Application Note

Food

Brewing Excellence: Quantitating Over 200 Pesticides in Black Tea with Steady Performance and Maximized Uptime by GC/MS/MS

Authors

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Abstract

This application note presents results for the sensitive and robust quantitation of 246 pesticides in black tea extract with the Agilent 7010D Triple Quadrupole Mass Spectrometer (GC/TQ) featuring a second-generation High Efficiency Source 2.0 (HES 2.0), that addresses the challenges posed by residual pesticide analysis in complex matrices. By optimizing sample preparation and using state-of-the-art GC/MS hardware, including ion source technology and midcolumn backflushing, excellent calibration performance and sensitivity at low-ppb levels were achieved. The method demonstrated exceptional ruggedness and robustness over 800 consecutive injections of a black tea extract spiked with pesticides at 2 ppb, with high precision and low RSDs, ensuring prolonged instrument uptime and maximum throughput. The demonstrated limits of quantitation (LOQs) were as low as 0.01 ppb for over a third of evaluated compounds, and the calibration range spanned up to five orders of magnitude while meeting SANTE 11312/2021 guidelines.

This application note highlights intelligent GC/TQ features, such as early maintenance feedback and an instrument health status dashboard, maintaining confidence in the results for a high-throughput analysis. The updated data acquisition platform provides enhanced user experience, including a new implementation of the retention time locking functionality.

Introduction

Tea is among the most common nonalcoholic beverages consumed worldwide. Like many foods, tea cultivation relies heavily on pesticide application to combat pests, leading to concerns over pesticide residues intensifying.[1]

Assessing pesticide levels in tea is essential for evaluating safety, and is required by many regulatory bodies, including the European Commission and the US Environmental Protection Agency.[2,3] A complete workflow for pesticide testing in tea includes sample extraction via QuEChERS, followed by extract cleanup, and subsequent testing with liquid and gas chromatography coupled with triple quadrupole mass spectrometry (LC/TQ and GC/TQ).[4] Workflow performance should enable sufficient method sensitivity, calibration range, pesticide recovery from the extraction, and precision. Sensitivity requirements are set based on the maximum residue levels (MRLs), which are the highest levels of pesticide residue that are legally allowed in or on food or feed when pesticides are applied correctly. The ability to calibrate over a wide dynamic range allows the varying MRLs for individual compounds monitored in the commodity, which can vary from 10 ppb to 100 ppm. When a specific pesticide lacks an established MRL, a default limit of 10 ppb is commonly applied. Efficiency of extraction and cleanup are characterized in terms of recovery of matrix spikes, and precision is expressed in terms of relative standard deviation (RSD) of repeat analyses.

This application note presents a complete GC/TQ workflow solution for the accurate and reliable analysis of 246 volatile and semivolatile pesticides in black tea. Excellent analytical performance of the workflow was achieved through a combination of cutting-edge technology and optimized methodology that included:

- Sample preparation using QuEChERS extraction, followed by EMR mixed-mode pass-through cleanup using Agilent Captiva EMR–GPD cartridges
- Agilent 8890 GC hardware and GC supplies
- Novel electron ionization (EI) source technology with HES 2.0
- Built-in GC/TQ MS intelligence and new software functionality for method setup, maintenance, and system health evaluation

The presented workflow allowed for quantitating 246 pesticide residues in black tea with LOQs as low as 0.01 ppb for 34% of the targets, at or below 0.1 ppb for 74% of compounds, and below 2 ppb for 96%. Matrix-matched calibrations demonstrated excellent accuracy over a wide dynamic range, spanning up to five orders of magnitude over 0.01 to 1,000 ppb in the complex black tea extract. Method ruggedness was demonstrated through maintaining measurement accuracy with good precision (RSDs < 20% for 176 compounds) for black tea extract spiked at 2 ppb sequentially analyzed over 800 runs spanning 17 days of continuous analysis. The new HES 2.0 ion source is equipped with a novel dipolar radiofrequency (RF) lens that redirects the carrier gas ions and, as a result, enables improved system robustness and maximizes uptime while maintaining unparalleled analytical sensitivity.

Experimental

GC/TQ analysis

The 8890 GC and 7010D GC/TQ systems (Figure 1A) were used and configured to achieve the best sensitivity, maintain a wide calibration range, and provide the most rugged method performance. 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 (also known as cold splitless). The injection parameters were optimized for maximizing sensitivity while limiting carryover. Midcolumn backflush capability was provided by the Agilent Purged Ultimate Union (PUU) installed between two identical 15 m columns, and the Agilent 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 provides the capability for large multi-analyte assays and the accurate quantitation of narrow peaks by an automatically determined most-efficient dwell time distribution. The dMRM capability enabled successful analysis for a large panel of 246 pesticides, with 749 total MRM transitions with up to 64 concurrent MRMs. Furthermore, dMRM allows 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 Pesticides and Environmental Pollutants MRM Database 4.0 (P&EP 4.0)[5],

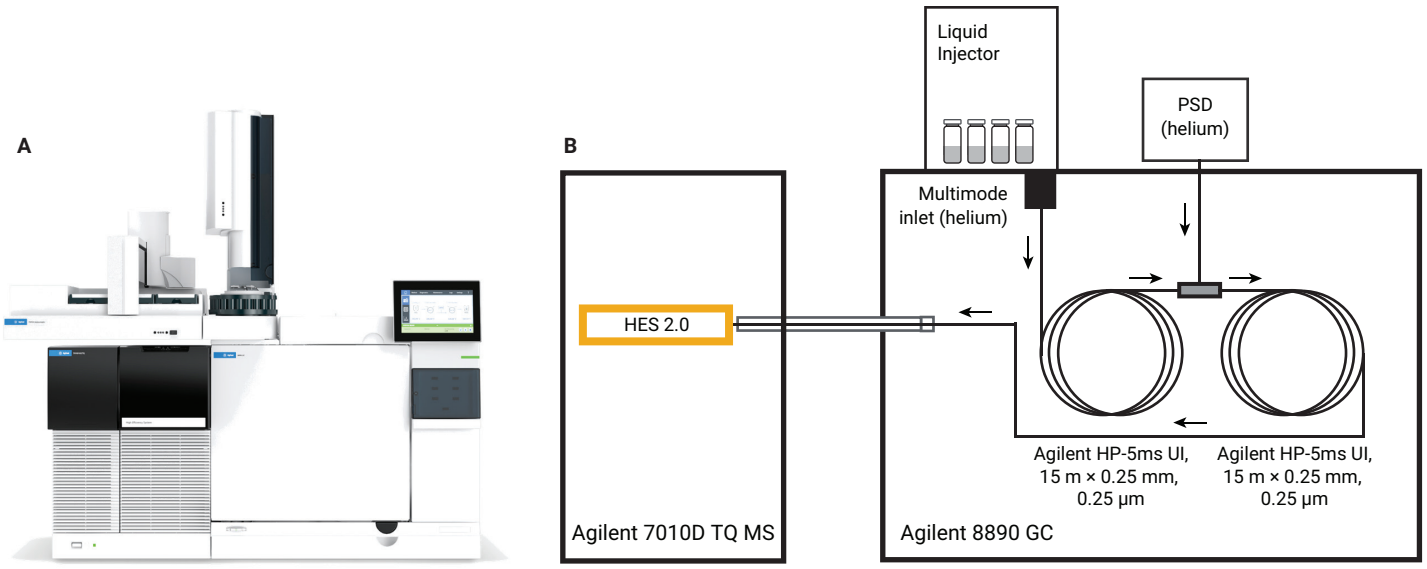


Figure 1. The Agilent 8890 GC system with the Agilent 7010D GC/TQ system (A) and system configuration (B).

which was used to seamlessly create the MS method. The use of P&EP 4.0 increased the ease and speed of setting up a targeted dMRM method. High method selectivity in the presence of coeluting matrix components was achieved by selecting the best MRM transitions from up to nine transitions available for each compound in the P&EP 4.0 database.

Three targets were not available in the P&EP 4.0 database (flonicamid, bioallethrin, and cycloxydim). For these compounds, MRM transitions were developed using Agilent MassHunter Optimizer for GC/TQ, operating in Start from Full Scan mode. The Optimizer is fully integrated into MassHunter Acquisition 13.0 for GC/MS (Figure 2).

The acquisition method was retention time locked to the P&EP database with chlorpyrifos-methyl eluting at 9.143 minutes. The retention time locking functionality, integrated in MassHunter Acquisition 13.0 for GC/MS, has an updated user-friendly and intuitive interface (Figure 3). It allows for semi-automated or manual compound selection, provides a choice to use three or five points for retention time locking calibration, and features both a visual and quantitative assessment of the calibration curve fit, while providing the tools to maintain excellent precision of retention times, even after column trimming.

Full scan data acquisition mode was used for the initial screening of the matrix extract. This screening was used to evaluate in-source loading, and for monitoring the efficiency of the sample cleanup procedure that followed QuEChERS extraction.

Agilent MassHunter Workstation software, including Agilent MassHunter Acquisition 13.0 for GC/MS, MassHunter Quantitative Analysis 12.1, and MassHunter Qualitative Analysis 12.0 packages were used in this work.

Table 1. Agilent 8890 GC system with Agilent 7010D gas chromatograph and mass spectrometer conditions for pesticide analysis.

Parameter	Value
GC	Agilent 8890 with fast oven, auto injector and tray
Inlet	MMI
Mode	Cold splitless
Purge Flow to Split Vent	60 mL/min at 3 min
Septum Purge Flow	3 mL/min
Septum Purge Flow Mode	Switched
Injection Volume	1.0 µL
Injection Type	Reversed 2-layer (L2, L1)
L1 Airgap	0.2 µL
L2 Volume (ISTD)	0.2 µL
L2 Airgap	0.2 µL
Gas Saver	On at 30 mL/min after 5 min
Inlet Temperature	60 °C for 0.1 min, then to 280 °C at 600 °C/min, hold for 5 min, then to 325 °C at 600 °C/min
Postrun Inlet Temperature	310 °C
Postrun Total Flow	25 mL/min
Carrier Gas	Helium
Inlet Liner	Agilent Ultra Inert 2 mm dimpled liner (p/n 5190-2297)
Oven	
Oven Program	60 °C for 1 min; 40 °C/min to 170 °C; Hold 0 min; 10 °C /min to 310 °C; Hold 2.25 min
Total Run Time	20 min
Postrun Time	1.5 min
Equilibration time	0.5 min
Column 1	
Type	Agilent HP-5ms UI, 15 m × 0.25 mm, 0.25 µm (p/n 19091S-431UI-KEY)
Control Mode	Constant flow
Flow	1.0 mL/min (then retention time locked)
Inlet Connection	MMI
Outlet Connection	PSD (PUU)
PSD Purge Flow	5 mL/min
Postrun Flow (Backflushing)	–7.873

Parameter	Value
Column 2	
Type	Agilent HP-5ms UI, 15 m × 0.25 mm, 0.25 µm (p/n 19091S-431UI-KEY)
Control Mode	Constant flow
Flow	1.2 mL/min (then retention time locked)
Inlet Connection	PSD (PUU)
Outlet Connection	MSD
Postrun Flow (Backflushing)	8.202
MSD	
Model	Agilent 7010D
Source	HES 2.0
Vacuum Pump	Performance turbo
Tune File	atunes.eihs2.jtune.xml
Solvent Delay	3.75 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)	749
Minimum Dwell Time	5.42 ms
Minimum Cycle Time	85.01 ms
Maximum Concurrent MRMs	64
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

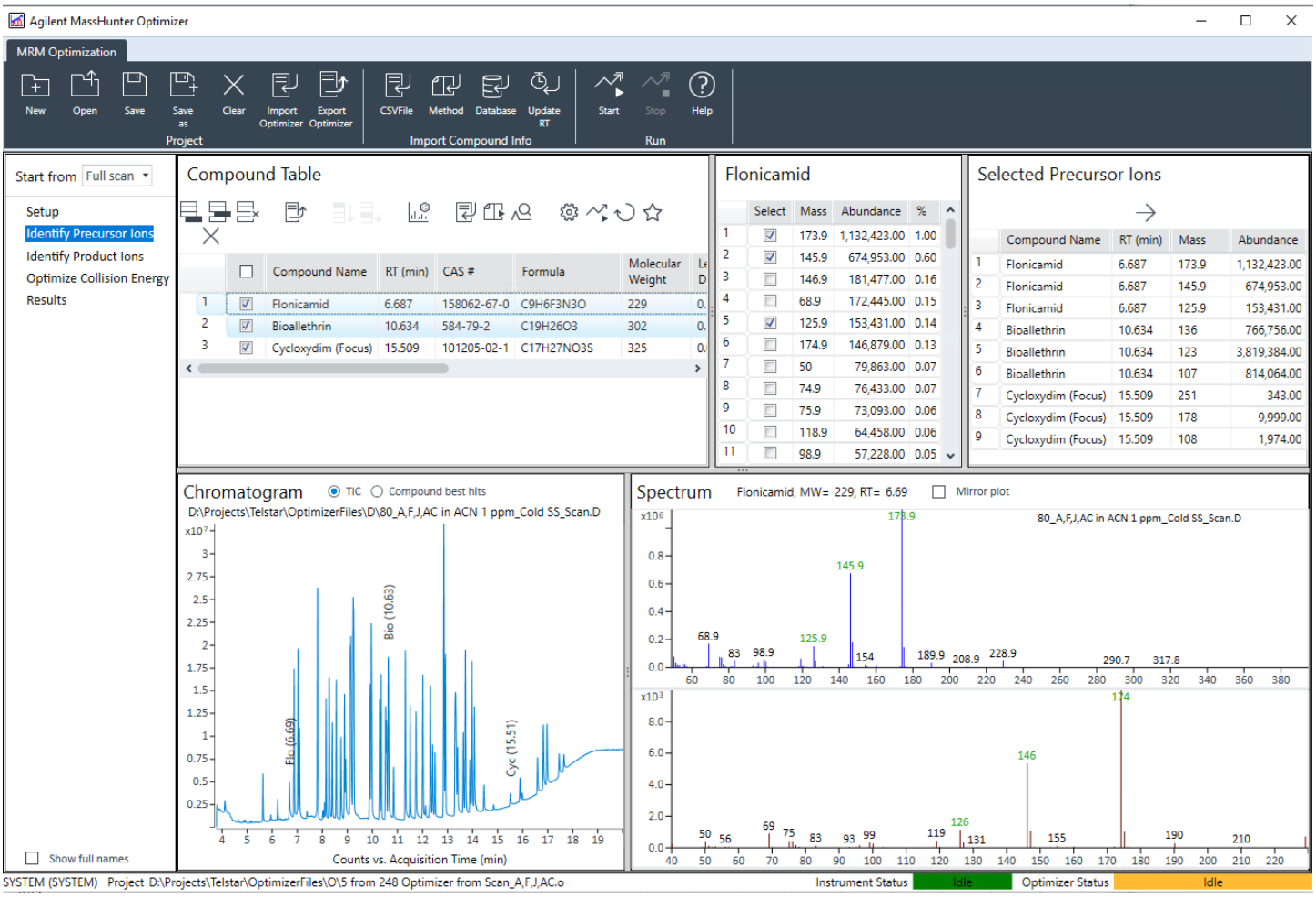


Figure 2. Agilent MassHunter Optimizer software for GC/TQ, used for the automated development of MRM transitions.

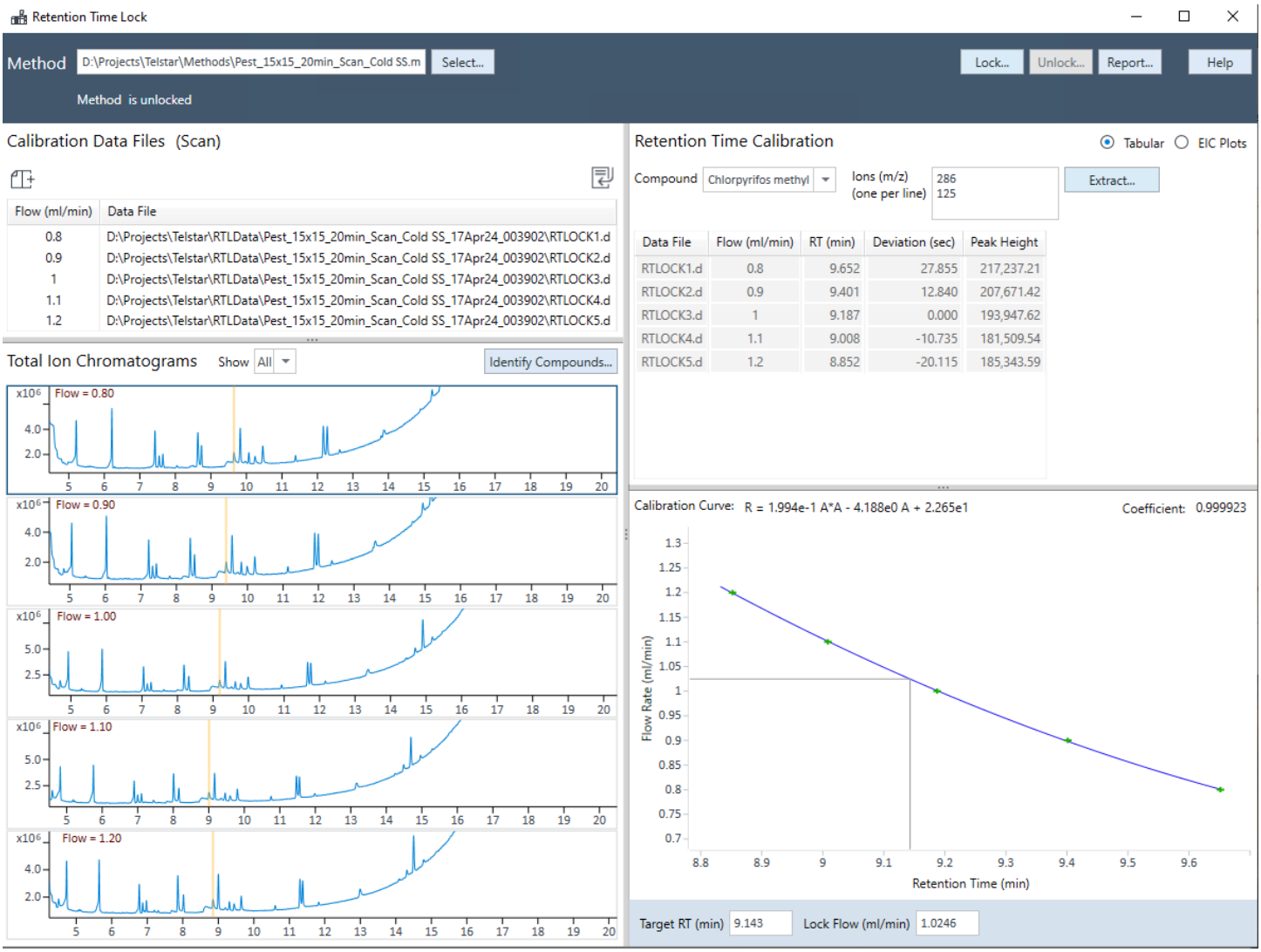


Figure 3. New Agilent retention time locking software in Agilent MassHunter Acquisition 13.0 for GC/MS.

Sample preparation

Black tea powder was obtained from a local grocery store. Black tea powder (2 g) was extracted with a modified QuEChERS extraction using acetonitrile (ACN) with 2% formic acid and EN extraction salt. The crude tea extract then was mixed with 2% of acidic buffer. The sample mixture was cleaned by EMR mixed-mode pass-through cleanup using Agilent Captiva EMR–GPD 6 mL. The sample eluent was dried with anhydrous $MgSO_4$ to remove water residue completely before GC/MS/MS analysis. The sample preparation procedure flowchart is shown in Figure 4, and details will be discussed in a separate application note. The entire sample preparation procedure resulted in a 5x dilution factor.

Pesticide standards

Agilent GC pesticide standards 1 through 12 (part numbers PSM-100-A through -L) and Agilent GC/LC pesticide standards 1, 2, and 3 (part numbers PSM-100-AA, PSM-100-AB, PSM-100-AC) were used for preparing matrix matched calibration standards. A combination of the 15 used standards yielded a mix of 246 pesticides commonly regulated by the FDA, USDA, and other global governmental agencies.

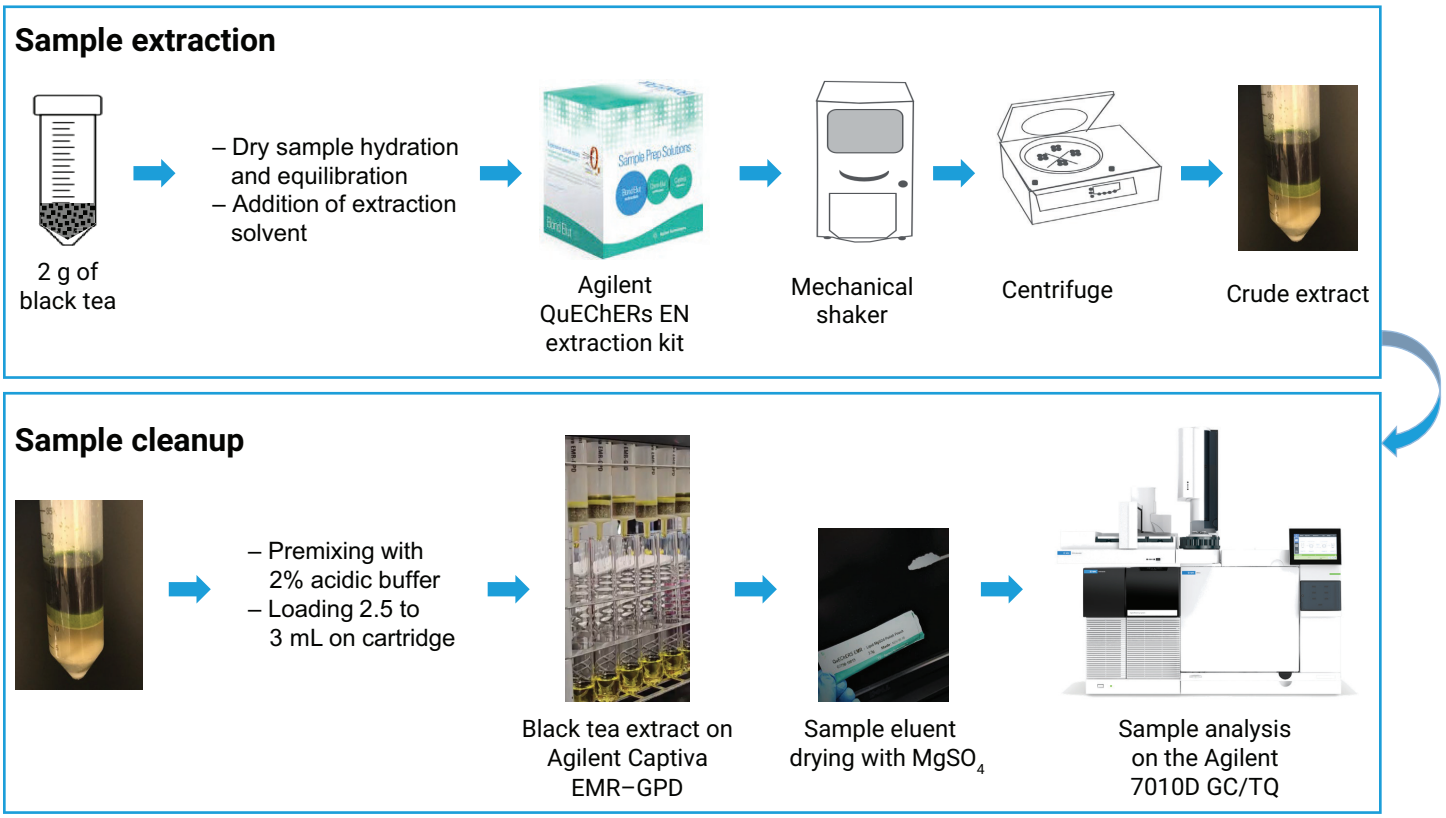


Figure 4. QuEChERS sample preparation and cleanup method for black tea.

Matrix-matched calibration

Calibration performance was evaluated using a series of matrix matched calibration standards, ranging from 0.01 to 1,000 ppb, including 0.01, 0.05, 0.1, 0.5, 1, 2, 5, 10, 50, 100, 200, 500, and 1,000 ppb. The standard parathion-d_{10} (Agilent QuEChERS IS standard number 6, part number PPS-610-1) was used as the internal standard for quantitation of the target pesticides. It was added at 0.2 µL through reversed sandwich injection with the ALS to a final concentration of 10 ppb in the injected sample.

An appropriate calibration function, either linear or quadratic, guided by the lower value of the relative standard error (RSE) was used. A weighting factor of 1/x allowed for maintaining accuracy across the entire calibration range. The deviation of the back-calculated concentrations of the calibration standards from the true concentrations, using the calibration curve in the relevant region, did not exceed ± 20%.

The concentrations expressed in ppb (w:v) correspond to the pesticide concentration in the injected sample. The QuEChERS sample preparation procedure described in the Sample preparation section resulted in a dilution factor of 5. Hence, the concentrations measured in the injected samples were five times lower than the corresponding concentration in the black tea sample, expressed in µg/kg.

Analyte protectants were not used in this work. The preliminary investigation showed that analyte protectants did not have a response enhancement effect on most of the compounds when analyzed in the rich and complex black tea matrix. It is of note that analyte protectants often significantly enhance target analyte response and stability as is described in-depth in the peer-reviewed literature.[6]

Recovery evaluation

Sample preparation efficiency was evaluated by performing recovery studies. The surrogate black tea matrix was spiked at two different levels, 10 and 50 ppb, with six replicates at each level. The samples were extracted and cleaned up. Assuming 100% recovery, pesticide concentrations in the prespiked samples were expected to be 2 and 10 ppb due to a 5x dilution rate. A blank black tea extract was postspiked with the pesticide standard to achieve final concentrations of 2 and 10 ppb. The prespiked and postspiked samples were analyzed, and the response areas were compared. The recovery was measured as the ratio of the pesticide peak area in the prespiked sample to the area in the postspiked samples.

Results and discussion

As contemporary GC/MS technology continues to advance, so do the expectations for high sample throughput, intuitive user-friendly system setup and configuration, and streamlined maintenance. The demands for enhanced analytical performance are driven by the evolving regulations in pesticide residue analysis and food safety.

Several best practices to achieve the best GC/TQ performance in pesticide residue analyses were described in Agilent application note 5994-4965EN.[7] This work presents a complete workflow for analyzing 246 pesticides in black tea, while implementing the previously described best practices and offering further method and technology enhancements. The innovative HES 2.0 yielded enhanced GC/TQ performance stability, as evidenced by precise results at the low concentration of 2 ppb over 800 consecutive injections of complex black tea extract.

The technology and method enhancements that enable unparalleled GC/TQ performance while ensuring stable and reliable results in a high-throughput setting are outlined in this application note and grouped into four categories: sample preparation, GC instrumentation and supplies, MS electron ionization technology advancements, and instrument intelligence and software functionality.

Effective matrix cleanup

Sample preparation is a key component of performing successful pesticide analysis. Performing analysis of samples prepared by QuEChERS extraction, particularly when analyzing complex pigmented samples such as black tea without adequate cleanup, can lead to increased system maintenance. The parts of the system that are affected without adequate sample cleanup include liner replacement, GC column trimming, and inlet and MS source cleaning. As a result, throughput is decreased. Further, the presence of large amounts of matrix can affect the accuracy of results, often most pronounced with difficult to analyze pesticides. The EMR mixed-mode pass-through cleanup using Captiva EMR with Carbon S cartridges is a simplified procedure that demonstrates an improvement on both sample matrix removal, and overall recovery and reproducibility of targets. As shown in Figure 5, the abundance of the TIC signal in full scan data acquisition mode was noticeably reduced for black tea extract after cleanup when comparing the crude extracts before cleanup.

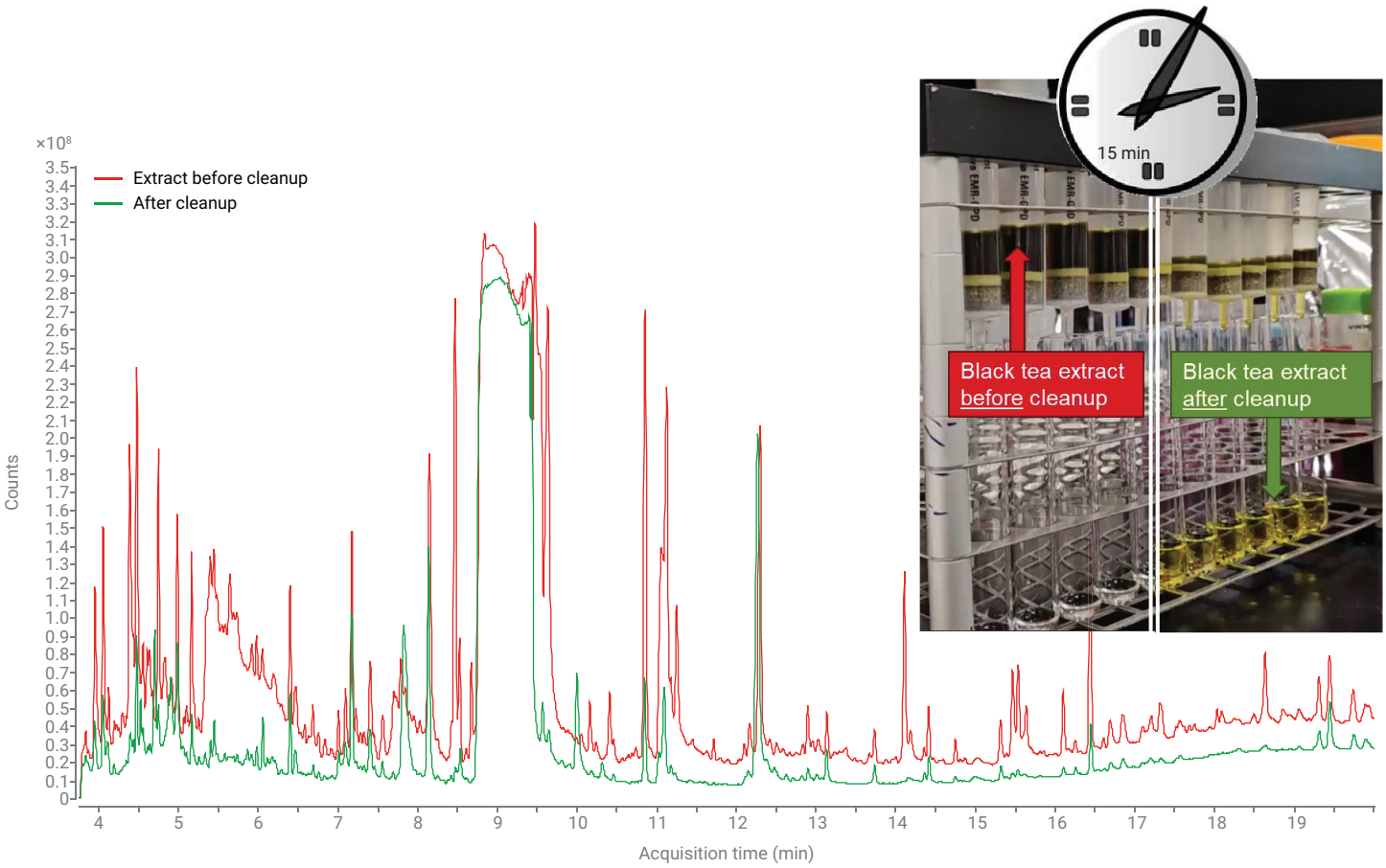


Figure 5. Scan TIC of black tea extract. The green trace corresponds to matrix sample with Agilent Captiva-EMR cleanup, and the red trace corresponds to matrix sample without cleanup.

Performing matrix screening in full scan data acquisition mode, as shown in Figure 5, facilitates the evaluation of in-source matrix loading, as discussed in 5994-4965EN.[7] Every MS source has a limitation on the amount of material present in the source, at any point in time, to maintain optimal performance. Quantitation accuracy of the analysis can be significantly compromised if the source is overloaded with matrix.

Hence, it is essential to analyze the matrix in full scan mode to evaluate the TIC and maintain optimal GC/TQ performance. For best performance with the HES 2.0 source, it is recommended to have a TIC full scan abundance below 7×10^7 counts when analyzing with an EM gain set to 1. As shown in Figure 5, black tea extract is complex, featuring abundant matrix components. Cleaning up the extract is key to lowering the matrix background that leads to adequate in-source loading, enhancing selectivity and sensitivity, widening the dynamic range, and allowing for less frequent system maintenance, increasing productive uptime.

GC instrumentation and supplies

Midcolumn backflushing: The Agilent 8890 GC provides an easy-to-use midcolumn backflushing functionality that results in increased sample throughput through shorter analysis times and less frequent column maintenance.

Midcolumn backflush allows for the elution of the high boiling point matrix components from the column in a shorter time and without eluting high-boiling matrix into the MS. Midcolumn backflushing is a technique in which the carrier gas flow is reversed after the last analyte has exited the column and all MS data are collected. The oven is then held at the final temperature in postrun mode, with the reversed carrier gas flow through the first column. The high boilers are eluted back out the head of the column and into the split vent trap. The ability to reverse the flow is provided by the 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 PSD 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 Agilent 8890 GC system can be found in Agilent application note 5994-0550EN.[8]

Figure 6 illustrates the effectiveness of the backflush technique in reducing cycle time without carryover of the black tea matrix. 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 backflushing, excess column bleed and heavy residues are not introduced into the MSD, thereby reducing ion source contamination.

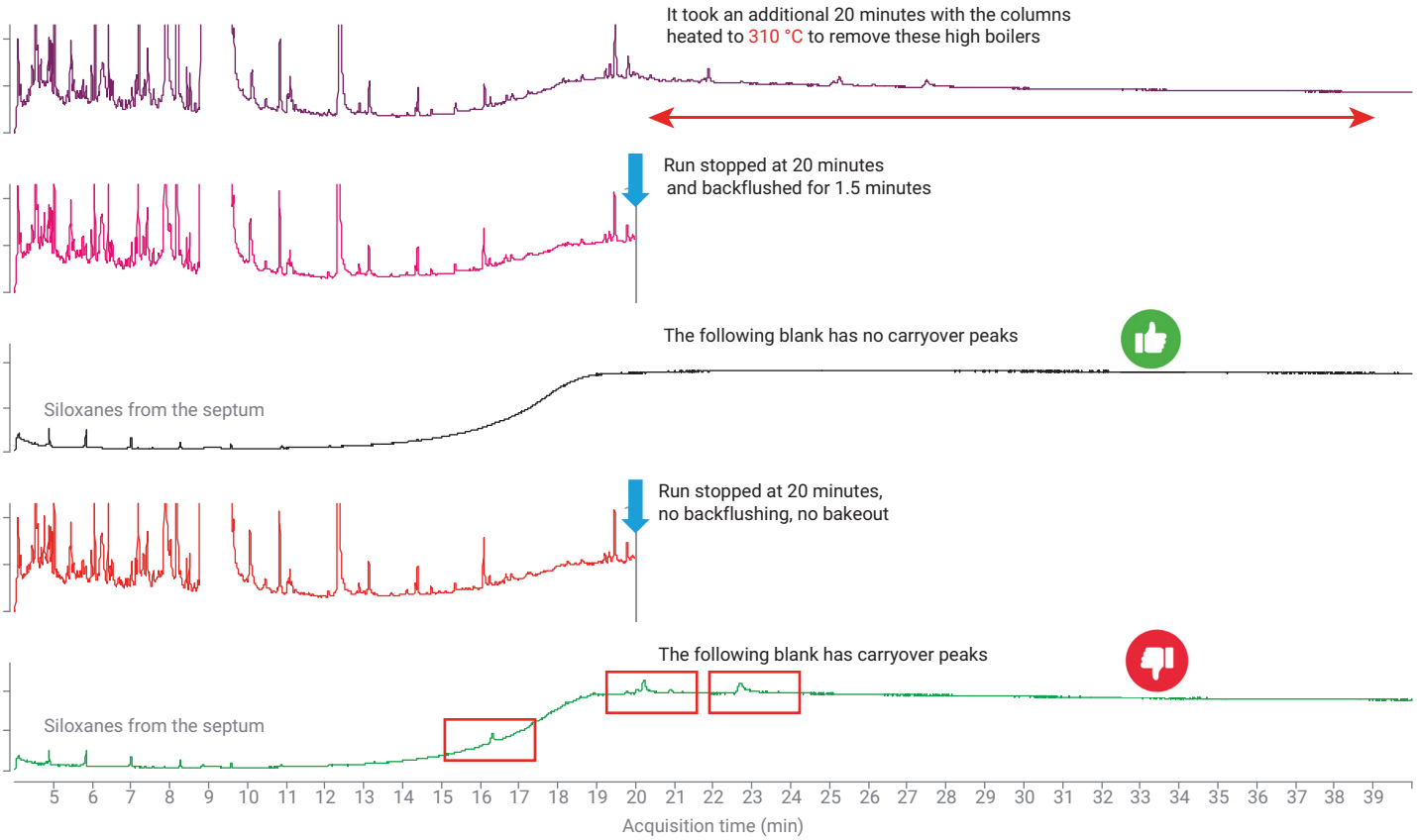


Figure 6. TIC Scan chromatograms of black tea extract, followed by analysis of an instrument blank with: column bake-out, with backflush, and without backflush or bake-out.

The backflush setup process has been simplified with the introduction of new tools that allow for making a capillary flow technology (CFT) connection with ease. These tools include the gold-plated flexible metal ferrules (part number G2855-28501) and the GC column installation preswaging tool for Flexible Metal ferrules into Capillary Flow Technology devices (part number G3440-80227)—shown in Figure 7.

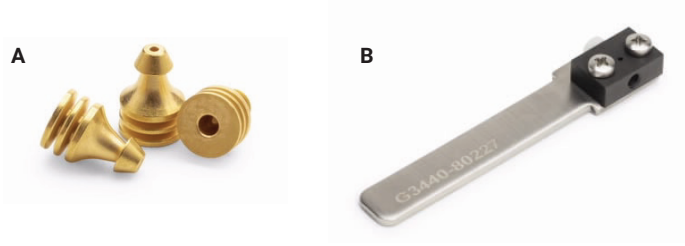


Figure 7. Flexible metal ferrules (part number G2855-28501) (A) and the GC column installation preswaging tool for Flexible Metal ferrules into Capillary Flow Technology devices (part number G3440-80227) (B).

Additionally, MassHunter Acquisition 13.0 for GC/MS provides intuitive guides for backflushing setup and review. Figure 8 shows the backflush overview tab in the GC Method Editor in MassHunter Acquisition 13.0 for GC/MS.

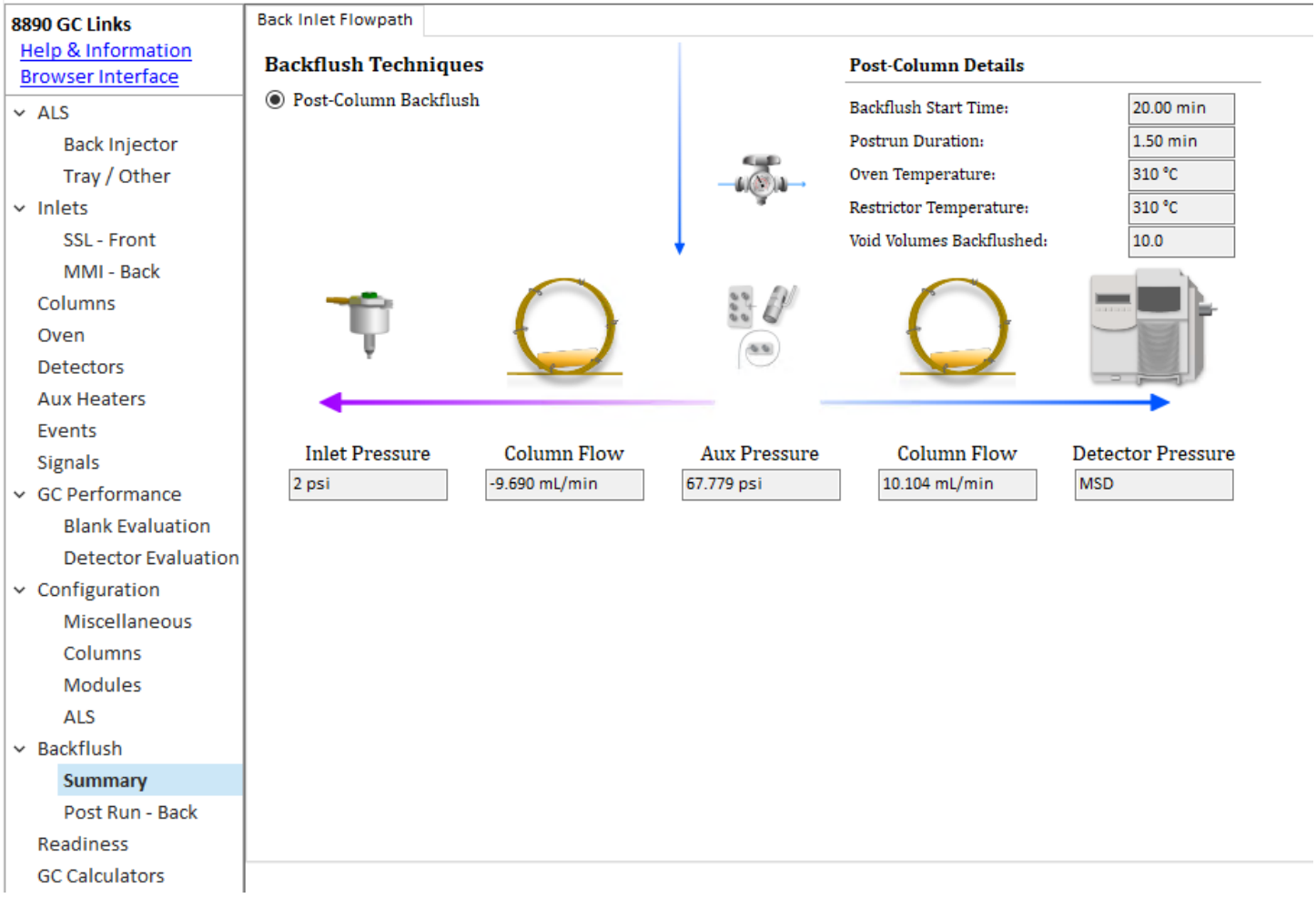


Figure 8. Backflush summary in Agilent MassHunter Acquisition 13.0 for GC/MS.

GC injection optimization: Efficiently volatilizing the sample in the GC inlet is an essential component of successful GC/MS analysis. Various sample introduction techniques are aimed at preserving thermally labile and active compounds. In this work, cold splitless and solvent vent injection modes were evaluated.

As shown on the left in Figure 9, the use of solvent vent mode for analyzing black tea extract resulted in very large caffeine carryover into the subsequent analyses. To reduce caffeine carryover, cold splitless injection mode was used (Figure 9, at right). Increase of the splitless purge time to 3 minutes resulted in enhanced method sensitivity without deteriorating the chromatographic peak shape for the targets.

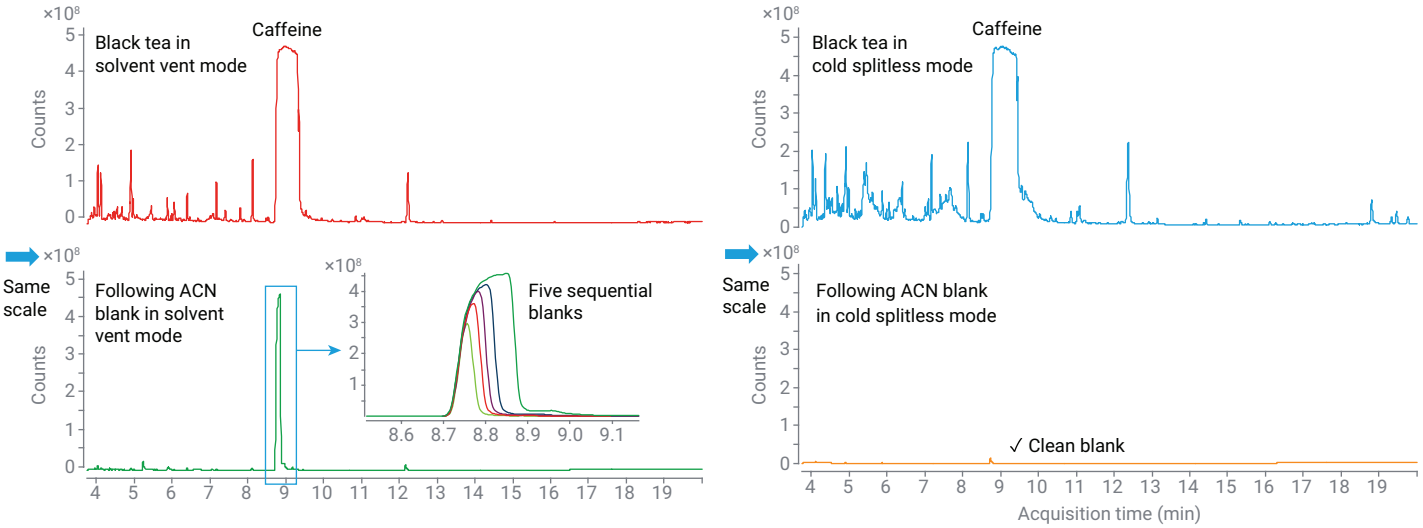


Figure 9. Injection optimization for analyzing black tea: cold splitless (on the right) reduces carryover of caffeine compared to solvent vent mode (on the left).

HES 2.0: Novel electron ionization (EI) source technology

Equipped with the novel HES 2.0 EI source, the 7010D demonstrated sensitivity that allows for ultra-trace level detection when analyzing pesticides. The new HES 2.0 ion source is equipped with a novel dipolar RF lens that redirects the carrier gas ions and, as a result, enables improved system robustness and unparalleled analytical sensitivity.

Figure 10 shows MRM chromatograms for selected pesticides at 0.01 ppb in black tea extract. The overlaid chromatograms show repeatability over seven replicate injections, and the response RSD% as a measure of precision. Appendix Table 1 shows the LOQs for all analyzed pesticides. LOQs as low as 0.01 ppb were observed for 34% of the targets, at or below 0.1 ppb for 74% of compounds, and below 2 ppb for 96%. The number of compounds expressed in percent, with their respective LOQs, are plotted in Figure 11.

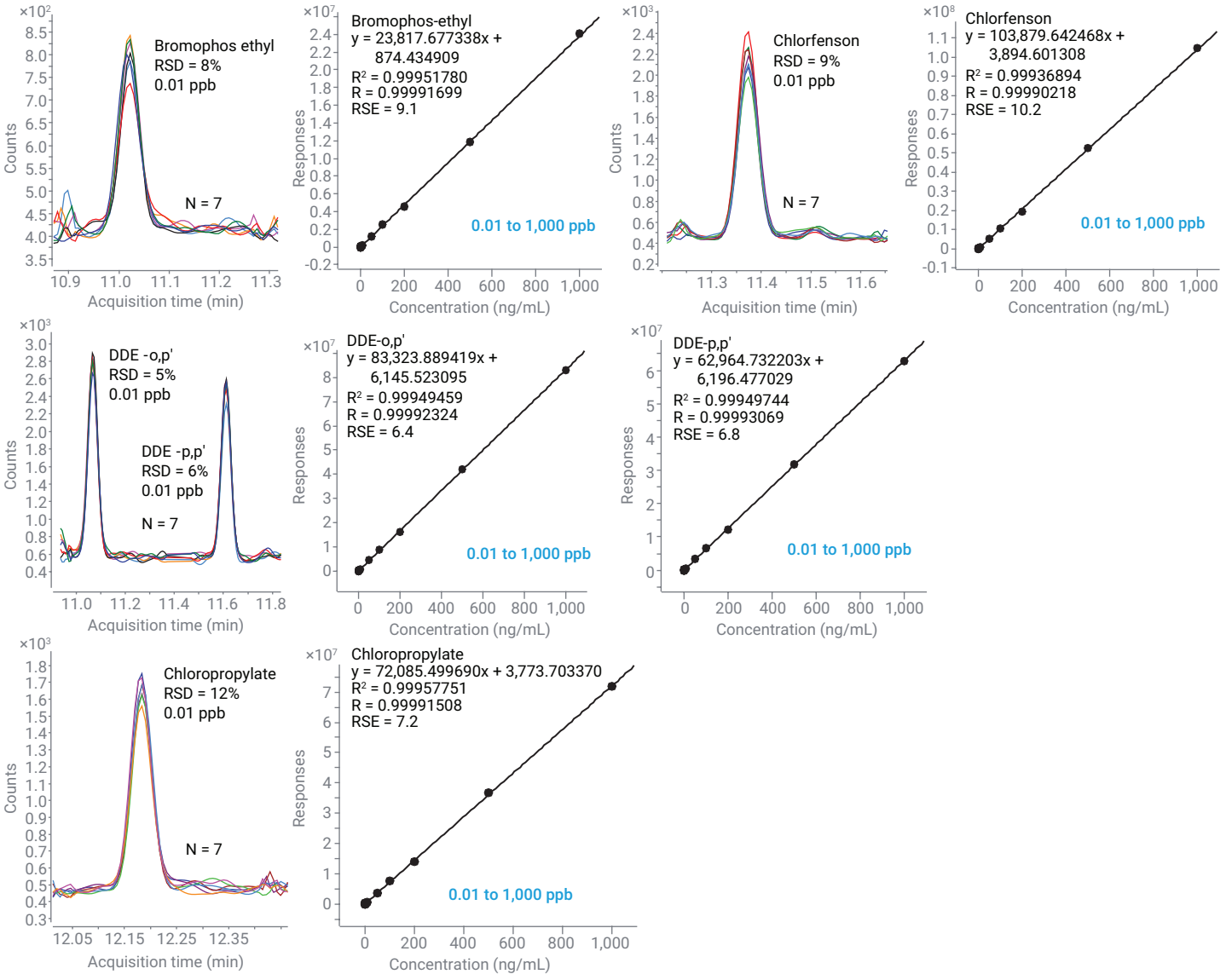


Figure 10. MRM chromatograms with seven replicate injections for the selected pesticides at the LOQ of 0.01 ppb in black tea extract and their calibration curves.

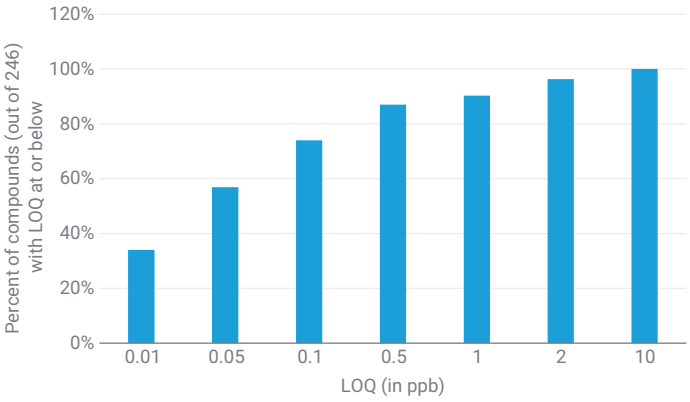


Figure 11. Percentage of compounds with their respective LOQ levels (in ppb) in black tea extract.

Figure 10 also shows the matrix-matched calibration performance in black tea extract with excellent linearity maintained over five orders of magnitude, ranging from 0.01 to 1,000 ppb. All calibration curves were inspected, and if needed, were trimmed to comply with SANTE 11312/2021 guidelines.[2] Appendix Table 1 provides information on calibration ranges and quality of calibration fit for all compounds. The R^2 correlation coefficient for all targets was > 0.99. The RSE was used as an additional criterion for demonstrating the calibration curve quality. The RSE provides an improved criterion for evaluation of calibration curves, as it is consistent for evaluation of all curve fitting types.[9] In this work, the calibration curves for all compounds had RSE values below 20.

For the compounds for which quadratic calibration fit was used, a linear calibration curve fit can be used instead by narrowing the calibration range. For example, oxyfluorfen could be calibrated over five orders of magnitude, from 0.01 to 1,000 ppb using quadratic calibration fit with R^2 = 0.9995 and RSE = 14. Alternatively, a linear calibration fit could be applied over a calibration range of 0.01 to 500 ppb with R^2 = 0.9960 and RSE = 26. The selection of the calibration curve fit was guided by the lower RSE value.

Some pesticides are known to present a particular challenge for analysis. As stated in the EURL Analytical Observation Report[10], captan and folpet are analytically among the most challenging pesticides due to their nonamenability to LC/TQ, and their tendency to degrade both in solution as well as in the GC inlet. Figure 12 demonstrates that captan and folpet could be quantitated with great precision at LOQs as low as 2 and 0.5 ppb, respectively. Freshly diluted standard, acidified sample extracts, and optimized injection conditions with cold splitless injection were key to achieving high recoveries and precision in analyzing captan and folpet. Deltamethrin, a synthetic pyrethroid, elutes at the end of the chromatographic run and is also known to be difficult for GC/MS analysis.[11] As shown in Figure 12, deltamethrin could be reliably quantitated down to 0.5 ppb using the developed method. Other compounds shown in Figure 12 include organochlorine pesticides, aldrin, dieldrin, and endrin, and the two most widely used multipurpose pyrethroids, cypermethrin and cyfluthrin, quantitated with great precision and excellent linearity over a wide dynamic range.

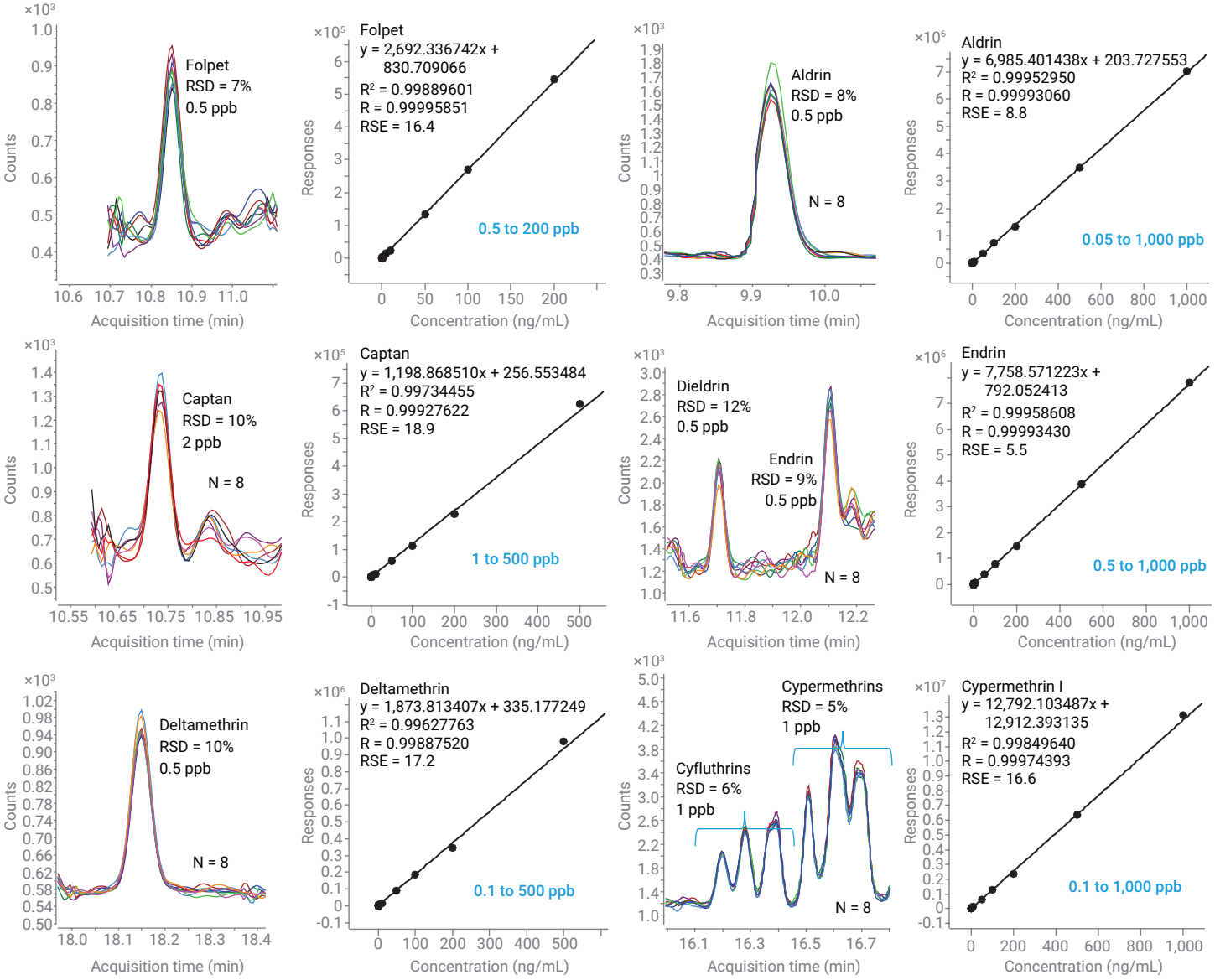


Figure 12. MRM chromatograms with eight replicate injections for the selected challenging pesticides. Included are LOQ levels and their calibration curves.

Recovery and precision

To validate the complete workflow solution and ensure that enhanced matrix cleanup did not have a negative impact on pesticide recovery, a study aimed at recovery and precision evaluation was performed. Two concentrations were selected for the study (10 and 50 ng/g) in dry black tea, resulting in 2 and 10 ppb in the final extract due to the 5x dilution factor. Figure 13 shows target results at 10 and 50 ng/g in black tea, demonstrating the acceptable recoveries achieved for the majority of pesticides, even for the common problematic pesticides such as planar and labile.

Longevity and maximized throughput with confidence

The ruggedness of the analysis was demonstrated by analyzing a challenging black tea extract spiked with pesticides at 2 ppb. The area of the analyte response was monitored over 800 consecutive injections. Analyte response, normalized by the internal standards (ISTD), remained consistent over 800 injections that spanned over 400 hours of continuous running with RSDs < 20% for 176 compounds. Figure 14 shows the response for 60 compounds, normalized by the ISTD and by the average response for each analyte.

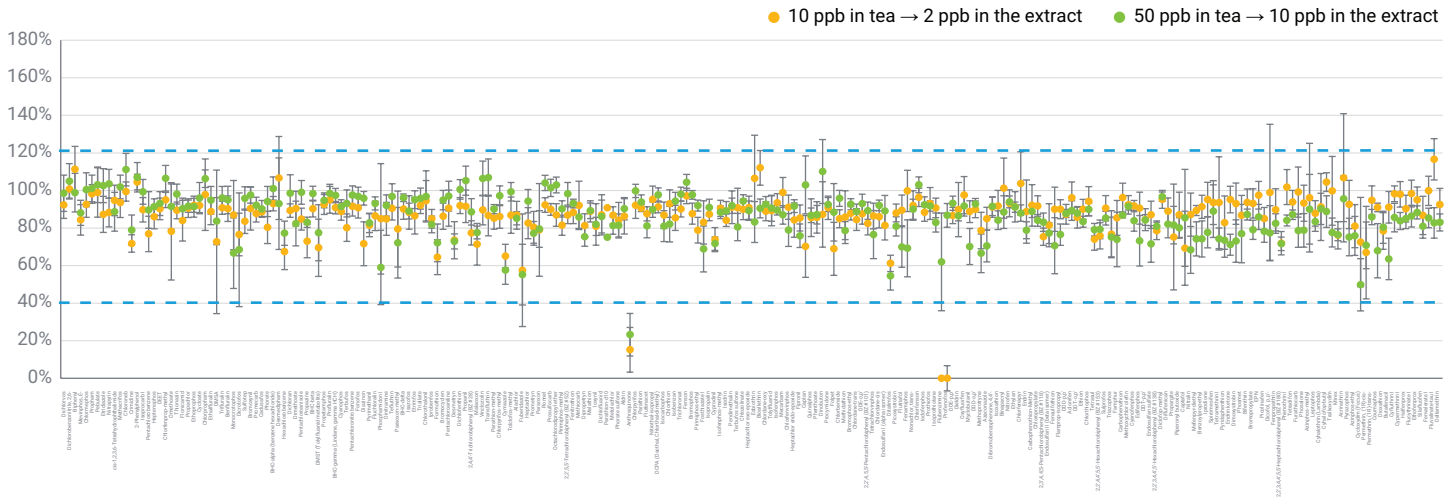


Figure 13. Pesticide recoveries in black tea at 10 and 50 ppb shown for all 244 pesticides.

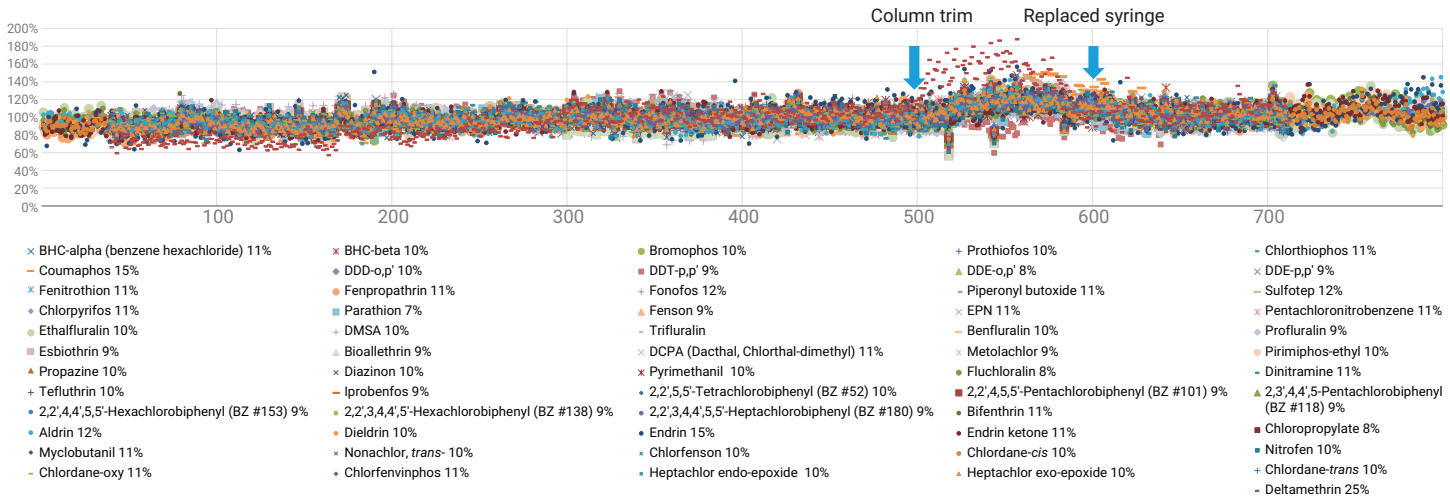


Figure 14. Stability of the peak area for pesticides spiked at 2 ppb into black tea extract, normalized by the ISTD and the average response, over 800 consecutive injections with the Agilent 8890 GC and 7010D GC/TQ systems.

The graph shows that analyte responses were stable and within 80 to 120% throughout the entire study that lasted over 17 days of continuous analysis. The RSDs for each of the target responses are shown in the legend in Figure 14, with most of them below 12%. The absolute responses in terms of peak areas also remained consistent throughout the longevity study. For example, the RSDs on the peak areas over 800 injections for early-eluting BHC-beta, mid-range eluting fenson, and late-eluting coumaphos were 9%, 10%, and 16%, respectively.

The maintenance performed during the robustness testing involved septum and liner replacement every 100 injections. With the midcolumn backflush configuration and the use of the temperature-programmed MMI inlet, inlet liner and septum replacement could be performed in under four minutes, providing a productivity boost to the workflow.

Two inches of the GC column head were trimmed after 500 injections. The use of the backflushing allowed for a substantial increase in the number of injections before column head maintenance was needed when analyzing a complex black tea extract. Similar to GC inlet maintenance, column trimming could be performed efficiently in a short amount of time (5 to 10 minutes) and did not require MS cool-down and venting due to the midcolumn configuration coupled with the temperature-programmed MMI.

The autoinjector syringe was replaced after 600 injections in the longevity study, as noted in Figure 14, with a total of 1,000 injections made with the syringe. The decision to replace the syringe was driven by the decreased measurement precision resulting from a higher variability in the target and ISTD responses. The replacement procedure was performed as guided by the user manual for the 7693A ALS.[12] The precision of measurements was restored after the syringe replacement. As a result, the graph in Figure 14 shows an increased response variability between 500 and 600 injections. This effect was particularly pronounced for deltamethrin, which can present a challenge for achieving good precision at low concentrations. Washing the syringe needle support foot is an additional autoinjector maintenance procedure to consider when analyzing challenging samples to minimize carryover and ensure precision.

It is of note that there was no need to perform GC inlet or MS source cleaning during the entire study, which spanned over 1,000 injections, including the calibration assessment and precision and recovery studies.

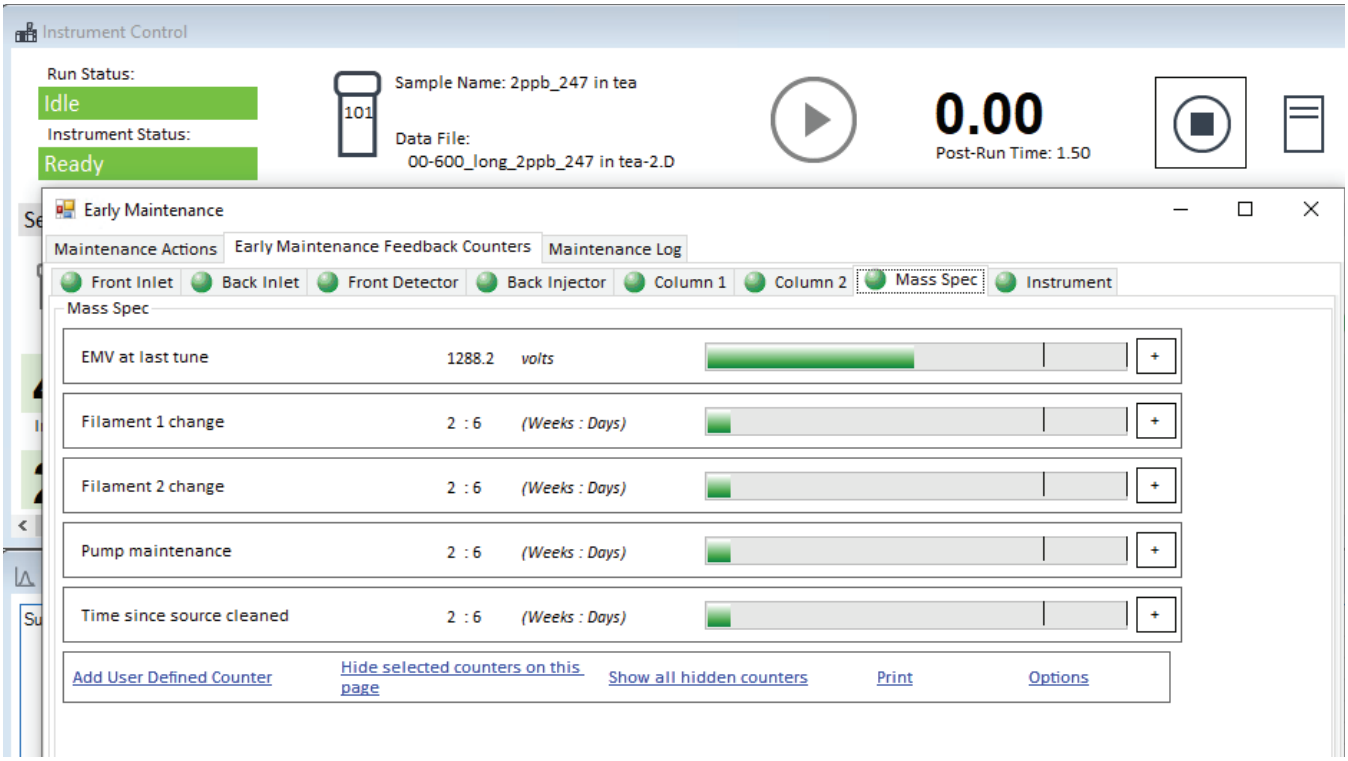
The exceptional method ruggedness shown in this work was achieved by:

- Following the key practices to successful pesticide analysis outlined in this application note and in another application note[7]
- Performing effective sample preparation and cleanup
- Using the state-of-the art GC and MS technology in the 8890 and 7010D GC/TQ systems

GC/TQ intelligence and new software functionality

The health and status of the GC/TQ system was continuously monitored though the longevity study by using the Early Maintenance Feedback functionality in MassHunter Acquisition 13.0 for GC/MS. Figure 15A shows a screenshot of the MS health status, featuring the electron multiplier (EM) voltage at last tune, filament age, pump maintenance schedule, and time since the source was cleaned. The dashboard allows for daily tracking for essential maintenance procedures and reminds the user to perform maintenance on time. In addition to the dashboard view, the built-in intelligent functionality in the 7010D GC/TQ system allows for plotting tune-related parameters over time to track the EI source health and performance. The plot for the EM voltage is shown in Figure 15B. The routine tune check procedures, which could be built into the sequence table via keywords, are helpful in guiding when the EM gain curve needs to be updated. This procedure allows for adjusting the EM voltage to maintain a stable response while not altering tune parameters and ion ratio, maintaining MS tune and method calibration validity.

A



B

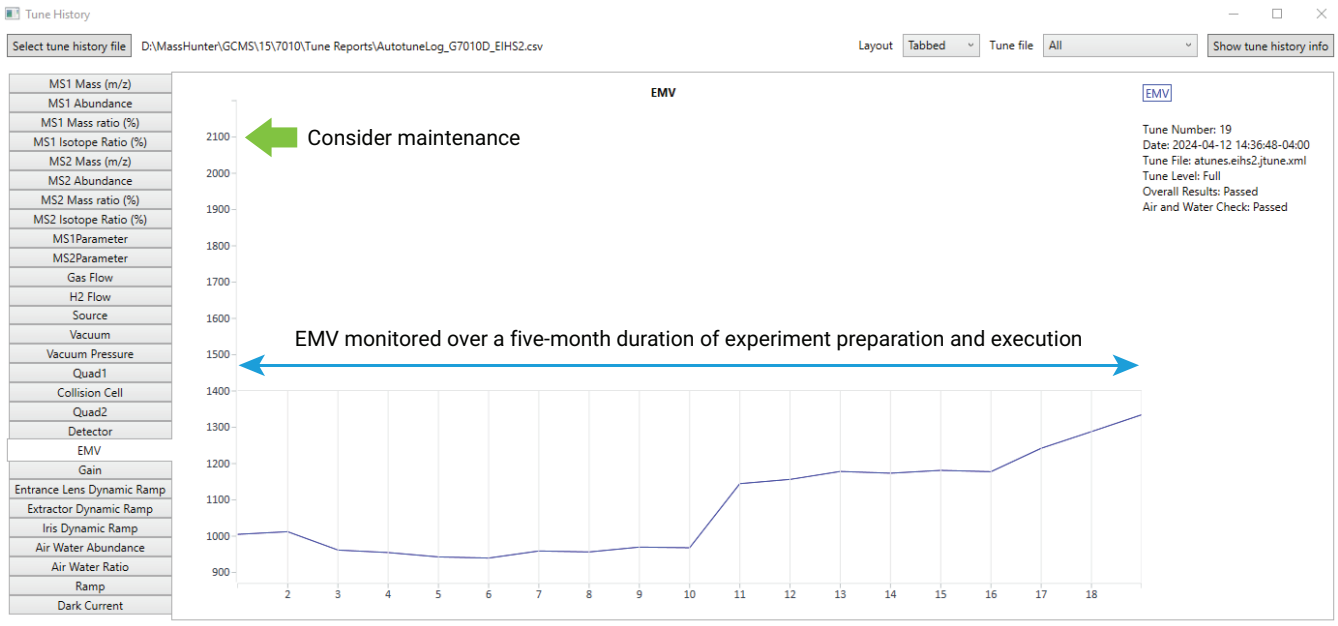


Figure 15. The early maintenance dashboard for GC/TQ (A) and the EM voltage plot for the tune history (B) shown in Agilent MassHunter Acquisition 13.0 for GC/MS.

Conclusion

This application note presents a workflow solution for analyzing pesticides in black tea with the new 7010D GC/TQ, allowing for the quantitation of 246 pesticide residues at trace levels with LOQs as low as 0.01 ppb for 34% of the targets, at or below 0.1 ppb for 74% of compounds, and below 2 ppb for 96%. Matrix-matched calibration allowed for excellent accuracy over a wide dynamic range, spanning up to five orders of magnitude over the 0.01 to 1,000 ppb range in a complex black tea extract. Method ruggedness was demonstrated through maintaining measurement accuracy with good precision (RSDs < 20% for 176 compounds) for black tea extract spiked at 2 ppb sequentially analyzed over 800 runs and spanning over 17 days of continuous analysis. The key components for a robust workflow included a combination of efficient sample preparation and cleanup, the Agilent 8890 GC hardware, functionality, and GC supplies, the novel EI source technology with HES 2.0, and lastly, the built-in GC/TQ intelligence and new software functionality.

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Appendix Table 1. Calibration performance for 246 pesticides in black tea using the Agilent 7010D GC/TQ equipped with the Agilent High-Efficiency Source (HES) 2.0.

Name	RT	Transition	Calibration Range (ppb)			CF	CF R^2	Relative Standard Error
Methamidophos	4.520	141.0 → 64.0	0.1	–	1,000	Linear	0.9994	7.5
Dichlorvos	4.643	184.9 → 93.0	0.05	–	1,000	Linear	0.9988	11.2
Dichlorobenzonitrile, 2,6-	5.210	171.0 → 100.0	0.01	–	1,000	Linear	0.9990	10.4
Biphenyl	5.390	154.1 → 153.1	0.5	–	1,000	Quadratic	0.9991	11.8
Mevinphos, E-	5.578	127.0 → 94.9	0.5	–	1,000	Linear	0.9994	7.9
Acephate	5.679	136.0 → 94.0	5	–	1,000	Quadratic	0.9990	8.1
Chlormephos	5.687	153.9 → 121.1	0.5	–	1,000	Linear	0.9979	5.0
Propham	5.740	178.9 → 137.1	1	–	1,000	Linear	0.9986	9.6
Pebulate	5.774	128.0 → 57.1	0.5	–	1,000	Linear	0.9983	6.6
Etridiazole	5.798	213.1 → 185.0	0.1	–	500	Linear	0.9986	10.7
Nitrapyrin	5.804	194.0 → 158.0	0.05	–	1,000	Quadratic	0.9994	8.7
cis-1,2,3,6-Tetrahydrophthalimide	5.956	151.1 → 80.0	0.1	–	1,000	Linear	0.9994	6.1
Methacrifos	6.027	207.9 → 180.1	0.05	–	1,000	Quadratic	0.9996	11.4
Chloroneb	6.110	191.0 → 113.0	0.01	–	1,000	Linear	0.9995	8.2
Crimidine	6.212	170.9 → 142.1	0.1	–	1,000	Linear	0.9994	10.4
2-Phenylphenol	6.213	169.1 → 115.1	0.5	–	1,000	Linear	0.9995	5.6
Isoprocarb I	6.295	136.0 → 121.1	0.5	–	1,000	Linear	0.9994	9.3
Pentachlorobenzene	6.311	251.9 → 217.0	0.01	–	1,000	Linear	0.9984	11.4
Heptenophos	6.585	124.0 → 89.0	0.01	–	500	Linear	0.9990	12.5
DEET	6.600	191.0 → 190.0	0.5	–	1,000	Linear	0.9981	11.5
Chlorfenprop-methyl	6.696	165.0 → 102.0	0.01	–	1,000	Linear	0.9989	14.0
Omethoate	6.773	110.0 → 47.0	0.1	–	1,000	Quadratic	0.9997	8.8
Thionazin	6.781	143.0 → 79.0	0.1	–	1,000	Quadratic	0.9998	9.5
Flonicamid	6.859	173.9 → 68.9	0.01	–	1,000	Linear	0.9994	11.5
Propachlor	6.865	176.1 → 57.1	0.05	–	1,000	Quadratic	0.9997	8.5
Ethoprophos	6.996	157.9 → 97.0	0.1	–	1,000	Quadratic	0.9997	8.2
Cycloate	7.017	154.1 → 83.1	0.05	–	1,000	Linear	0.9991	16.2
Chlorpropham	7.080	171.0 → 127.1	0.05	–	500	Linear	0.9993	13.7
Ethalfluralin	7.109	275.9 → 202.1	0.05	–	1,000	Quadratic	0.9997	11.4
DMSA	7.169	200.0 → 108.0	2	–	1,000	Quadratic	0.9963	17.5
Trifluralin	7.217	306.1 → 264.0	0.05	–	1,000	Quadratic	0.9997	11.8
Benfluralin	7.251	292.0 → 264.0	0.1	–	1,000	Quadratic	0.9996	12.0
Monocrotophos	7.258	192.0 → 127.0	0.1	–	1,000	Quadratic	0.9998	7.4
Dicrotofos	7.264	193.0 → 127.1	0.5	–	1,000	Quadratic	0.9998	10.1
Sulfotep	7.349	321.8 → 201.9	0.05	–	1,000	Quadratic	0.9997	10.4
Bromoxynil	7.395	276.8 → 88.0	0.05	–	1,000	Quadratic	0.9997	7.1
Promecarb	7.399	135.1 → 115.1	2	–	1,000	Linear	0.9967	16.1
Cadusafos	7.405	158.8 → 97.0	0.01	–	1,000	Quadratic	0.9997	13.1
Phorate	7.475	121.0 → 47.0	0.5	–	1,000	Linear	0.9983	11.1
BHC-alpha (Benzene Hexachloride)	7.609	218.9 → 183.0	0.01	–	1,000	Quadratic	0.9998	9.9
Desmedipham	7.690	181.0 → 122.0	2	–	1,000	Linear	0.9985	11.8
Hexachlorobenzene	7.741	283.8 → 213.9	0.01	–	1,000	Quadratic	0.9996	10.7
Dichloran	7.771	160.1 → 124.1	0.01	–	1,000	Linear	0.9996	6.7
Dimethoate	7.781	87.0 → 46.0	0.01	–	1,000	Linear	0.9997	11.8
Pentachloroanisole	7.797	279.9 → 236.8	0.05	–	1,000	Linear	0.9993	8.0

Name	RT	Transition	Calibration Range (ppb)			CF	CF R^2	Relative Standard Error
Propazine	7.933	229.1 → 58.1	0.01	–	1,000	Linear	0.9988	13.5
BHC-beta	8.010	218.9 → 183.1	0.01	–	1,000	Linear	0.9994	12.2
DMST (Tolylfluanid Metabolite)	8.032	214.0 → 106.0	2	–	1,000	Quadratic	0.9954	17.7
Propetamphos	8.079	138.0 → 64.0	0.1	–	1,000	Linear	0.9988	6.9
Profluralin	8.087	318.1 → 199.1	0.05	–	1,000	Quadratic	0.9997	12.7
BHC-gamma (Lindane, Gamma HCH)	8.119	216.9 → 181.0	0.01	–	1,000	Linear	0.9981	15.6
Cyanophos	8.135	242.9 → 109.0	0.05	–	1,000	Linear	0.9993	12.8
Terbufos	8.137	230.9 → 129.0	0.1	–	1,000	Linear	0.9994	12.5
Pentachloronitrobenzene	8.195	141.9 → 106.9	0.01	–	1,000	Quadratic	0.9996	9.4
Fonofos	8.223	246.1 → 109.0	0.01	–	500	Linear	0.9981	11.9
Diazinon	8.264	137.1 → 84.0	0.05	–	1,000	Quadratic	0.9997	17.0
Pyrimethanil	8.269	198.0 → 118.1	0.01	–	500	Linear	0.9990	12.6
Fluchloralin	8.299	325.8 → 62.9	0.05	–	500	Quadratic	0.9995	13.5
Phosphamidon I	8.339	127.0 → 95.0	0.5	–	500	Linear	0.9981	17.4
Dinitramine	8.382	260.7 → 241.0	0.05	–	1,000	Quadratic	0.9997	11.6
Tefluthrin	8.400	177.1 → 127.1	0.01	–	1,000	Linear	0.9986	16.0
Paraoxon-methyl	8.411	229.9 → 106.1	0.05	–	500	Linear	0.9947	18.3
BHC-delta	8.489	219.0 → 183.1	0.5	–	1,000	Quadratic	0.9998	16.5
Isazofos	8.504	256.9 → 162.0	0.01	–	1,000	Quadratic	0.9997	13.8
Etrimfos	8.523	292.0 → 153.1	0.01	–	500	Linear	0.9985	16.7
Triallate	8.540	268.0 → 184.1	0.05	–	1,000	Linear	0.9995	10.8
Chlorothalonil	8.568	265.9 → 168.0	0.1	–	500	Quadratic	0.9971	10.7
Iprobenfos	8.673	203.9 → 91.0	0.01	–	1,000	Linear	0.9986	13.9
Formothion	8.763	124.9 → 47.0	0.1	–	1,000	Quadratic	0.9997	16.0
Bromocyclen	8.764	271.8 → 236.9	0.1	–	1,000	Linear	0.9996	8.6
Pentachloroaniline	8.897	158.0 → 123.0	0.5	–	1,000	Linear	0.9986	14.7
Desmetryn	8.916	213.0 → 58.1	0.05	–	1,000	Linear	0.9972	11.7
Dichlofenthion	8.961	279.0 → 223.0	0.01	–	500	Linear	0.9975	11.4
Propanil	8.980	161.0 → 99.0	0.01	–	1,000	Linear	0.9983	16.8
2,4,4'-Trichlorobiphenyl (BZ #28)	9.030	256.0 → 186.0	0.05	–	1,000	Linear	0.9981	11.7
Malaoxon	9.103	126.9 → 99.0	2	–	1,000	Quadratic	0.9989	15.0
Vinclozolin	9.128	187.0 → 124.0	0.05	–	1,000	Linear	0.9962	15.8
Transfluthrin	9.129	163.1 → 143.1	0.1	–	1,000	Linear	0.9972	14.3
Parathion-methyl	9.151	262.9 → 109.0	0.5	–	500	Quadratic	0.9991	18.2
Chlorpyrifos-methyl	9.151	288.0 → 93.0	0.05	–	1,000	Quadratic	0.9995	12.0
Cymiazole	9.213	218.0 → 144.1	2	–	1,000	Linear	0.9986	12.3
Tolclofos-methyl	9.242	267.0 → 93.0	0.5	–	1,000	Linear	0.9987	12.8
Alachlor	9.280	237.0 → 160.1	1	–	1,000	Linear	0.9969	12.2
Fuberidazole	9.306	184.0 → 156.2	5	–	500	Linear	0.9921	19.5
Heptachlor	9.330	271.7 → 236.9	0.1	–	200	Linear	0.9990	15.4
Prometryn	9.339	241.0 → 58.2	5	–	200	Quadratic	0.9967	19.4
Paraoxon	9.383	148.9 → 119.0	50	–	1,000	Quadratic	0.9982	11.3
Ronnel	9.411	286.9 → 272.0	1	–	1,000	Linear	0.9989	11.7
Prosulfocarb	9.424	251.0 → 128.2	0.1	–	1,000	Quadratic	0.9995	14.9
Octachlorodipropyl Ether	9.431	129.9 → 94.9	0.5	–	1,000	Quadratic	0.9996	10.0
Pirimiphos-methyl	9.610	290.0 → 125.0	0.01	–	1,000	Quadratic	0.9996	9.3

Name	RT	Transition	Calibration Range (ppb)			CF	CF R^2	Relative Standard Error
2,2',5,5'-Tetrachlorobiphenyl (BZ #52)	9.617	289.9 → 219.9	0.01	–	1,000	Linear	0.9997	11.9
Fenitrothion	9.622	125.1 → 47.0	0.01	–	1,000	Linear	0.9994	11.3
Methiocarb	9.628	168.0 → 109.1	2	–	1,000	Quadratic	0.9998	11.3
Dipropetryn	9.748	255.1 → 222.1	0.01	–	500	Linear	0.9982	13.5
Malathion	9.759	172.9 → 99.0	0.01	–	1,000	Quadratic	0.9997	12.1
Ioxynil	9.780	370.8 → 117.0	0.05	–	1,000	Linear	0.9982	12.2
Dichlofluanid	9.785	167.0 → 97.0	1	–	500	Quadratic	0.9991	13.8
Metolachlor	9.913	238.0 → 162.2	0.01	–	1,000	Linear	0.9993	12.5
Phorate Sulfone	9.914	199.0 → 97.0	0.1	–	500	Linear	0.9975	11.7
Aldrin	9.932	254.9 → 220.0	0.05	–	1,000	Linear	0.9995	8.8
Anthraquinone	9.941	208.0 → 152.2	0.05	–	1,000	Linear	0.9990	19.1
Chlorpyrifos	9.968	313.8 → 257.8	0.05	–	1,000	Linear	0.9994	11.7
Parathion	9.983	291.0 → 109.0	0.01	–	1,000	Linear	0.9985	15.2
Flufenacet	10.004	151.0 → 95.0	0.5	–	1,000	Linear	0.9994	11.9
Nitrothal-isopropyl	10.057	254.0 → 212.0	0.5	–	500	Linear	0.9967	16.3
DCPA (Dacthal, Chlorthal-dimethyl)	10.068	298.9 → 221.0	0.01	–	1,000	Linear	0.9993	14.1
Isocarbophos	10.114	136.0 → 69.0	0.5	–	1,000	Linear	0.9985	13.1
Chlorthion	10.156	125.1 → 47.1	0.05	–	1,000	Quadratic	0.9995	14.7
Isobenzan	10.186	274.7 → 240.0	0.1	–	1,000	Linear	0.9992	11.2
Trichloronat	10.199	296.8 → 268.9	0.01	–	1,000	Linear	0.9987	14.5
Fenson	10.210	141.0 → 77.1	0.01	–	1,000	Linear	0.9996	6.7
Bromophos	10.294	330.9 → 315.9	0.01	–	1,000	Linear	0.9986	15.8
Pirimiphos-ethyl	10.294	318.1 → 166.1	0.05	–	1,000	Linear	0.9977	14.8
Fosthiazate I	10.299	195.0 → 103.0	0.05	–	1,000	Quadratic	0.9997	12.1
Isopropalin	10.350	280.1 → 238.1	0.01	–	500	Linear	0.9975	16.4
Cyprodinil	10.413	225.2 → 224.3	0.05	–	1,000	Linear	0.9990	14.4
Isofenphos-methyl	10.420	199.0 → 121.0	0.01	–	1,000	Quadratic	0.9995	9.9
Isodrin	10.442	193.0 → 123.0	0.05	–	1,000	Linear	0.9985	10.9
Pendimethalin	10.522	251.8 → 162.2	0.05	–	1,000	Quadratic	0.9995	11.5
Terbufos Sulfone	10.573	264.0 → 199.0	0.05	–	1,000	Quadratic	0.9996	8.7
Chlozolinate	10.586	186.0 → 109.0	0.1	–	1,000	Quadratic	0.9995	8.6
Heptachlor Exo-epoxide	10.616	354.8 → 264.9	0.01	–	1,000	Linear	0.9993	15.3
Esbiothrin	10.622	123.0 → 93.0	2	–	1,000	Linear	0.9975	15.2
Bioallethrin	10.629	123.0 → 81.0	2	–	1,000	Linear	0.9924	12.2
Chlordane-oxy	10.629	114.9 → 51.1	0.5	–	1,000	Linear	0.9996	3.8
Tolylfluanid	10.639	238.0 → 137.0	0.05	–	1,000	Quadratic	0.9996	14.6
Isofenphos	10.674	212.9 → 121.1	0.01	–	1,000	Quadratic	0.9994	10.7
Mecarbam	10.675	130.9 → 86.0	0.5	–	1,000	Quadratic	0.9992	13.0
Chlorfenvinphos	10.679	266.9 → 159.0	0.01	–	200	Linear	0.9986	11.0
Heptachlor Endo-epoxide	10.683	135.0 → 99.0	0.5	–	1,000	Linear	0.9993	6.6
Fipronil	10.698	366.8 → 212.8	0.05	–	1,000	Quadratic	0.9997	8.8
Captan	10.738	149.0 → 70.0	1	–	500	Linear	0.9973	18.9
Quinalphos	10.738	298.0 → 156.0	0.01	–	500	Quadratic	0.9992	17.6
Phenthoate	10.741	274.0 → 125.0	0.01	–	1,000	Quadratic	0.9988	8.1
Dinobuton	10.743	211.0 → 163.0	0.5	–	1,000	Quadratic	0.9999	9.0
Procymidone	10.850	282.8 → 96.0	0.01	–	1,000	Linear	0.9996	8.3

Name	RT	Transition	Calibration Range (ppb)			CF	CF R^2	Relative Standard Error
Folpet	10.851	259.8 → 130.1	0.5	–	200	Linear	0.9989	16.4
Chlorbenside	10.904	125.0 → 89.0	0.01	–	1,000	Linear	0.9993	8.2
Methidathion	11.007	125.0 → 47.0	0.5	–	1,000	Linear	0.9993	16.2
Bromophos-ethyl	11.022	358.7 → 302.8	0.01	–	1,000	Linear	0.9995	9.1
Chlordane-*trans*	11.024	271.7 → 236.9	0.05	–	1,000	Linear	0.9995	8.4
DDE-o,p'	11.073	246.0 → 176.2	0.01	–	1,000	Linear	0.9995	6.4
2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	11.111	325.9 → 255.9	0.01	–	1,000	Linear	0.9995	7.7
Tetrachlorvinphos	11.166	329.0 → 108.9	0.01	–	1,000	Linear	0.9972	16.9
Chlordane-*cis*	11.288	372.8 → 265.9	0.01	–	1,000	Linear	0.9994	15.4
Endosulfan I (Alpha Isomer)	11.290	194.9 → 160.0	0.1	–	1,000	Linear	0.9993	14.8
Ditalimfos	11.299	242.9 → 148.1	0.05	–	500	Linear	0.9977	14.8
Picoxystrobin	11.307	145.0 → 102.1	0.05	–	1,000	Linear	0.9994	14.1
Flutriafol	11.335	123.1 → 75.1	0.05	–	1,000	Linear	0.9995	11.9
Fenamiphos	11.360	303.0 → 154.0	0.1	–	500	Linear	0.9959	17.1
Nonachlor, *trans*-	11.369	406.8 → 299.8	0.05	–	1,000	Linear	0.9993	11.9
Chlorfenson	11.374	175.0 → 111.0	0.01	–	1,000	Linear	0.9994	10.2
Iodofenphos	11.466	376.8 → 361.8	0.05	–	1,000	Quadratic	0.9998	12.4
Prothiofos	11.488	308.9 → 238.9	0.05	–	500	Linear	0.9975	16.8
Isoprothiolane	11.498	162.1 → 85.0	0.01	–	1,000	Linear	0.9986	13.4
Flubenzimine	11.538	186.0 → 69.0	2	–	500	Quadratic	0.9974	10.5
Profenofos	11.544	207.9 → 63.0	0.1	–	200	Linear	0.9984	12.4
DDE-p,p'	11.613	246.1 → 176.2	0.01	–	1,000	Linear	0.9995	6.8
Dieldrin	11.713	262.9 → 193.0	0.5	–	1,000	Linear	0.9990	13.8
Oxyfluorfen	11.721	252.0 → 146.0	0.01	–	1,000	Quadratic	0.9995	14.0
Myclobutanil	11.750	179.0 → 125.1	0.01	–	1,000	Quadratic	0.9995	12.6
DDD-o,p'	11.783	235.0 → 165.1	0.01	–	1,000	Linear	0.9993	12.7
Methoprotryne	11.788	256.0 → 212.1	0.01	–	1,000	Quadratic	0.9996	12.6
Azaconazole	11.865	217.0 → 173.1	0.01	–	1,000	Linear	0.9994	11.4
Dibromobenzophenone, 4,4'-	11.913	340.0 → 183.0	0.05	–	1,000	Quadratic	0.9997	7.6
Isoxathion	11.941	313.0 → 177.0	0.05	–	1,000	Quadratic	0.9993	14.9
Binapacryl	12.003	100.0 → 82.0	5	–	1,000	Quadratic	0.9988	18.9
Nitrofen	12.011	282.9 → 253.0	0.01	–	500	Linear	0.9963	14.5
Ethylan	12.041	223.1 → 193.1	0.05	–	500	Linear	0.9976	14.7
Chlorfenapyr	12.051	328.0 → 247.0	0.5	–	1,000	Linear	0.9983	14.8
Endrin	12.108	262.8 → 193.0	0.5	–	1,000	Linear	0.9996	5.5
Carbophenothion-methyl	12.167	125.0 → 47.0	0.1	–	1,000	Linear	0.9986	19.2
Chloropropylate	12.187	139.0 → 75.0	0.01	–	1,000	Linear	0.9996	7.2
2,3',4,4',5-Pentachlorobiphenyl (BZ #118)	12.222	325.9 → 255.9	0.01	–	1,000	Linear	0.9996	7.6
Endosulfan II (Beta Isomer)	12.274	206.9 → 172.0	0.1	–	1,000	Quadratic	0.9989	13.0
Fensulfothion	12.284	293.0 → 97.0	0.01	–	1,000	Linear	0.9978	14.8
Flamprop-isopropyl	12.305	276.0 → 105.1	0.05	–	1,000	Linear	0.9991	10.4
DDD-p,p'	12.369	237.0 → 165.1	0.01	–	1,000	Linear	0.9993	13.7
Aclonifen	12.397	264.1 → 194.2	0.1	–	1,000	Quadratic	0.9995	10.3
DDT-o,p'	12.430	235.0 → 199.1	0.01	–	1,000	Linear	0.9974	19.4
Ethion	12.431	231.0 → 129.0	0.01	–	1,000	Linear	0.9962	19.9

Name	RT	Transition	Calibration Range (ppb)			CF	CF R^2	Relative Standard Error
Chlorthiophos	12.484	268.9 → 205.1	0.05	–	1,000	Linear	0.9983	13.9
Tetrasul	12.572	321.7 → 252.0	0.01	–	1,000	Linear	0.9987	11.5
2,2',4,4',5,5'-Hexachlorobiphenyl (BZ #153)	12.610	359.9 → 289.9	0.01	–	1,000	Linear	0.9992	10.9
Sulprofos	12.650	322.0 → 156.0	0.01	–	500	Linear	0.9975	12.5
Triazophos	12.662	161.2 → 134.2	1	–	500	Quadratic	0.9995	15.0
Famphur	12.810	218.0 → 109.0	2	–	1,000	Linear	0.9982	14.6
Carbophenothion	12.826	342.0 → 157.0	0.05	–	500	Linear	0.9974	14.5
Methoxychlor Olefin	12.837	308.0 → 238.0	0.01	–	1,000	Linear	0.9984	13.5
Cyanofenphos	12.906	169.0 → 77.1	0.1	–	1,000	Linear	0.9988	10.7
Edifenphos	12.940	309.9 → 172.9	0.5	–	1,000	Quadratic	0.9998	13.3
DDT-p,p'	13.027	235.0 → 165.2	0.01	–	1,000	Linear	0.9976	19.9
Endosulfan Sulfate	13.032	271.9 → 237.0	0.5	–	1,000	Quadratic	0.9997	18.2
2,2',3,4,4',5'-Hexachlorobiphenyl (BZ #138)	13.118	359.9 → 289.9	0.01	–	1,000	Linear	0.9996	6.5
Diclofop-methyl	13.284	339.9 → 252.9	0.01	–	500	Linear	0.9973	13.1
Diflufenican	13.310	266.0 → 246.1	0.01	–	1,000	Linear	0.9971	18.7
Propargite	13.327	231.0 → 135.0	0.5	–	1,000	Linear	0.9993	13.7
Piperonyl Butoxide	13.380	176.1 → 103.1	0.1	–	1,000	Quadratic	0.9995	9.0
Captafol	13.440	310.8 → 78.8	10	–	1,000	Quadratic	0.9987	19.3
Nitralin	13.551	315.9 → 274.0	0.1	–	500	Quadratic	0.9993	13.9
Mefenpyr-diethyl	13.608	253.0 → 189.0	0.01	–	500	Quadratic	0.9989	15.8
Benzoylprop-ethyl	13.699	292.0 → 105.0	0.1	–	1,000	Linear	0.9991	11.8
Iprodione	13.721	313.8 → 55.9	0.1	–	500	Linear	0.9984	12.4
Spiromesifen	13.722	272.0 → 254.2	0.1	–	500	Quadratic	0.9994	15.7
Tetramethrin I	13.814	164.0 → 77.1	5	–	1,000	Quadratic	0.9990	17.1
Pyridaphenthion	13.822	340.0 → 199.0	0.05	–	1,000	Quadratic	0.9996	12.9
Endrin Ketone	13.876	316.9 → 101.0	0.01	–	500	Quadratic	0.9993	13.6
Dimoxystrobin	13.880	205.0 → 58.0	0.1	–	1,000	Quadratic	0.9996	8.4
Phosmet	13.917	160.0 → 77.1	2	–	1,000	Quadratic	0.9993	10.6
Bifenthrin	13.922	181.2 → 165.2	0.1	–	500	Quadratic	0.9990	13.8
Bromopropylate	13.928	338.8 → 182.9	0.05	–	1,000	Quadratic	0.9993	10.7
EPN	13.935	169.0 → 77.1	0.05	–	1,000	Quadratic	0.9991	13.3
Picolinafen	13.958	376.0 → 238.1	0.01	–	200	Linear	0.9978	17.1
Bifenazate	13.975	168.1 → 61.9	10	–	1,000	Quadratic	0.9990	6.6
Dicofol, p, p'-	13.976	183.9 → 141.2	1	–	1,000	Linear	0.9972	18.8
Fenpropathrin	14.056	265.0 → 89.0	0.01	–	1,000	Quadratic	0.9996	13.5
2,2',3,4,4',5,5'-Heptachlorobiphenyl (BZ #180)	14.299	393.8 → 323.8	0.01	–	1,000	Linear	0.9992	12.2
Phenothrin I	14.399	122.9 → 81.1	0.1	–	1,000	Linear	0.9987	11.5
Tetradifon	14.424	158.9 → 111.0	0.01	–	1,000	Linear	0.9992	7.4
Furathiocarb	14.437	163.1 → 135.1	2	–	1,000	Linear	0.9992	6.1
Phosalone	14.590	182.0 → 75.0	0.05	–	500	Linear	0.9958	19.2
Azinphos-methyl	14.626	160.0 → 77.0	2	–	1,000	Quadratic	0.9993	11.4
Leptophos	14.638	171.0 → 51.0	0.05	–	1,000	Quadratic	0.9995	12.4
Cyhalothrin (Lambda)	14.698	181.1 → 152.1	5	–	1,000	Quadratic	0.9979	12.9
Cyhalofop-butyl	14.703	357.1 → 229.1	0.01	–	500	Linear	0.9958	16.1

Name	RT	Transition	Calibration Range (ppb)			CF	CF R^2	Relative Standard Error
Tralkoxydim	14.830	137.0 → 57.0	0.05	–	1,000	Linear	0.9990	7.9
Mirex	14.865	271.8 → 236.8	0.01	–	1,000	Linear	0.9994	13.5
Acrinathrin	15.045	247.0 → 68.0	1	–	1,000	Quadratic	0.9996	12.8
Pyrazophos	15.144	221.0 → 149.0	0.01	–	1,000	Quadratic	0.9994	14.1
Azinphos-ethyl	15.228	160.0 → 77.1	0.5	–	1,000	Quadratic	0.9997	12.4
Cycloxydim (Focus)	15.500	178.0 → 80.9	0.1	–	1,000	Quadratic	0.9997	8.0
Permethrin, (1R)-*cis*-	15.622	163.0 → 91.0	2	–	1,000	Quadratic	0.9978	18.4
Permethrin, (1R)-*trans*-	15.744	163.0 → 127.0	0.01	–	1,000	Linear	0.9990	12.0
Coumaphos	15.880	361.9 → 109.0	0.05	–	500	Linear	0.9972	16.0
Dioxathion	15.963	271.0 → 96.9	0.1	–	500	Linear	0.9969	19.8
Butafenacil	15.988	331.0 → 180.0	0.01	–	500	Linear	0.9973	14.4
Cyfluthrin I	16.202	163.0 → 127.0	0.5	–	1,000	Linear	0.9980	15.8
Cypermethrin I	16.510	163.0 → 127.0	0.1	–	1,000	Linear	0.9985	16.6
Halfenprox	16.565	262.9 → 169.0	0.05	–	1,000	Quadratic	0.9994	11.9
Flucythrinate I	16.725	156.9 → 107.1	0.01	–	1,000	Linear	0.9992	13.7
Ethofenprox	16.798	163.0 → 107.1	0.1	–	1,000	Linear	0.9989	14.3
Silafluofen	16.944	286.0 → 207.0	0.1	–	1,000	Quadratic	0.9995	9.7
Fenvalerate I	17.428	167.0 → 125.1	0.05	–	1,000	Linear	0.9988	12.6
Fluvalinate-tau I	17.601	250.0 → 200.0	0.1	–	1,000	Quadratic	0.9996	15.2
Deltamethrin	18.152	252.9 → 174.0	0.1	–	500	Linear	0.9963	17.2

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