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

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Introduction

Analysis of GC-amenable pesticides at low concentrations can present analytical challenges given the diverse and labile nature of many pesticides and the complex matrices in which they are analyzed.

A critical goal in GC/MS/MS analysis of pesticides is to augment instrument uptime to optimize sample throughput. A combination of the best practices in GC/MS/MS analysis with the state-of-the-art triple quadrupole GC/MS system enhances detection limits and increases maintenance-free instrument uptime.

This poster will provide tips and tricks for a sensitive and robust GC/MS/MS method for a panel of 246 pesticides. Method ruggedness was shown with 800 consecutive injections of a black tea extract, spiked with pesticides at 2 ppb.

A Combination of the Cutting-Edge Technology and Optimized Methodology

- Sample preparation via QuEChERS extraction followed by EMR mixed-mode passthrough cleanup using Captiva EMR–GPD cartridges
- 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.

Experimental

The 8890/7010D GC/TQ system (Figure 1) was used and configured to achieve the best sensitivity, maintain a wide calibration range, and provide the most rugged method performance.

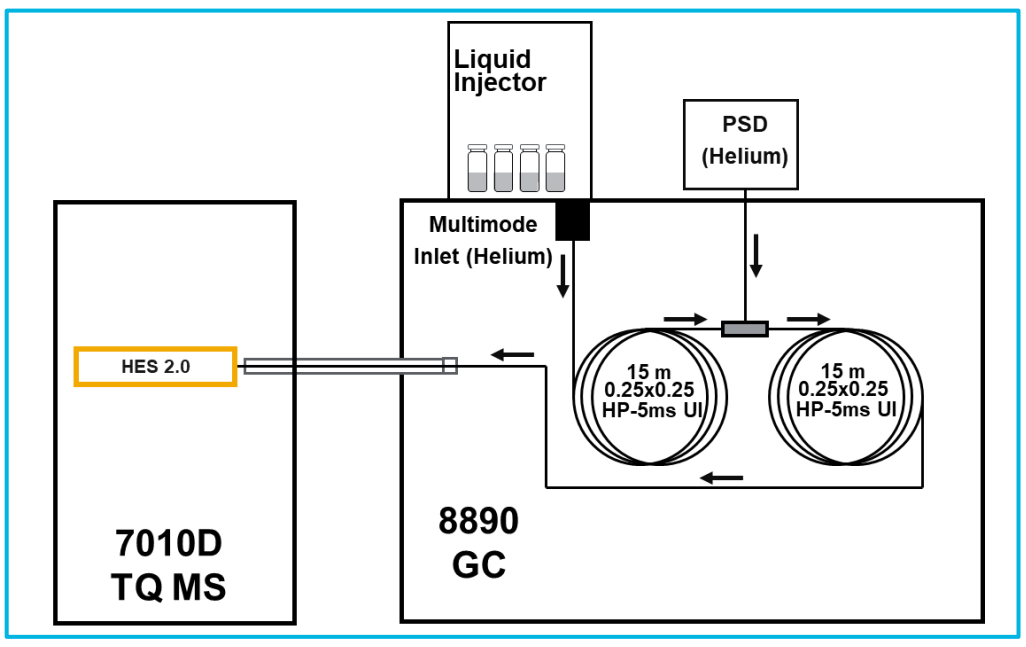

Figure 1. The Agilent 8890/7010D GC/TQ system configuration.

Experimental

Pesticides and Environmental Pollutants 4.0 MRM Database

Data was acquired in dynamic MRM (dMRM) mode with 749 total MRM transitions for 246 pesticides.

The use of the Agilent MassHunter Pesticides and Environmental Pollutants MRM Database 4.0 (P&EP 4.0) [1] increased the ease and speed of setting up a targeted dMRM method. P&EP 4.0 includes up to 9 MRM transitions for over 1,100 compounds allowing for high flexibility and selectivity.

New Retention Time Locking Tool in MassHunter 13

The acquisition method was retention time-locked (RTL) to match the retention times in P&EP 4.0. RTL allows for semi-automated or manual compound selection, provides a choice to use three or five points for RTL calibration, and provides the tools to maintain excellent precision of retention times, even after column trimming.

Figure 2. New Agilent Retention Time Locking software in MassHunter Acquisition 13 for GC/MS

Sample Preparation

The black tea powder (2 g) was extracted with the modified QuEChERS extraction (10 mL of ACN) followed by the EMR mixed-mode pass-through cleanup using Agilent Captiva EMR–GPD 6 mL. The sample eluent was dried with anhydrous MgSO4 to remove water residue completely before GC/MS/MS detection.

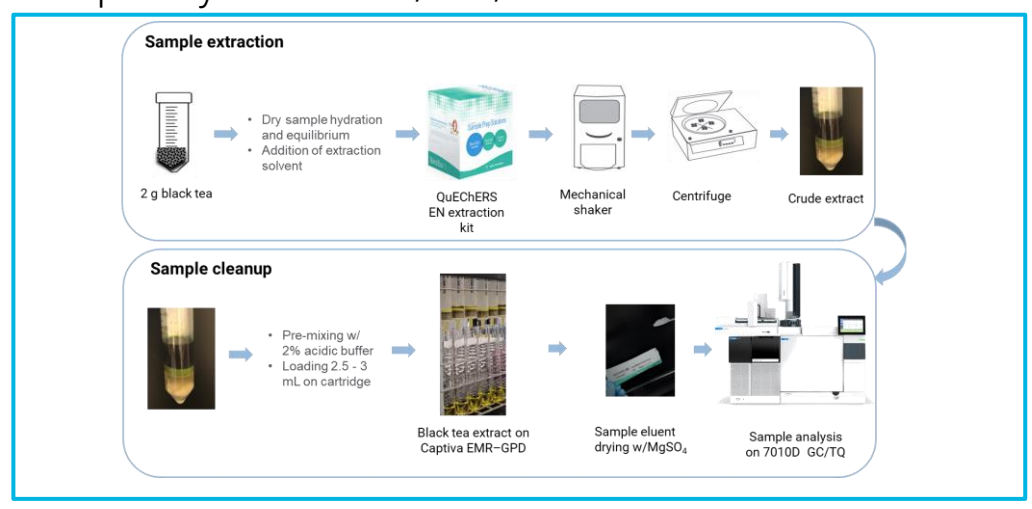

Figure 3. QuEChERS sample preparation and cleanup method for black tea.

Effective Matrix Cleanup and Pesticide Recovery

Adequate sample preparation is the key to successful pesticide analysis. Performing an efficient matrix cleanup following QuEChERS extraction reduces in-source matrix loading and interference with targets, while improving the signal-to-noise ratio, accuracy, and reproducibility for target pesticides.

As shown in Figure 4, the abundance of the total ion chromatogram signal in full scan data acquisition mode was noticeably reduced for black tea extract after cleanup when comparing the crude extracts before cleanup.

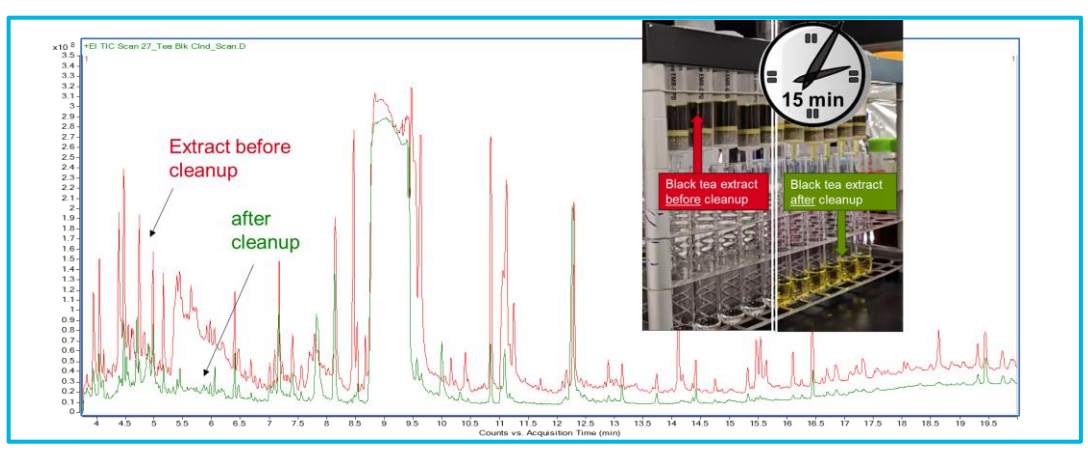

Figure 4. Scan TIC of the black tea extract: matrix sample with Agilent Captiva-EMR cleanup (green); matrix sample without cleanup (red).

The EMR mixed-mode passthrough cleanup using Captiva EMR with Carbon S cartridges is a simplified procedure that improves both sample matrix removal, and overall recovery and reproducibility of targets.

To validate the complete workflow solution, a study aimed at recovery and precision evaluation was performed. The acceptable recoveries (40-120%) were achieved for 243 and 241 pesticides at 10 and 50 ppb (v/w), respectively, including for the common problematic pesticides such as planar and labile.

Enhanced Robustness with Backflushing

Figure 5 illustrates the effectiveness of the backflush technique in reducing cycle time without 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 TQ MS, thereby reducing ion source contamination.

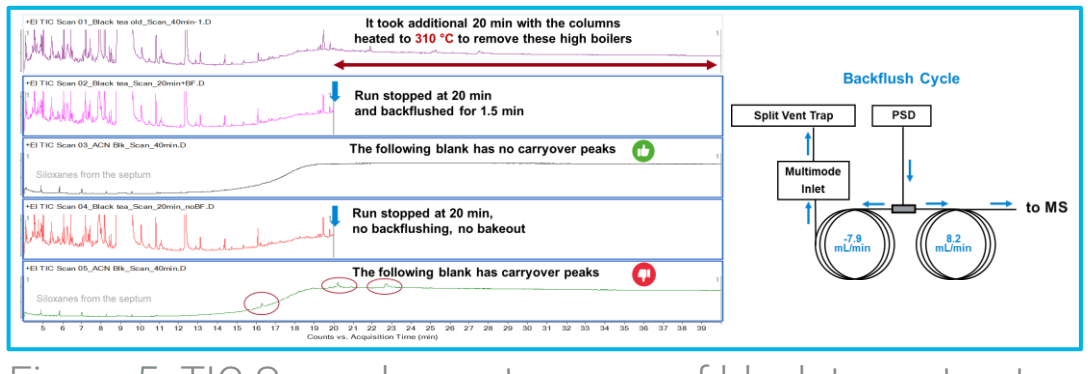

Figure 5. TIC Scan chromatograms of black tea extract, followed by analysis of an instrument blank

HES 2.0: Novel EI Source Technology

Equipped with the novel HES 2.0 EI source, the 7010D GC/TQ demonstrated unparalleled sensitivity when analyzing pesticides. 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 unparalleled analytical sensitivity.

Figure 6 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. 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%.

Excellent linearity was maintained over five orders of magnitude, ranging from 0.01 to 1,000 ppb as shown with the matrix-matched calibration in black tea extract.

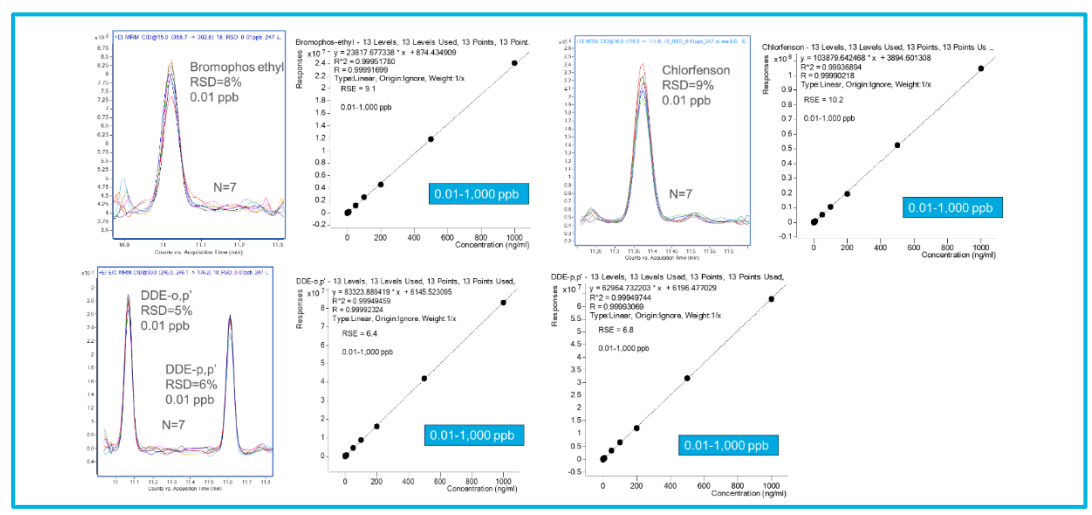

Figure 6. MRM chromatograms with seven replicate injections for the selected pesticides at the LOQ of 0.01 ppb in black tea extract and their calibration curves.

Excellent Performance for Challenging Pesticides

Captan and folpet are analytically among the most challenging pesticides due to their non-amenability to LC/TQ, and their tendency to degrade both in solution as well as in the GC inlet. Figure 7 demonstrates that captan and folpet could be quantitated with great precision at LOQs as low as 2 and 0.5 ppb, respectively.

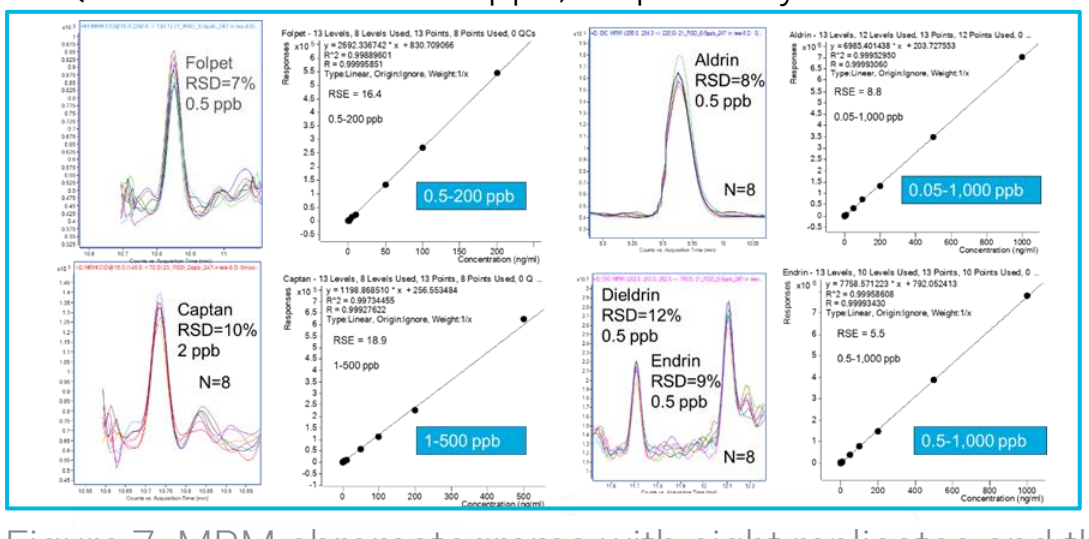

Figure 7. MRM chromatograms with eight replicates and the calibration curves for the selected challenging pesticides.

Results and Discussion

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.

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.

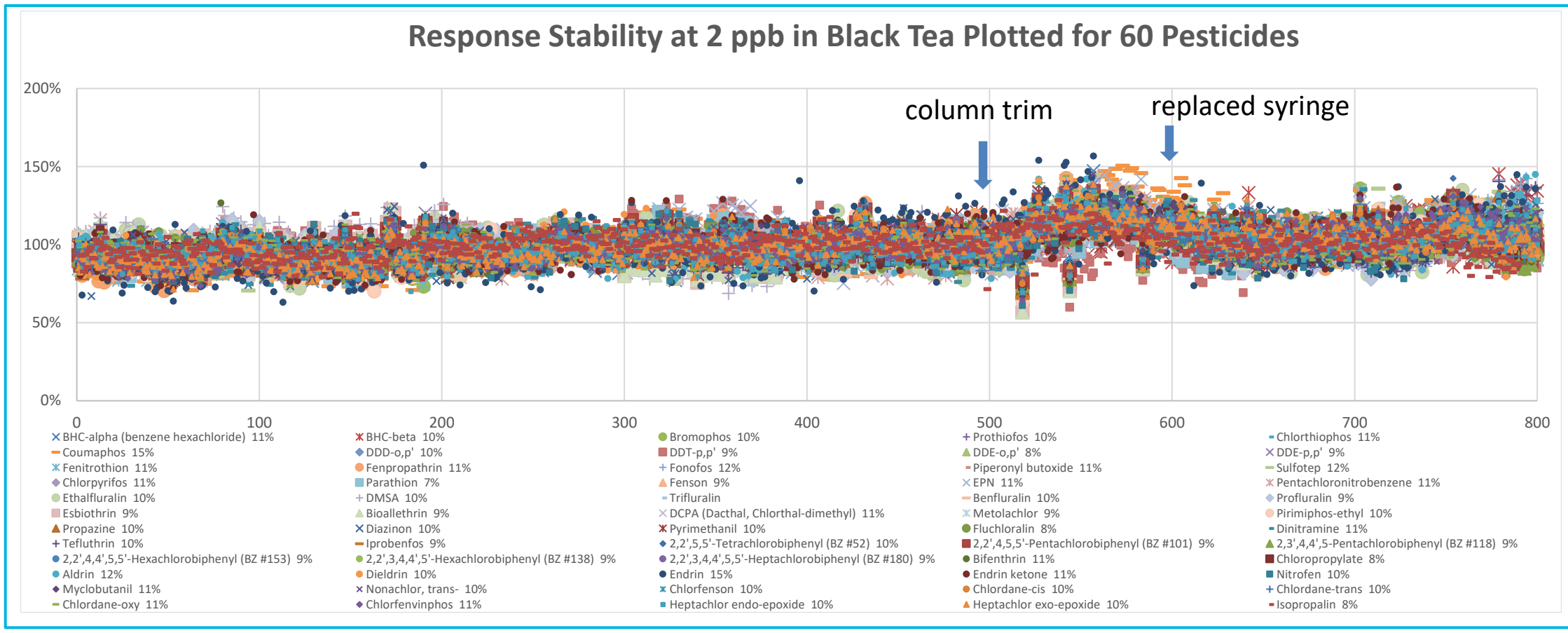

Figure 8. Stability of the peak area for pesticides spiked at 2 ppb into black tea extract, normalized by the ISTD and the average response, over 800 consecutive injections with the Agilent 8890 GC system and Agilent 7010D GC/TQ system.

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. Figure 9 shows a screenshot of the MS health status, featuring the electron multiplier, voltage at last tune, filament age, pump maintenance schedule, and time since the source was cleaned.

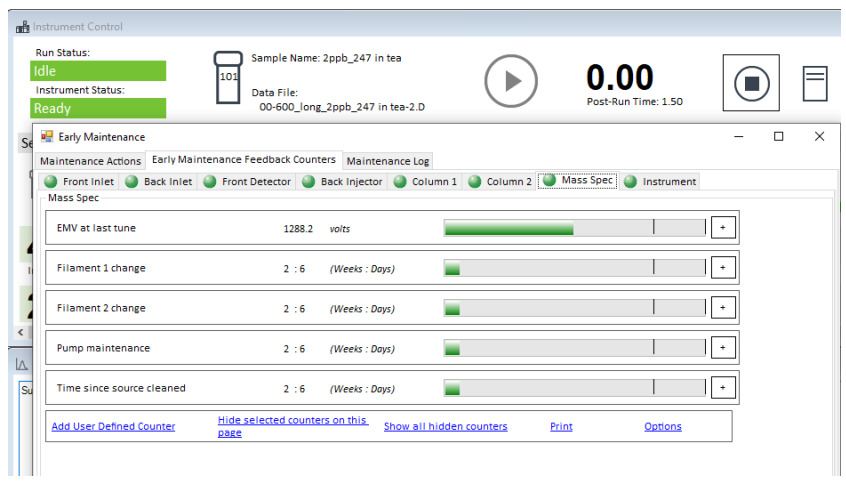

Figure 9. The early maintenance dashboard for GC/TQ.

https://www.agilent.com/en/promotions/asms

Conclusions

Excellent analytical performance was demonstrated for analyzing pesticides in black tea with the new 7010D GC/TQ:

- LOQs: 0.01 ppb for 34% of the targets, ≤0.1 ppb for 74%, ≤ 2 ppb for 96%
- Dynamic range up to five orders of magnitude 0.01-1,000 ppb
- RSDs<20% for 176 compounds in the black tea extract spiked at 2 ppb over 800 runs (17 days).

Key workflow features included modified QuEChERS sample preparation, 8890 GC hardware and GC supplies, novel HES, built-in GC/MS intelligence and software functionality.

References

1 Agilent MassHunter pesticide and environmental pollutants MRM database (P&EP 4.0) G9250AA. https://www.agilent.com/en/product/gas-chromatography-mass-spectrometry-gc-ms/gc-ms-application-solutions/pesticides-environmental-pollutants-4-0-mrm-database

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