a given food can vary widely, requiring a broad dynamic range. For example, MRLs for spinach range from 60,000 ppb for boscalid to only 10 ppb for fludioxonil. Five key components support successful pesticide analysis. First, effective sample extraction and matrix cleanup (Captiva EMR pass-through cleanup for the relevant sample type) maintain high pesticide recoveries and reduce matrix background and their interferences. Second, matrix evaluation in full scan data acquisition mode with a high-efficiency source can ensure efficient performance. Third, midcolumn backflushing minimizes column trimming and source cleaning, reduces analysis time, and extends maintenance-free operation. Fourth, the use of temperature-programmed MMI ensures even thermally stable compounds are volatilized. Fifth, a leak-free GC/TQ system using the self-tightening collared columns, capillary flow technology gold-plated flexible metal ferules, and monitoring supports a maintenance-free and reliable MS performance with longer GC column life. The calibration performance of the 8890/7000E and 8890/7010C GC/TQ systems for 203 pesticides in spinach, walnut, and cayenne pepper shows linear fits ($R^2>0.99$) for most compounds at 0.1 to 5000 μg/L and 0.1 to 0.1000μg/L, respectively (Fig. 5).

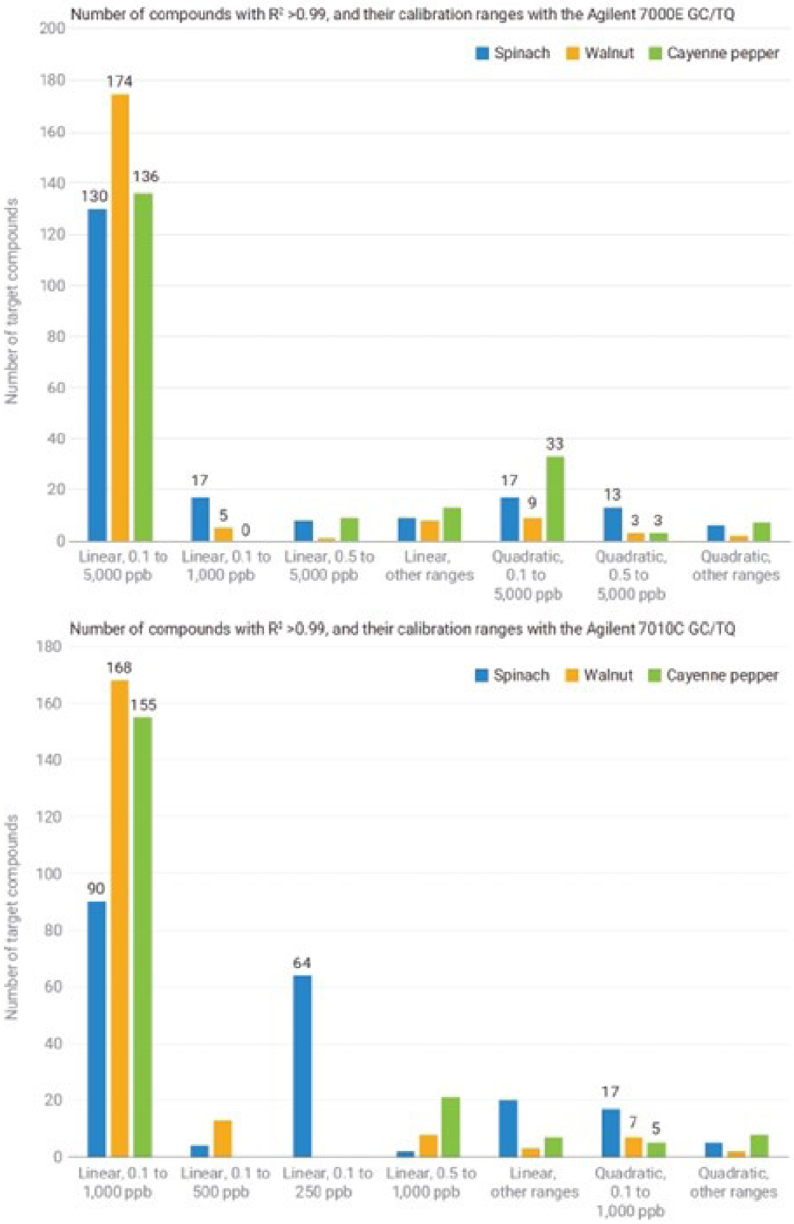

Figure 5. Calibration performance for the 203 pesticides in spinach, walnut, and cayenne pepper with the 8890/7000E (top) and 8890/7010C GC/TQ (bottom) systems.

Dynamic MRM/Scan Mode: Adding More Confidence to Sensitive Quantitation in Complex Foods by GC/TQ

Adapted from an article by Andrianova, A.A., Quimby, B.D., and Zhao, L.

Concerns about pesticides and food contaminants drive the demand for reliable, robust, and rapid methods for identifying and quantifying contaminants and chemical residues in food matrices. Approaches that combine screening and analysis for licensed chemical residues and unknown contaminants would improve efficiency. The described GC/TQ system (Table 1, column 6) in the simultaneous dMRM/scan data acquisition modes provides retrospective analysis for identifying unknowns and target compounds with excellent quantitative performance comparable to dMRM mode. The full scan from one analytical run evaluates the matrix in full scan and supports retrospective analysis and identification of regulated pesticides in food. It can confirm targets and unknowns with library match scores (LMS). From the same analytical run, the dMRM data can confirm targets with RT, qualifiers, and quantifiers; and secondly, dMRM data quantify targets with a highly sensitive dynamic range (e.g., bifenthrin in Fig. 6, chlorpyrifos, metolachlor in cayenne pepper). Of the 203 pesticides analyzed in spinach, walnuts, and cayenne pepper, the calibration ranges of 67% to 79% of compounds analyzed on an 8890/7000E GC/TQ system in dMRM/scan mode exhibited excellent linearity ($R^2>99\%$) for 0.1 to 5000 ppb. Likewise, the calibration ranges procured with the 8890/7010C GC/TQ in dMRM/scan modes for 72% to 81% of compounds exhibited excellent linearity ($R^2>99\%$) for 0.1 to 1000 ppb. Simultaneous dMRM/scan mode provides an attractive tool for compound identification and reliable quantitation in one run.

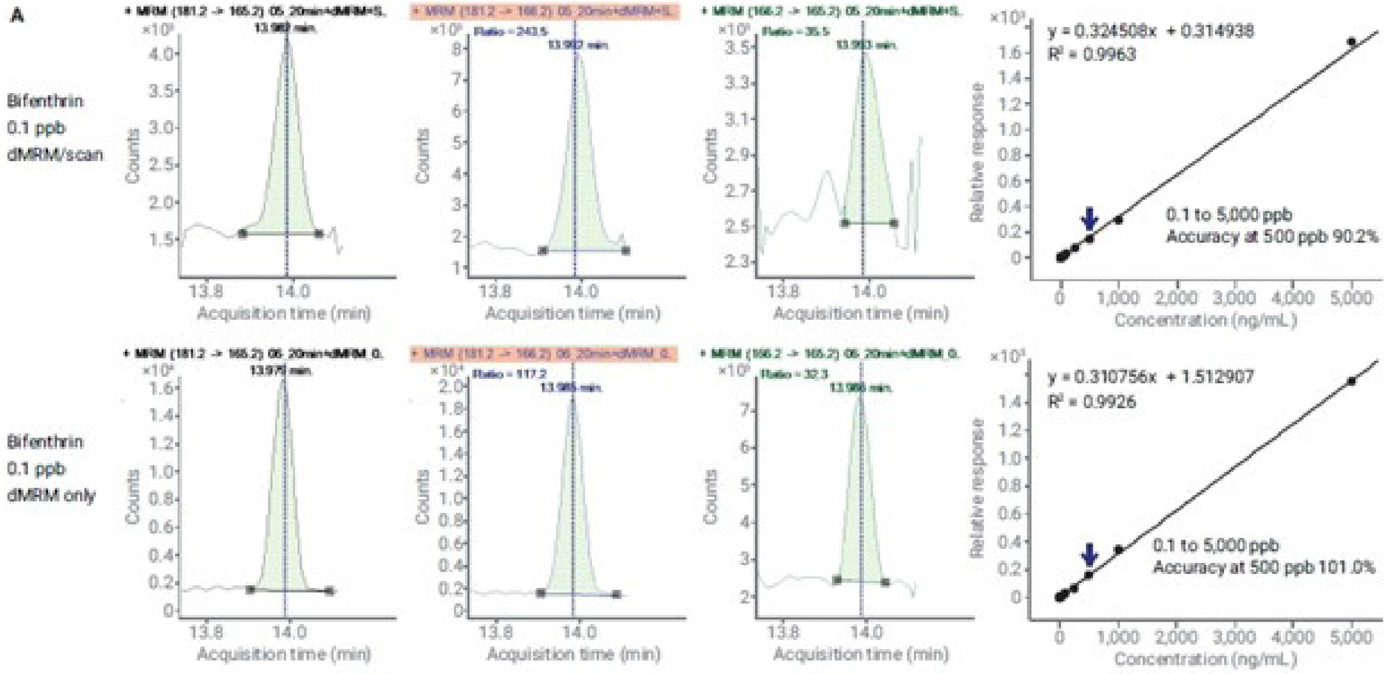

Figure 6. The Agilent 8890/7000E GC/TQ provided quantifier and qualifier ion profiles for bifenthrin spiked at 100 ppb in cayenne pepper. Matrix-matched calibration curves ranged from 0.1 to 5000 ppb. Top row: Data acquisition mode was dMRM/scan; Bottom row: Data acquisition mode was dMRM only.

A Fast and Robust GC/MS/MS Analysis of 203 Pesticides in 10 Minutes in Spinach

Adapted from an article by Andrianova, A.A., Quimby, B.D., and Zhao, L.

Spinach is a challenging, high chlorophyll matrix. Two approaches with GC/MS/MS (Table 1, column 7) achieved robust, multi-residue pesticide analysis with sufficient chromatographic resolution to identify and quantify 200 pesticides in spinach in a 10-minute run time. Both GC/TQ approaches (Table 1, column 7) used midcolumn backflushing which minimized column trimming and supported more efficient liner change and source cleaning, thereby extending maintenance-free operation and increasing method robustness. The first approach used the traditional (15 m x 0.25mm x 0.25 mm) backflush configuration with an accelerated oven ramp. The second approach used a minibore 10 m (0.18 x 0.18 mm) midcolumn backflush configuration with a GC oven insert (pillow). Sample preparation included sample extraction with QuEChERS followed by spinach matrix cleanup with Captiva EMR–High Chlorophyll Fresh with NH_2. Results showed that both approaches yielded excellent linearity (R^2>0.99) over a calibration dynamic range of 0.1 to 1000 ppb or 0.5 to 1000 ppb for 73% to 83% of 203 compounds. The results demonstrated the robustness and reproducibility of the 10-minute analysis by monitoring the area of nine analytes over 700 consecutive injections: the responses remained consistent over 175 hours of continuous running (Fig. 7).

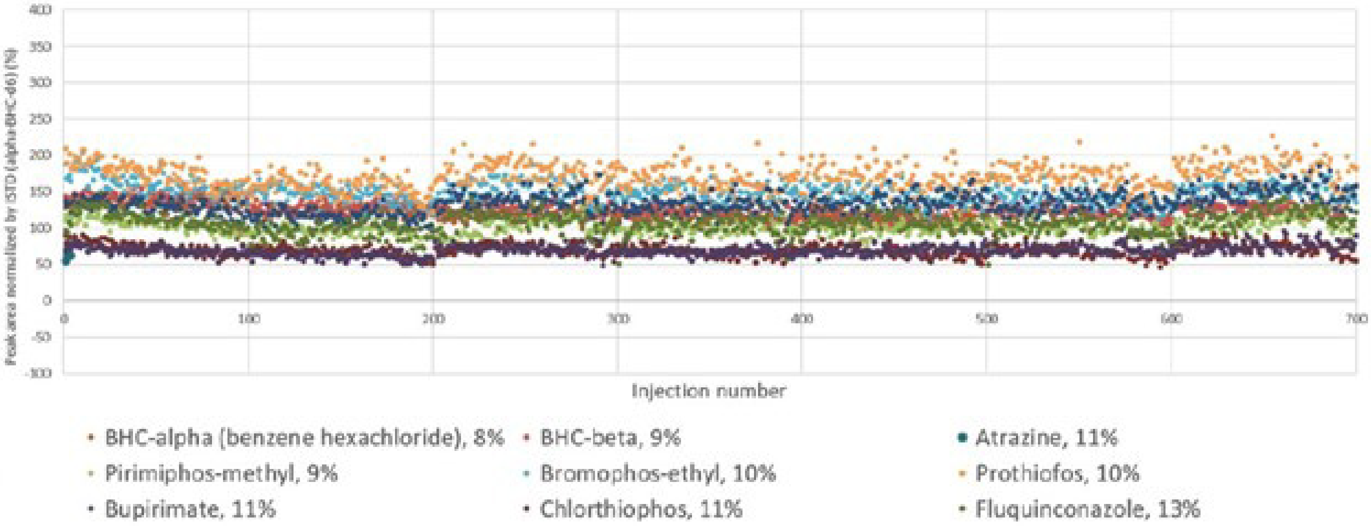

Figure 7. Stability of the peak area for nine pesticides analyzed by GC/MS/MS over 700 consecutive injections in sequential 10-min runs. The nine pesticides were spiked at 20 ppb into spinach extract. The extracted and cleaned samples were analyzed by Agilent 8890C/7000E triple quadrupole GC/TQ using the midcolumn backflushing procedure for the 15 m column configuration.

Analysis of Pesticides in Kale Using the Agilent 7010C Triple Quadrupole GC/MS with Agilent Bond Elut QuEChERS High Pigment dSPE with Carbon S Cleanup

Adapted from an article by Westland, J. and Andrianova, A.A.

Today's regulated environment of the food supply chain suggests analytical testing at every step for safety and quality. The Agilent 8890E/7010C triple quadrupole GC/MS delivers high-throughput routine monitoring, with sensitive detection levels and quantitative analysis for hundreds of pesticides in a single 20-min run. The parameters for Agilent GC/TQ are described in Table 1, column 9. An industry standard for pesticide extraction and cleanup on foods is the QuEChERS method followed by the Agilent Captiva EMR pass-through cleanup. The percent recovery and percent RSD for 150 pesticides spiked at 24 ppb into organic kale were investigated. Calibration analysis of matrix-matched pesticides in organic kale matrix by the GC/MS system indicated 98.6% of pesticides had recoveries between 130% and 70% (e.g., Fig. 8). Relative standard deviations (RSDs; n=6) of 99.3% of the pesticides' recoveries were <25%, confirming the precision and accuracy of the analyses.

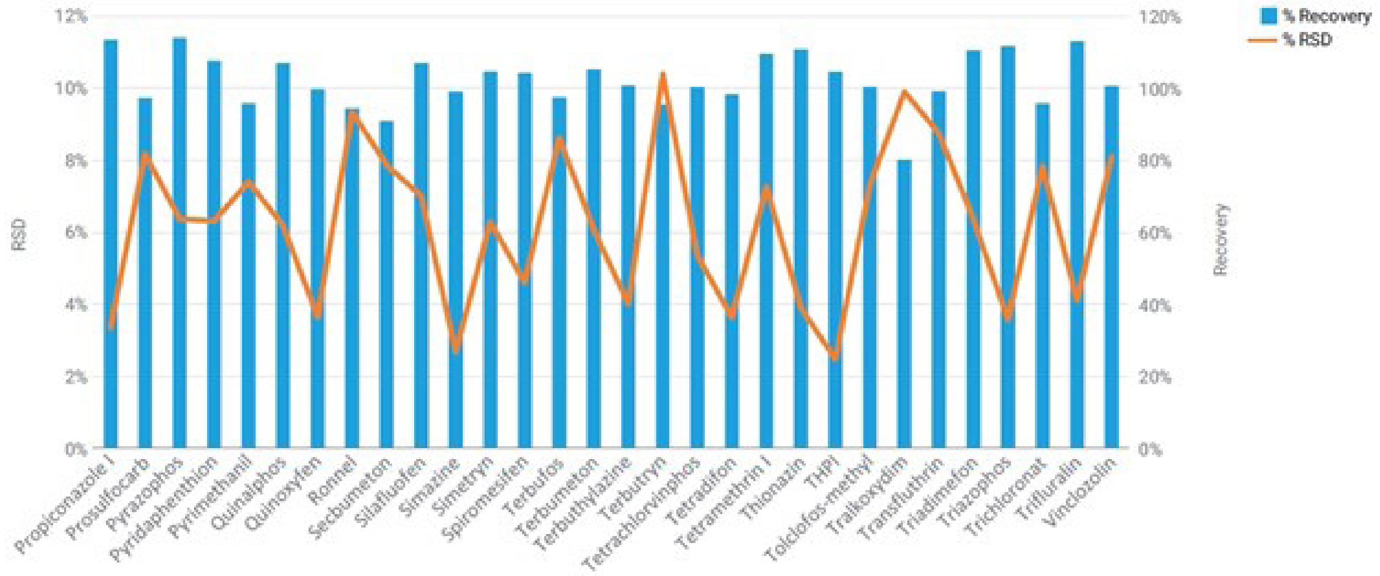

Figure 8. Percent recovery and percent RSD of the indicated pesticides spiked at 24 ppb into organic kale. Studies (n=6) were performed using an Agilent 8890/7010C GC/TQ system configured with automatic liquid sampler, MMI, midcolumn backflushing equipment, MassHunter workstation software.