Application Note

Food & Beverage Testing

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

Authors

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Abstract

This application note describes five best practices to enhance analytical performance in the analysis of over 200 pesticides in challenging matrices including spinach, walnut, and cayenne pepper. The novel Agilent Captiva EMR passthrough cleanup procedure following the Agilent QuEChERS extraction enabled a cleaner matrix background. The cleanup and extraction reduced matrix interferences with target analytes and extended the maintenance-free operation time of the instrument. Calibration performance was demonstrated over a wide dynamic range to over four orders of magnitude. It was shown that the Agilent 8890/7000E triple quadrupole GC/MS system achieved excellent linearity over a concentration range of 0.1 to 5,000 ppb. The Agilent 8890/7010C triple quadrupole GC/MS system demonstrated superior sensitivity yielding a higher signal-to-noise ratio at lower concentrations.

Introduction

The global agriculture industry uses over a thousand different pesticides in the production of food. Producers require pesticides to meet the increasing demand for reasonably priced food. This growing demand has increased the use of pesticides and encouraged problematic agricultural practices that have elevated risks in the food supply and the environment. Concerns about trace level chemical pollutants in food are driving the demand for more rapid and reliable methods for the identification and quantitation of chemical residues. The Agilent 8890/7000E and 8890/7010C triple quadrupole GC/MS systems (GC/TQ) are ideally suited to meet this need.

The US Environmental Protection Agency (EPA) sets tolerances as part of the food safety equation.[1] The tolerance corresponds to the maximum residue limit (MRL), which is the maximal level of pesticide residue allowed to remain in or on the treated food commodity. The MRLs may vary over a broad concentration range depending on different pesticides and food commodities. For example, the MRLs established for 68 pesticides regulated in spinach vary from 10 ppb for fludioxonil to 60,000 ppb for boscalid.[2] This range of limits presents a challenge for the analysis, requiring both high sensitivity and the ability to calibrate over a wide dynamic range.

Five key components of successful pesticide analysis discussed in this application note are:

1. Effective sample extraction and matrix cleanup, which allow for minimal matrix background and interferences while maintaining high pesticide recoveries. Also, a robust analytical method that achieves the required method performance while increasing maintenance-free uptime.
2. Evaluation of the matrix in full scan data acquisition mode to ensure the most efficient performance, especially with the high efficiency source (HES).
3. Postrun backflushing to extend maintenance-free operation of the system. This technique minimizes column trimming and source cleaning while also allowing reduced analysis time.
4. A leak-free GC/TQ system enables extended GC column life and facilitates maintenance-free consistent and reliable MS performance.
5. Use of the temperature-programmed Agilent multimode inlet (MMI) with a 2 mm dimpled liner (no glass wool) to ensure efficient volatilization of even the most thermally labile compounds.

This application note demonstrates the analysis of over 200 pesticides in three challenging matrices, including a high chlorophyll fresh matrix spinach, a complex dry matrix cayenne pepper, and an oily dry matrix walnut. The achieved wide dynamic ranges with high method sensitivity enabled accurate quantification of pesticides in these matrices, at their MRLs.

Matrix-matched calibrations with R^2 >0.99 over a dynamic range as wide as 0.1 to 5,000 ppb were achieved with the 7000E GC/TQ and 0.1 to 1,000 ppb with the 7010C GC/TQ. The 7010C GC/TQ equipped with the HES enabled superior sensitivity yielding high signal-to-noise ratio even at low concentrations and allowed for accurate quantification at concentrations below 0.1 ppb. However, this was not required in this work as the MRLs for pesticides regulated in the commodities of interest did not require sub-0.1 ppb quantification.

Experimental

GC/TQ analysis

The 8890/7000E and 8890/7010C GC/TQ systems (Figure 1A) were used and configured to achieve the best performance over a wide calibration range. This calibration range encompassed the varying MRLs for pesticides regulated in the analyzed commodities. The GC was configured with the Agilent 7693A automatic liquid sampler (ALS) and 150-position tray. The system used a multimode inlet (MMI) operated in temperature-programmed splitless injection mode. Midcolumn backflush capability was provided by the Agilent Purged Ultimate Union (PUU) installed between two identical 15 m columns, and the 8890 pneumatic switching device (PSD) module (Figure 1B). The instrument operating parameters are listed in Table 1.

Data were acquired in dynamic MRM (dMRM) mode, which enables the capability for large multi-analyte assays and to accurately quantitate narrow peaks by an automated and most-efficient dwell time distribution. The dMRM capability enabled a successful analysis for a large panel of 203 pesticide with 614 total MRM transitions with up to 52 concurrent MRMs (Figure 2). Furthermore, dMRM enables the analyst to add and remove additional analytes with ease. The acquisition method was retention time-locked to match the retention times in the Agilent MassHunter Pesticide & Environmental Pollutant MRM Database (P&EP 4), which was used to seamlessly create the MS method. The use of P&EP 4 increased the ease and speed of setting up a targeted dMRM method. The acquisition method was retention time locked to the P&EP library.

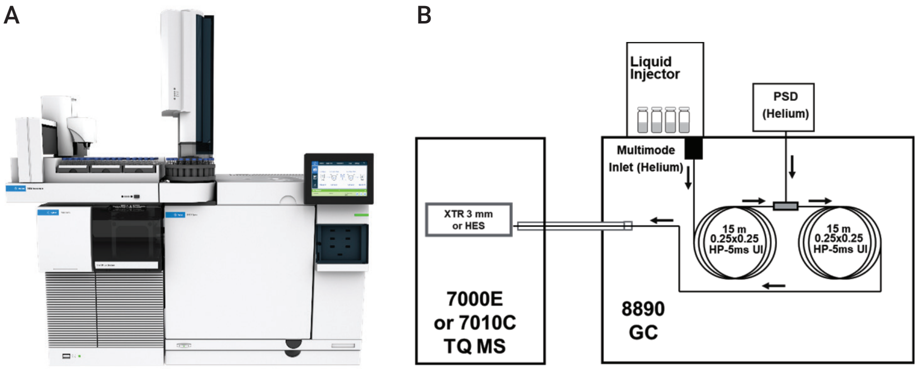


Figure 1. The Agilent 8890/7000E and 8890/7010C GC/TQ system (A) and system configuration (B).

Table 1. Agilent 8890/7000E and 8890/7010C gas chromatograph and mass spectrometer conditions for pesticide analysis.

GC	
Agilent 8890 with fast oven, auto injector, and tray	
Inlet	Multimode inlet (MMI)
Mode	Splitless
Purge Flow to Split Vent	60 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 Airgap	0.2 µL
Gas Saver	On at 30 mL/min after 3 min
Inlet Temperature	60 °C for 0.1 min, then to 280 °C at 600 °C/min
Post Run Inlet Temperature	310 °C
Post Run 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 Temp 1	170 °C
Final Hold 1	0 min
Ramp Rate 2	10 °C /min
Final Temp 2	310 °C
Final Hold 2	2.25 min
Total Run Time	20 min
Post Run Time	1.5 min
Equilibration Time	0.25 min

Column 1	
Type	Agilent HP-5ms UI (p/n 19091S-431UI-KEY)
Length	15 m
Diameter	0.25 mm
Film Thickness	0.25 µm
Control Mode	Constant flow
Flow	1.016 mL/min
Inlet Connection	Multimode inlet (MMI)
Outlet Connection	PSD (PUU)
PSD Purge Flow	5 mL/min
Post Run Flow (Backflushing)	–7.873
Column 2	
Type	Agilent HP-5ms UI (p/n 19091S-431UI-KEY)
Length	15 m
Diameter	0.25 mm
Film Thickness	0.25 µm
Control Mode	Constant flow
Flow	1.216 mL/min
Inlet Connection	PSD (PUU)
Outlet Connection	MSD
Post Run Flow (Backflushing)	8.202

MSD	
Model	Agilent 7000E or 7010C
Source	Inert Extractor Source with a 3 mm lens or HES
Vacuum Pump	Performance turbo
Tune File	Atunes.eiex.jtune.xml or Atunes.eihs.jtune.xml
Solvent Delay	3 min
Quad Temperature (MS1 and MS2)	150 °C
Source Temperature	280 °C
Mode	dMRM or Scan
He Quench Gas	2.25 mL/min
N_2 Collision Gas	1.5 mL/min
MRM Statistics	
Total MRMs (dMRM Mode)	614
Minimum Dwell Time	6.85 ms
Minimum Cycle Time	69.8 ms
Maximum Concurrent MRMs	52
EM Voltage Gain Mode	10
Scan Parameters	
Scan Type	MS1 Scan
Scan Range	45 to 450 *m/z*
Scan Time (ms)	220
Step Size	0.1 amu
Threshold	0
EM Voltage Gain Mode	1

Full scan data acquisition mode was used for the preliminary screening of the matrix extract. This screening was used to evaluate the in-source loading and for monitoring the efficiency of the sample cleanup.

Agilent MassHunter Workstation revisions 10.1 and 10.2 including MassHunter Acquisition software for GC/MS systems 10.2, MassHunter Quantitative 10.1, and MassHunter Qualitative 10 packages were used in this work.

Calibration performance was evaluated using a series of matrix-matched calibration standards ranging from 0.1 to 5,000 ppb, including 0.1, 0.5, 1, 5, 10, 50, 100, 250, 500, 1,000, and 5,000 ppb. The standard α-BHC-d_6 at a final concentration of 20 ppb in vial was used as the internal standard for quantitation of the target pesticides. A linear or quadratic regression fit with a weighting factor of 1/x was applied to all calibration curves.

Sample preparation

A sample preparation workflow chart is shown in Figure 3. The sample preparation included two major steps: sample extraction by traditional QuEChERS extraction, followed with Captiva EMR pass-through clean up. Different Captiva EMR products were used for different matrices based on different matrix challenges. A Captiva EMR–HCF cartridge was used for high-chlorophyll fresh matrix spinach. Captiva EMR–LPD was used for the low pigmented but oily dry matrix walnut. Captiva EMR–GPD was used for a very challenging dry matrix cayenne pepper. The new sample preparation workflow demonstrates a simplified procedure with improvement on both sample matrix removal and targets quantitation data quality.

As shown in Figure 3, samples were first extracted by the traditional QuEChERS EN extraction kit (part number 5892-5650). For fresh spinach, 10 g of homogenized spinach sample was used for extraction. For walnut, 5 g of walnut powder was used, followed with the addition of 10 mL of water and 10 minutes of vortexing. For cayenne pepper, 2 g of cayenne pepper powder was used, followed with the addition of 10 mL water and 10 minutes vortexing. The 10 mL of ACN with 1% acetic acid was then added for extraction, followed with QuEChERS EN extraction. After extraction, 3 mL of crude extract or with 10% of water mixture was transferred to Captiva EMR cartridges for pass-through cleanup.

The following cartridges were used: Captiva Enhanced Matrix Removal High Chlorophyll Fresh, with NH_2, (Captiva EMR–HCF1, part number 5610-2088) for spinach, the Captiva Enhanced Matrix Removal Low Pigment Dry (Captiva EMR–LPD, part number 5610-2092) for walnut, and the Captiva Enhanced Matrix Removal General Pigmented Dry (Captiva EMR–GPD, part number 5610-2091) for cayenne pepper. The sample eluent was collected and further dried by anhydrous $MgSO_4$, (part number 5982-0102) and samples were then ready for GC/TQ analysis. The positive pressure manifold 48 processor (PPM-48, part number 5191-4101) was used for Captiva EMR pass-through clean up processing.

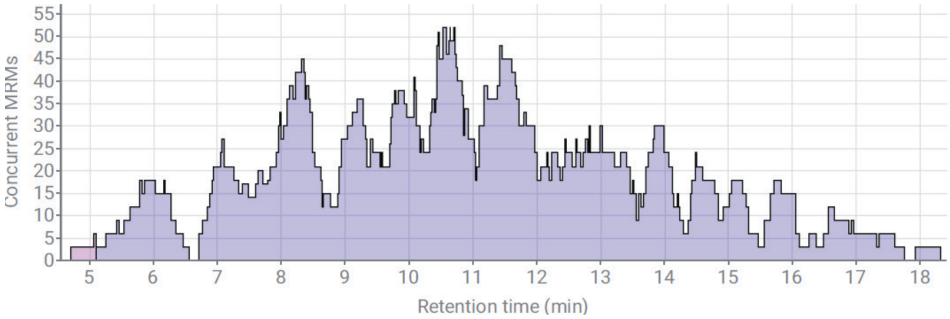


Figure 2. The distribution of 614 MRM transitions with up to 52 concurrent MRMs monitored during the analysis enabling most efficient dwell time distribution.

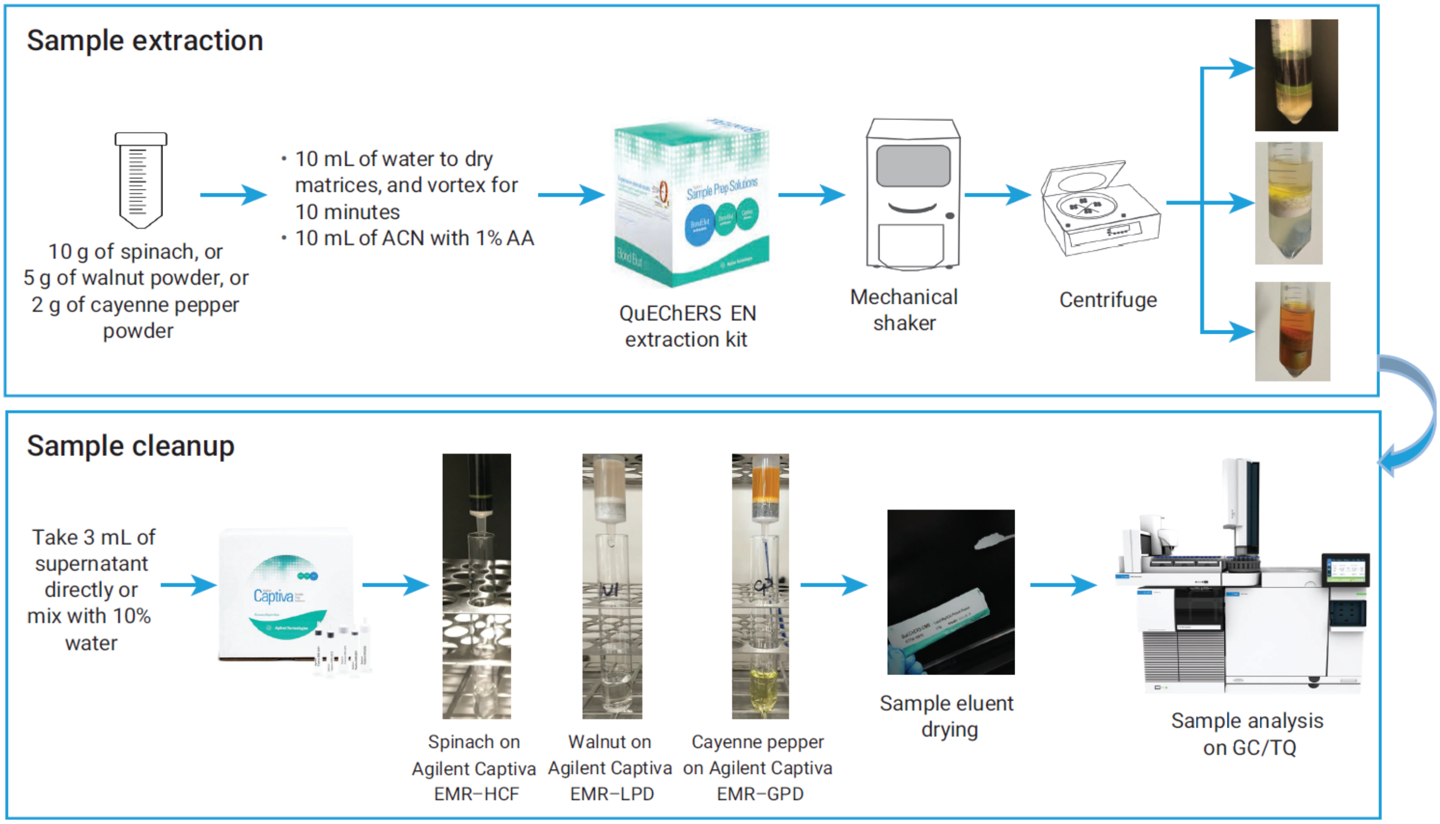


Figure 3. Sample preparation flowchart including traditional QuEChERS extraction, followed with Captiva EMR pass-through cleanup.

Results and discussion

Robust pesticide analysis that supports a high-throughput workflow must provide an extended maintenance-free operation with minimal downtime. The workflow must also meet the required sensitivity that can be at sub-ppb level. It must also enable calibration performance over a wide dynamic range that would encompass the MRLs for the compounds monitored in the commodity, which often vary over a wide dynamic range. The five key strategies outlined in this application note allowed achieving limits of quantification (LOQs) of up to 0.1 ppb while maintaining the calibration performance over a range up to 5,000 ppb for the 7000E and 1,000 ppb for the 7010C. In addition, the strategies would enable minimal instrument downtime limited to liner and septum replacement every ~100 injections.

The work presented in this application note and the system robustness study with 700 consecutive injections described elsewhere[3] resulted in over 1,000 injections of complex matrix extracts including spinach, walnut, and cayenne pepper. During this time, there was no need to perform TQ MS tuning, source cleaning, or GC column trimming.

Sample preparation

Efficient sample extraction and matrix cleanup are the keys to successful pesticide analysis. Analysis of crude QuEChERS extracts, especially of complex pigmented and oily matrices, can significantly increase the need for liner replacement, inlet cleaning, GC column trimming, and MS source cleaning. Such maintenance procedures decrease throughput of the analysis. Performing an efficient matrix cleanup following QuEChERS extraction reduces in-source matrix loading and interferences with targets, while improving signal-to-noise ratio, accuracy, and reproducibility for target pesticides. Captiva EMR passthrough clean up following the traditional QuEChERS extraction was used in this work. The new sample cleanup protocol is a simplified procedure that demonstrates an improvement on both sample matrix removal and targets overall recovery and reproducibility. As shown in Figure 4, the abundance of TIC signal in full scan data acquisition mode was noticeably reduced for spinach, walnut, and cayenne pepper extracts after clean up when comparing the crude extracts before cleanup.

Matrix screening in full scan data acquisition mode

Performing sample screening in full scan data acquisition mode facilitates the evaluation of in-source matrix loading. Every MS source has a limitation on the amount of material present in the source, at any point of time, to maintain the optimal performance. Quantitation accuracy of the analysis can be significantly compromised if the source is overloaded with matrix. Therefore, it is essential to analyze matrix in full scan mode to evaluate TIC and maintain the optimal GC/TQ performance. The abundance of TIC in full scan mode is recommended not to exceed 7×10^7 counts when analyzing with an EM gain set to 1. Out of the three analyzed matrices, cayenne pepper featured the highest matrix background, although noticeably reduced after the clean up procedure. This evaluation revealed that pesticides that elute between 11 and 12.5 minutes were expected to have sacrificed performance in the cayenne pepper matrix when evaluating sensitivity and the dynamic range. For example, Endosulfan I eluted at 11.273 minutes, and could be quantitated only starting at 5 ppb in the cayenne pepper matrix with both 7000E and 7010C, while spinach and walnut matrices had significantly lower matrix levels coeluting with Endosulfan I, with 0.1 ppb LOQ observed. Best practices on using the Agilent GC/TQ system in full scan data acquisition mode can be found in the application note 5994-3859EN.[4]

Some of the practices that can be employed to lower the matrix background include adequate sample cleanup, sample dilution, and smaller injection volume. The latter two approaches often result in better LOQs, especially with the HES-equipped 7010C GC/TQ system.

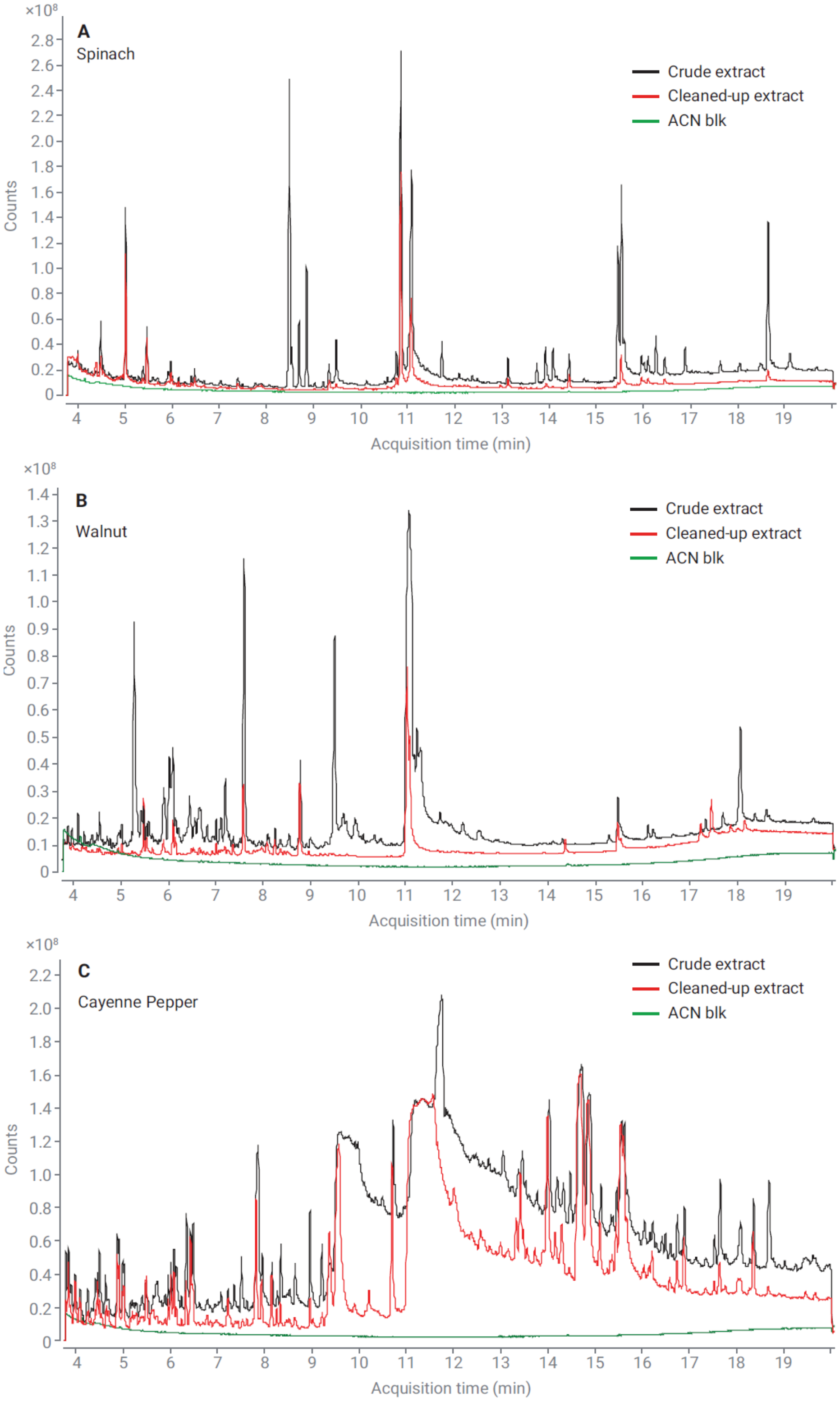


Figure 4. Scan TIC of the spinach (a), walnut (b), and cayenne pepper (c) extracts. The red trace corresponds to matrix sample with Captiva EMR cleanup, and the black trace corresponds to matrix sample without clean up. The green trace corresponds to the acetonitrile solvent blank.

Midcolumn backflushing

The use of the midcolumn backflushing configuration allows the analyst to limit the analysis time to the retention time of the last-eluting compound of interest. Challenging matrices, especially the oily ones, such as walnut, are rich in high-boiling components, with long retention times. These retention times often exceed that for the target pesticides. A common way to avoid ghost-peaks in the subsequent runs was to use an extended column bake-out after the last target analyte eluted from the column. However, this approach has several disadvantages including the deposition of high-boilers and GC column stationary phase into the EI source, contamination of the head of the GC column, a decrease of the column lifetime, and a longer cycle time due to the extended bake-out.

Midcolumn backflush allows the elution of the high boiling matrix components from the column without the sacrifices encountered with the bake-out approach. Midcolumn backflushing is a technique in which the carrier gas flow is reversed after the last analyte has exited the column. After the MS data are collected, the oven is held at the final temperature in post run mode, and the carrier gas flow through the first column is reversed. This reversed flow carries any high boilers that were in the column at the end of data collection. The high boilers are carried out of the head of the column and into the split vent trap (Figure 5A). The ability to reverse the flow is provided by the Agilent Purged Ultimate Union (PUU). The PUU is a tee that is inserted, in this case, between two identical 15 m columns. During the analysis, a small makeup flow of carrier gas from the 8890 pressure switching device (PSD) module is used to sweep the connection. During backflushing, the makeup flow from the PSD is raised to a much higher value, sweeping high boilers backward out of the first column while simultaneously providing forward flow in the second column. For the configuration in this application, the backflushing time was 1.5 minutes. More details about using PSD for backflushing in the 8890 GC system can be found in the application note 5994-0550EN.[5]

The chromatograms shown in Figure 5B illustrate the effectiveness of the backflush technique in reducing cycle time sample carryover. The cycle time was reduced by 50% and the columns did not have to be exposed to the higher bake-out temperatures for an extended time. Using backflush, excess column bleed and heavy residues are not introduced into the MSD, thereby reducing ion source contamination.

In addition, the midcolumn backflushing configuration provides a significant time saving benefit when coupled with the MMI inlet. Maintenance procedures, such as septum and liner change, and column trimming can be performed without the need to cool down MS transfer line and source. When the septum is removed, the PSD provides the carrier gas flowing backward through column 1. The PSD also prevents air from entering the GC columns and the MS. MMI fast cooling capability enables more time savings. As a result, liner and septum replacement, which are the most common maintenance procedures, can be performed in a few minutes.

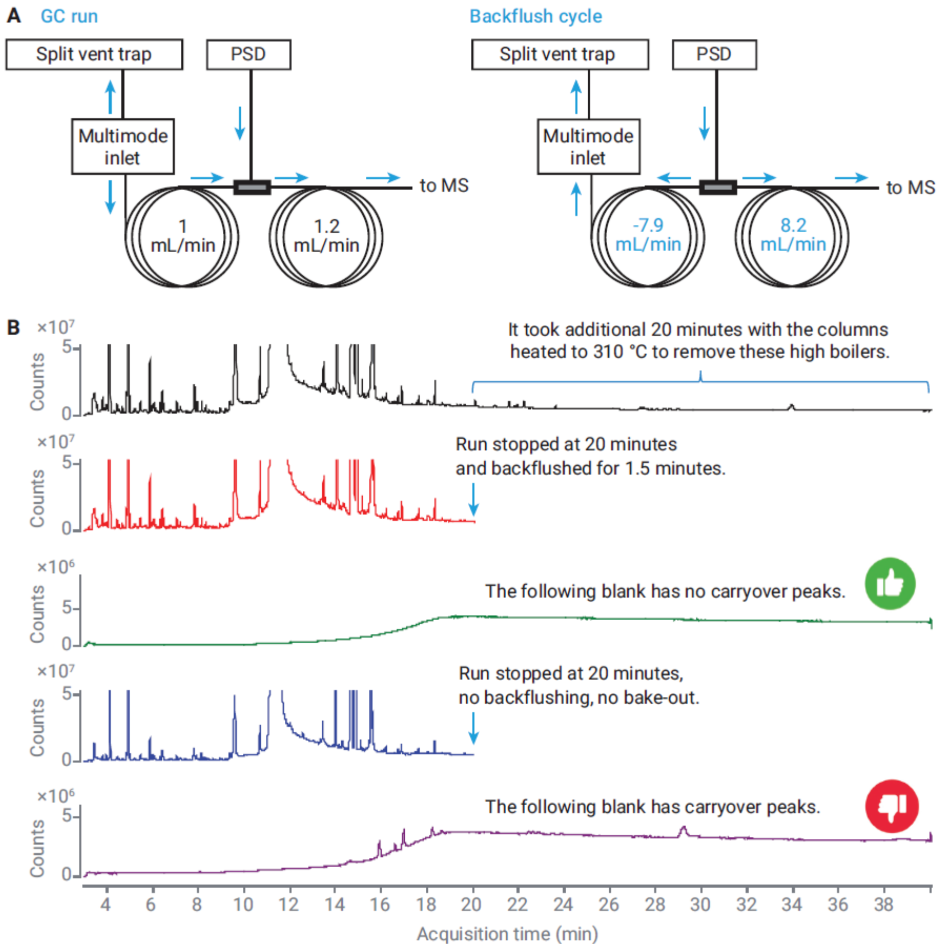


Figure 5. Midcolumn backflush configuration and gas flow during the GC run and the backflush cycle (A); TIC Scan chromatograms of a cayenne pepper extract followed by the analysis of an instrument blank with column bake-out, with backflush and without backflush or bake-out (B).

Leak-free GC/TQ system

Maintaining the GC/MS system leak-free is essential for the long-term performance of the instrument. Undesired leaks reduce the GC column lifetime and lead to oxidation of the EI source degrading its performance. The tools that enable tight connection make installation easy and reproducible and include the self-tightening collared column nuts for GC (Figures 6A and 6B part numbers G3440-81011 and G3440-81013) and CFT gold-plated flexible metal ferrules (Figure 6C, part number G2855-28501).

The self-tightening collared column nuts have an innovative spring-driven piston. The piston continuously presses against the short graphite/polyimide ferrule, maintaining a leak-free seal even after hundreds of temperature cycles of the oven. The addition of the collar makes column installation into the GC inlet and MS transfer line easy and reduces the possibility of variation. The locking collar allows locking the column in place, for accurate and repeatable installation results, time after time. The simplicity of the column installation process with the self-tightening collared column nuts is demonstrated in these videos.[6,7] When MS source maintenance is not required, the collared nut in combination with the column installation tool (part number G1099-20030) allows installation of the column into the MS without opening the side door.

Gold-plated flexible metal ferrules are inert and provide exceptionally reliable sealing. They prevent formation of microleaks at the CFT (PUU) connection and allow for maintaining high sensitivity of the GC/TQ.

Figure 6. Self-tightening collared column nuts for the inlet (A) and MS transfer line connection (B) and gold-plated flexible metal ferrules (C).

To confirm the leak-free status of the system, the air/water check, or autotune report, are often evaluated to determine how much of a leak is detected by the MS. However, this approach does not help to identify the source of the leak. Additionally, it may miss microleaks like those that may be present at user connections.

The novel leak test functionality is available with the 7000E and 7010C GC/TQ with MassHunter Data Acquisition 10.2 and above. The leak test can identify the source, and monitor the magnitude, of the leak. The tool monitors up to 10 user-specified ions (Figure 7A), including ions from a leak testing gas such as air duster (*m/z* 69 and 83, Figure 7B). The tool plots the corresponding chromatograms including EICs and TIC (Figure 7C).

Optimized injection with the temperature-programmable multimode inlet (MMI)

Efficiently volatilizing the sample in the GC inlet is an essential component of a successful GC/MS analysis. Some pesticides, such as captafol, captan, dicofol, folpet, and deltamethrin, are known to be thermally labile. They are anticipated to suffer thermal degradation during injection. Starting the injection at lower temperature of 60 °C and ramping up to 280 °C allows for volatilizing all the target analytes while maintaining their chemical integrity upon introduction to the GC column. Moreover, the ability to program the inlet temperature allows heating up the inlet further to 310 °C during the post run while backflushing. This heating enables the system to bake-out any matrix residue that may remain in the inlet.

Leak Test Parameters

Tune File: atunes.eiex.jtune

☐ Use lower temperatures (100°C/100°C/100°C)

Scan Range

Low (m/z): 30

High (m/z): 300

Monitored Ions

Monitor	Ion (m/z)
☑	32
☑	40
☑	44

Figure 7. The novel leak testing tool that enables monitoring of the user-specified ions to identify the source and the amount of leak.

The combination of temperature-programmable injection with an Ultra Inert 2 mm dimpled liner resulted in high sensitivity even for challenging pesticides like deltamethrin in a complex walnut matrix. Figure 8A demonstrates the response of deltamethrin, a pesticide with an established MRL in walnut, at 0.5 ppb with the 7000E and the 7010C GC/TQ. The 7010C GC/TQ is equipped with the HES that yields a higher sensitivity resulting in higher signal-to-noise ratio (S/N).

Pentachloronitrobenzene is a pesticide that is commonly analyzed by GC/MS in various food commodities as it has established MRLs in many vegetables and fruits (Crop Group 8 Fruiting Vegetables Group), peanuts, and soybean seeds that vary from 20 ppb to 1 ppm.[8] Pentachloronitrobenzene presents a challenge for LC/MS analysis, so GC/MS analysis is the technique of choice. Figure 8B demonstrates the chromatograms for a selective MRM transition for pentachloronitrobenzene in a walnut extract with the 7000E and the 7010C.

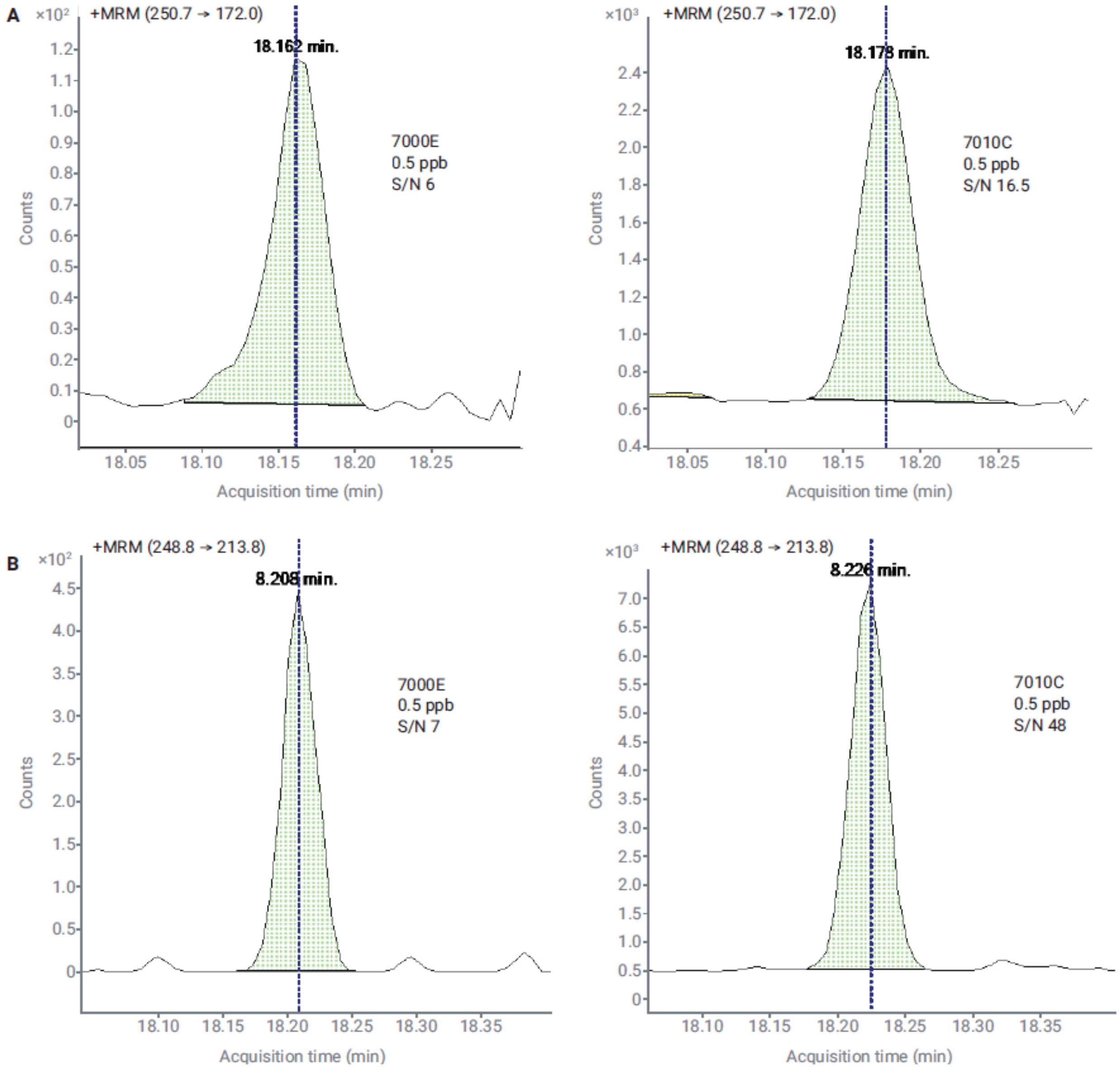


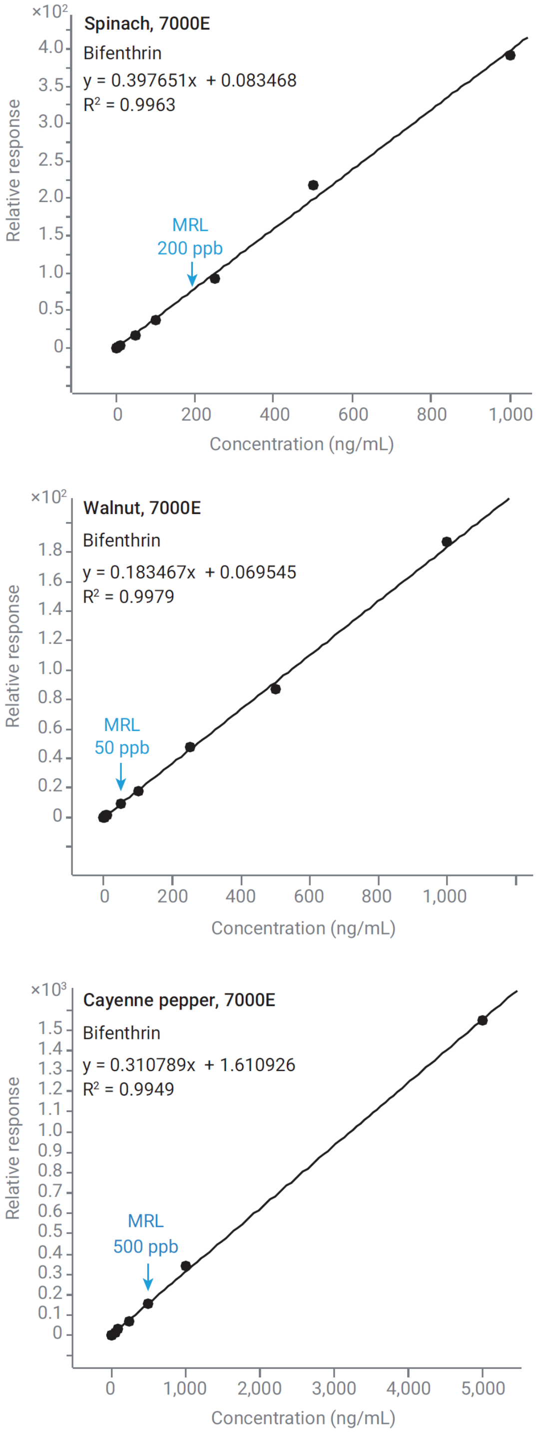
Figure 8. MRM chromatograms for deltamethrin (A) and pentachloronitrobenzene (B) at 0.5 ppb in walnut extract analyzed with the 7000E and the 7010C GC/TQ.

Calibration performance over a wide dynamic range with the 7000E and 7010C GC/TQ

The biggest challenge with the multiresidue analysis of food commodities is that the MRLs established for the pesticides vary over a wide range that may require undesirable sample reinjection. Achieving a broad dynamic calibration range can greatly reduce the need for diluting the sample and repeating the analysis.

Bifenthrin has established MRLs in spinach, walnut, and cayenne pepper that are 200, 50, and 500 ppb, respectively. Figure 9 demonstrates the linear calibration curves acquired with the 7000E over the calibration ranges of 0.1 to 1,000 ppb ($R^2 = 0.996$) in spinach, 0.1 to 5,000 ppb ($R^2 = 0.991$) in walnut, and 0.1 to 5,000 ppb ($R^2 = 0.995$) in cayenne pepper, encompassing the established MRL values.

MRLs for pesticide vary significantly not only across various commodities, but also for various pesticides regulated in one commodity. For example, pyriproxyfen and fludioxonil are monitored in spinach with the MRLs of 3,000 and 10 ppb, respectively. Figure 10A demonstrates that the 7000E GC/TQ maintained linear calibration performance for both pyriproxyfen and fludioxonil in spinach extract from 0.1 to 5,000 ppb, while demonstrating excellent accuracy even at low concentrations (see the zoomed in calibration for fludioxonil).



Spinach, 7000E

Walnut, 7000E

Cayenne pepper, 7000E

Figure 9. Matrix-matched calibration curves for bifenthrin in spinach, walnut, and cayenne pepper extracts with the 7000E GC/TQ.

As shown in Figure 10B, the 7010C GC/TQ also allowed for achieving a linear calibration curve over a broad range for both pesticides (0.1 to 1,000 ppb). However, the dynamic range of the 7010C would require an extra injection of a diluted sample to accommodate accurate quantitation of pyriproxyfen at its MRL of 3,000 ppb. While the upper limit of the calibration range achieved with the 7010C for pyriproxyfen and fludioxonil is lower than that with the 7000E, the 7010C delivers a higher sensitivity at lower concentrations. This is shown in Figure 10C and can be critical for the analysis of these pesticides in the commodities with lower established MRLs.

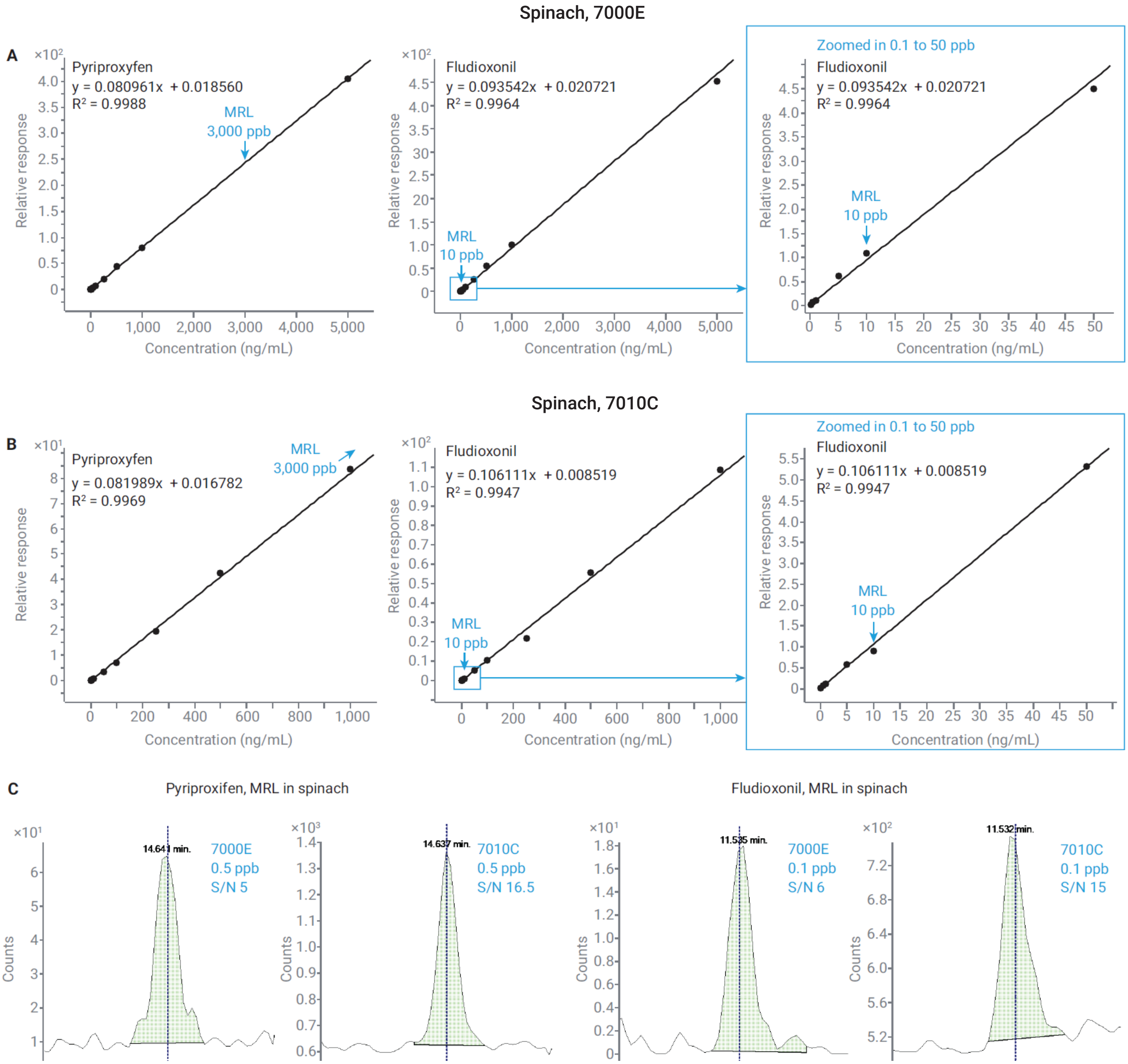


Figure 10. Matrix-matched calibration curves for pyriproxyfen and fludioxonil in spinach QuEChERS extracts with the 7000E GC/TQ (A) and with the 7010C GC/TQ (B); MRM chromatograms for pyriproxyfen and fludioxonil at 0.5 and 0.1 ppb in spinach QuEChERS extract analyzed with the 7000E and the 7010C GC/TQ (C).

Alternatively, samples with the MRLs above 1,000 ppb can be further diluted before the analysis with the 7010C GC/TQ. Superior sensitivity enabled with the HES allows for precise quantitation maintaining low LOQs even in the diluted sample. Additionally, injection of the dilutes samples increased maintenance-free operating time increased the number of injections that could be performed before the GC inlet liner needs replacement.

A summary in Figure 11 shows the calibration performance for the 203 pesticides that were analyzed in spinach, walnut, and cayenne pepper extracts with the 7000E and 7010C GC/TQ systems. The graph illustrates the number of compounds with the calibration correlation coefficient $R^2 > 0.99$, the calibration fit (linear or quadratic), and the calibration range.

As expected, considering the recommended loading for the HES not to exceed 1 ng per analyte, the upper calibration limit for the 7010C was lower when compared to the 7000E (1,000 ppb versus 5,000 ppb). However, the calibration range achieved with the 7010C was up to four orders of magnitude with a linear fit for most of the analyzed compounds. The 7010C GC/TQ equipped with the HES enables superior sensitivity yielding high S/N at low concentrations and allows for accurate quantitation at concentrations below 0.1 ppb. However, this was not required in this work as the MRLs for pesticides regulated in the commodities of interest did not require sub 0.1 ppb quantitation. Alternatively, samples with the MRLs above 1,000 ppb can be further diluted before the analysis with the 7010C GC/TQ. The HES enables maintaining high sensitivity at the LOQ level even in the dilutes sample.

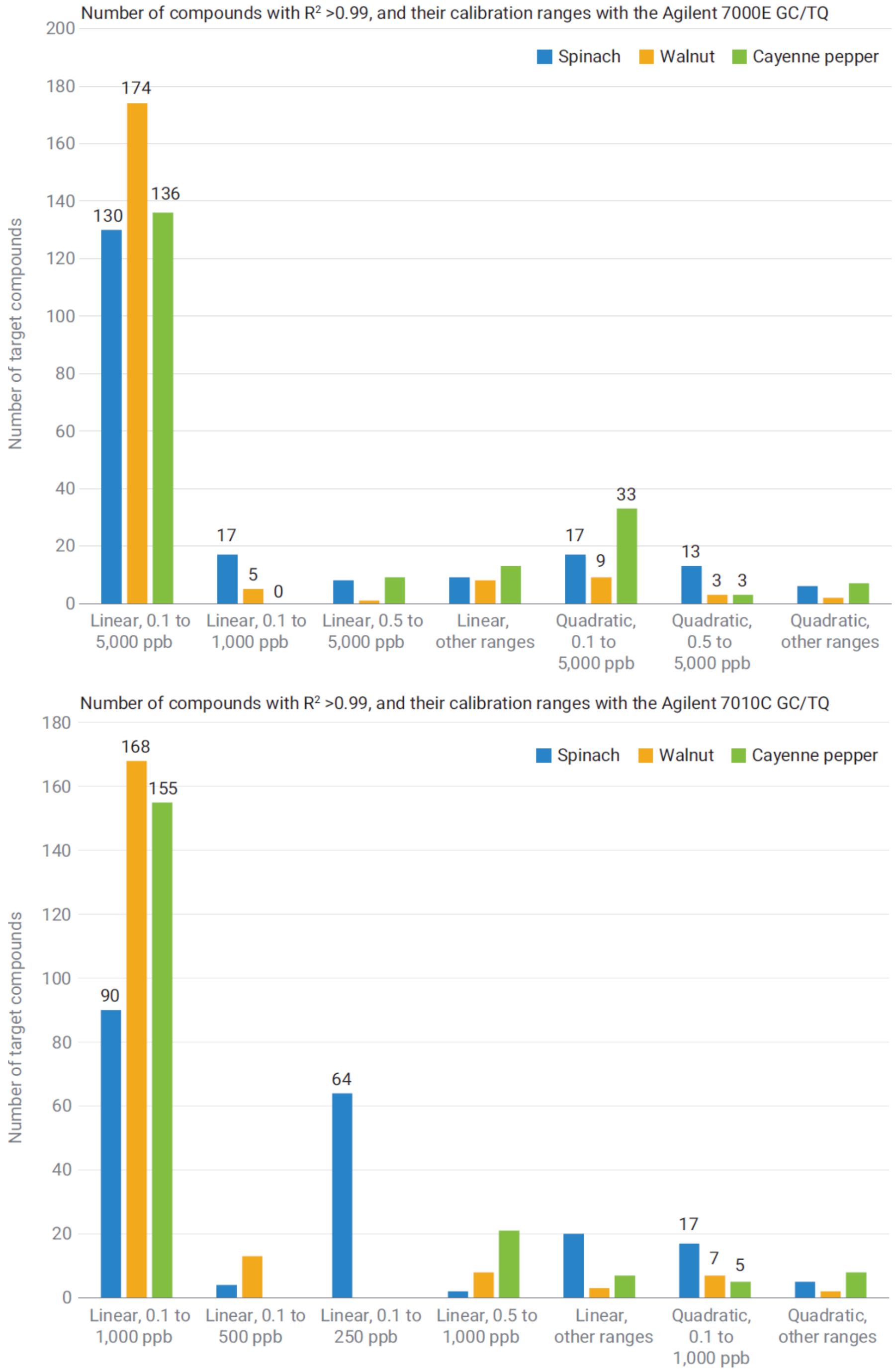


Figure 11. Calibration performance for the 203 pesticides with the 7000E and 7010C GC/TQ in spinach. The graph shows the number of compounds and their calibration ranges.

Conclusion

This application note described five best practices in sample preparation and Agilent 8890/7000E and 8890/7010C triple quadrupole GC/MS system analysis applied to 203 pesticides in challenging food matrices, including spinach, walnut, and cayenne pepper. These practices included:

- Simplified and improved sample preparation achieved with the novel and improved Agilent Captiva EMR pass-through clean up following the traditional Agilent QuEChERS extraction
- Evaluation of in-source loading of the matrix in full scan data acquisition mode
- Postrun backflushing
- Leak-free GC/triple quadrupole system enabled with the self-tightening collared column nuts and CFT gold-plated flexible metal ferrules
- Use of temperature-programmed multimode inlet with a 2 mm dimpled liner (no glass wool)

The resulting method allowed for excellent calibration performance over a wide dynamic range up to over four orders of magnitude. The calibration performance was as wide as 0.1 to 5,000 ppb and 0.1 to 1,000 for most of the compounds with the 7000E and the 7010C, respectively. The 7010C demonstrated superior sensitivity yielding a higher signal-to-noise ratio at lower concentrations. The wide dynamic ranges in combination with high sensitivity make the 7000E and the 7010C the ideal tools for analyzing pesticides at their MRLs in various commodities, including those with complex highly pigmented and oily matrices.

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Appendix 1

Compounds analyzed in this work and their observed retention times.

Name	Retenion Time (min)	Name	Retenion Time (min)	Name	Retention Time (min)
Allidochlor	4.893	Pyrimethanil	8.282	DCPA (Dacthal, Chlorthal-dimethyl)	10.062
Dichlorobenzonitrile, 2,6-	5.244	Diazinon	8.291	Fenson	10.201
Biphenyl	5.423	Fluchloralin	8.326	Diphenamid	10.288
Mevinphos, E-	5.597	Disulfoton	8.427	Bromophos	10.297
3,4-Dichloroaniline	5.708	Tefluthrin	8.431	Pirimiphos-ethyl	10.304
Pebulate	5.803	Terbacil	8.432	Isopropalin	10.358
Etridiazole	5.833	BHC-delta	8.504	Cyprodinil	10.407
cis-1,2,3,6-Tetrahydrophthalimide	5.966	Isazofos	8.527	MGK-264	10.443
N-(2,4-dimethylphenyl)formamide	5.973	Triallate	8.569	Isodrin	10.455
Methacrifos	6.055	Chlorothalonil	8.584	Metazachlor	10.532
Chloroneb	6.136	Endosulfan ether	8.857	Pendimethalin	10.535
2-Phenylphenol	6.246	Pentachloroaniline	8.913	Penconazole	10.562
Pentachlorobenzene	6.343	Propanil	8.942	Chlozolinate	10.584
Propachlor	6.888	Dimethachlor	8.996	Heptachlor exo-epoxide	10.621
Tecnazene	6.889	Acetochlor	9.093	Tolylfluanid	10.646
Diphenylamine	6.959	Vinclozolin	9.115	Allethrin	10.648
Cycloate	7.043	Transfluthrin	9.129	Fipronil	10.662
2,3,5,6-Tetrachloroaniline	7.059	Parathion-methyl	9.145	Chlorfenvinphos	10.676
Chlorpropham	7.102	Chlorpyrifos-methyl	9.146	Bromfenvinfos-methyl	10.683
Ethalfluralin	7.139	Tolclofos-methyl	9.233	Captan	10.732
Trifluralin	7.245	Alachlor	9.263	Triadimenol	10.746
Benfluralin	7.279	Propisochlor	9.333	Quinalphos	10.747
Sulfotep	7.376	Heptachlor	9.336	Triflumizole	10.77
Diallate I	7.481	Metalaxyl	9.337	Folpet	10.847
Phorate	7.498	Ronnel	9.396	Procymidone	10.858
BHC-alpha (benzene hexachloride)	7.636	Prodiamine	9.556	Chlorbenside	10.918
Hexachlorobenzene	7.768	Fenitrothion	9.596	Bromophos-ethyl	11.041
Dichloran	7.798	Pirimiphos-methyl	9.598	Chlordane-trans	11.043
Pentachloroanisole	7.823	Linuron	9.668	DDE-o,p'	11.09
Atrazine	7.885	Malathion	9.743	Paclobutrazol	11.106
Clomazone	7.982	Pentachlorothioanisole	9.758	Tetrachlorvinphos	11.169
BHC-beta	8.025	Dichlofluanid	9.764	Endosulfan I (alpha isomer)	11.273
Profluralin	8.117	Metolachlor	9.902	Chlordane-cis	11.305
Terbuthylazine	8.119	Anthraquinone	9.916	Flutriafol	11.322
BHC-gamma (Lindane, gamma HCH)	8.146	Fenthion	9.928	Fenamiphos	11.355
Terbufos	8.159	Aldrin	9.942	Chlorfenson	11.382
Propyzamide	8.175	Chlorpyrifos	9.964	Nonachlor, trans-	11.392
Pentachloronitrobenzene	8.219	Parathion	9.98	Bromfenvinfos	11.4
Fonofos	8.251	Triadimefon	10.011	Flutolanil	11.402
Pentachlorobenzonitrile	8.259	Dichlorobenzophenone, 4,4'-	10.033	Iodofenphos	11.479

Name	Retention Time (min)	Name	Retention Time (min)	Name	Retention Time (min)
Prothiofos	11.514	Carbophenothion	12.849	Phenothrin I	14.334
Fludioxonil	11.556	Carfentrazone-ethyl	12.851	Tetradifon	14.445
Profenofos	11.56	Methoxychlor olefin	12.865	Phosalone	14.61
Pretilachlor	11.592	Edifenphos	12.949	Azinphos-methyl	14.64
DDE-p,p'	11.637	Norflurazon	12.964	Pyriproxyfen	14.662
Tricyclazole	11.645	Lenacil	12.976	Leptophos	14.666
Oxadiazon	11.659	Endosulfan sulfate	13.04	Cyhalothrin (Lambda)	14.731
Dieldrin	11.73	DDT-p,p'	13.054	Mirex	14.898
Oxyfluorfen	11.737	Hexazinone	13.23	Acrinathrin	15.076
Myclobutanil	11.747	Methoxychlor, o,p'-	13.241	Fenarimol	15.121
DDD-o,p'	11.799	Tebuconazole	13.294	Pyrazophos	15.168
Flusilazole	11.8	Propargite	13.352	Azinphos-ethyl	15.252
Bupirimate	11.831	Piperonyl butoxide	13.404	Pyraclofos	15.303
Fluazifop-p-butyl	12.007	Resmethrin	13.44	Permethrin, (1R)-cis-	15.656
Nitrofen	12.023	Captafol	13.466	Permethrin, (1R)-trans-	15.772
Ethylan	12.063	Nitralin	13.563	Pyridaben	15.807
Chlorfenapyr	12.064	Iprodione	13.726	Fluquinconazole	15.895
Endrin	12.127	Tetramethrin I	13.836	Coumaphos	15.902
Chlorobenzilate	12.194	Pyridaphenthion	13.838	Prochloraz	15.958
Endosulfan II (beta isomer)	12.291	Endrin ketone	13.898	Cyfluthrin I	16.207
DDD-p,p'	12.383	Phosmet	13.931	Cypermethrin I	16.421
Ethion	12.453	Bromopropylate	13.952	Flucythrinate I	16.75
DDT-o,p'	12.457	EPN	13.955	Ethofenprox	16.829
Chlorthiophos	12.503	Bifenthrin	13.956	Fluridone	17.034
Nonachlor, cis-	12.508	Methoxychlor, p,p'-	14.062	Fenvalerate I	17.459
Endrin aldehyde	12.618	Fenpropathrin	14.077	Fluvalinate-tau I	17.646
Sulprofos	12.669	Tebufenpyrad	14.142	Deltamethrin	18.177
Triazophos	12.674				

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DE10556921

Printed in the USA, June 03, 2022
5994-4965EN