Application Note

Food Testing

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Ultrasensitive and Powerful GC/MS/MS for Analyzing Multipesticides in Black Pepper and Dried Tea

Using the Agilent 8890/7010B triple quadrupole GC/MS with backflush and Agilent JetClean self-cleaning ion source

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Abstract

This application note presents a deep dilution approach for the analysis of multipesticides in complex matrices such as black pepper and dried tea using the ultrasensitive Agilent 8890 GC coupled with the Agilent 7010B GC/TQ. A total of 284 pesticide compounds were used to evaluate the analytical method for both dried tea and black pepper matrices following EU SANTE/11312/2021 guidelines. Calibration curves were constructed in the range of 0.1–5 µg/L with R^2 > 0.99 for all compounds. Recovery efficiency was assessed at two prespike levels, 10 and 50 µg/kg, with over 95 and 87% of total pesticides achieving recovery rates between 70–120% for black pepper and dried tea, respectively. The method demonstrated good repeatability and reproducibility, with relative standard deviation (RSD) < 15%. The robustness of the Agilent 8890 GC/7010B GC/TQ system was evidenced by the stability of pesticide compound responses in quality control (QC) samples across nearly 1,000 injections, facilitated by Agilent's comprehensive solutions, including backflush and Agilent JetClean self-cleaning ion source features during sample analysis.

Introduction

Pesticides play a vital role in safeguarding crops and are indispensable in most farming settings to secure high yields.[1] Regulatory authorities, including the Codex Alimentarius and the European Commission mandate the monitoring and reporting of pesticide residues found in or on food product.[2] The analysis of pesticides in food faces several major challenges, such as the variety of pesticide classes, the complexity of different food matrices, the effects of these matrices, and the detection of target analytes at low concentrations.[3]

According to the EU's SANTE/11312/2021 guidelines, black pepper and dried tea are considered among the difficult or unique commodity matrices for multiresidue pesticide analysis.[4] The matrix interferences are complex and diverse, including carbohydrates, fats, piperine, terpenoids (for black pepper)[5], and caffeine (in dried tea). "For dried tea, matrix interferences include polyphenols, pigments, polysaccharides, alkaloids, free amino acids, high caffeine levels, and catechins".[6]

In addition to affecting the analyte signals, matrix interferences can cause the system to become contaminated more quickly. This leads to a rapid decline in the sensitivity of the analytical instrument, and necessitates frequent maintenance, significantly reducing laboratory productivity. These are the current challenges faced by laboratories when analyzing pesticides in difficult and complex matrices.

To overcome these challenges, Agilent offers a robust solution with its backflush and JetClean self-cleaning ion source technologies integrated into the high-sensitivity 7010B GC/TQ system. Backflush technology prevents high-boiling contaminants from reaching the detector, reducing the need for frequent maintenance and extending column life.[7] This ensures consistent performance and minimizes downtime, thereby enhancing laboratory productivity.

With JetClean technology, your lab can significantly increase instrument uptime, as fewer manual cleanings are needed, maximizing productivity. This technology helps maintain data quality by ensuring a clean ion source, which guarantees run-to-run reproducibility. Additionally, JetClean enhances operator convenience through automated cleaning, requiring virtually no user intervention.[8] Combined with the ultrasensitivity of the 7010B GC/TQ system, these technologies provide precise and reliable analysis of pesticides in complex matrices such as black pepper and dried tea. Agilent's comprehensive approach effectively mitigates matrix interferences, preserves instrument sensitivity, and significantly boosts overall efficiency in pesticide analysis.

This application note describes a detailed approach for the simultaneous quantification of 284 pesticides in black pepper and dried tea samples. Agilent's solution for complex matrices demonstrates the sensitivity of the 8890 GC/7010B GC/TQ and confirms its robustness when using backflush and JetClean techniques.

Experimental and chemicals

Chemicals and reagents

A total of 284 pesticide standards, each with a purity exceeding 98%, or stock solutions (1,000 mg/L) were acquired from either Sigma-Aldrich (St Louis, MO, USA) or LGC Standards (Teddington, Middlesex, UK). To prepare a 10 mg/L stock solution comprising all analytes, the required volume from the primary stock was added to a 10 mL volumetric flask and topped up to volume with acetonitrile. Acetonitrile, methanol (HPLC grade), and magnesium sulfate were purchased from Sigma-Aldrich (St. Louis, Missouri, United States). Ultrapure water was produced by a Milli-Q system from Millipore Sigma (Burlington, Massachusetts, United States).

GC/TQ parameters

The 8890 GC/7010B GC/TQ systems (Figure 1) were optimized for wide calibration range performance. Equipped with an Agilent 7693A automatic liquid sampler and a 150-position tray, the GC operated in temperature-programmed splitless injection mode with a multimode inlet. Detailed instrument parameters can be found in Table 1.

Data acquisition was in dynamic MRM (dMRM) mode, enabling analysis of 284 pesticides with 1233 MRM transitions and up to 74 concurrent MRMs (see Figure 2). Retention time was synchronized with the Agilent Pesticides and Environmental Pollutants (P&EP) 4.0 MRM Database, streamlining method setup.

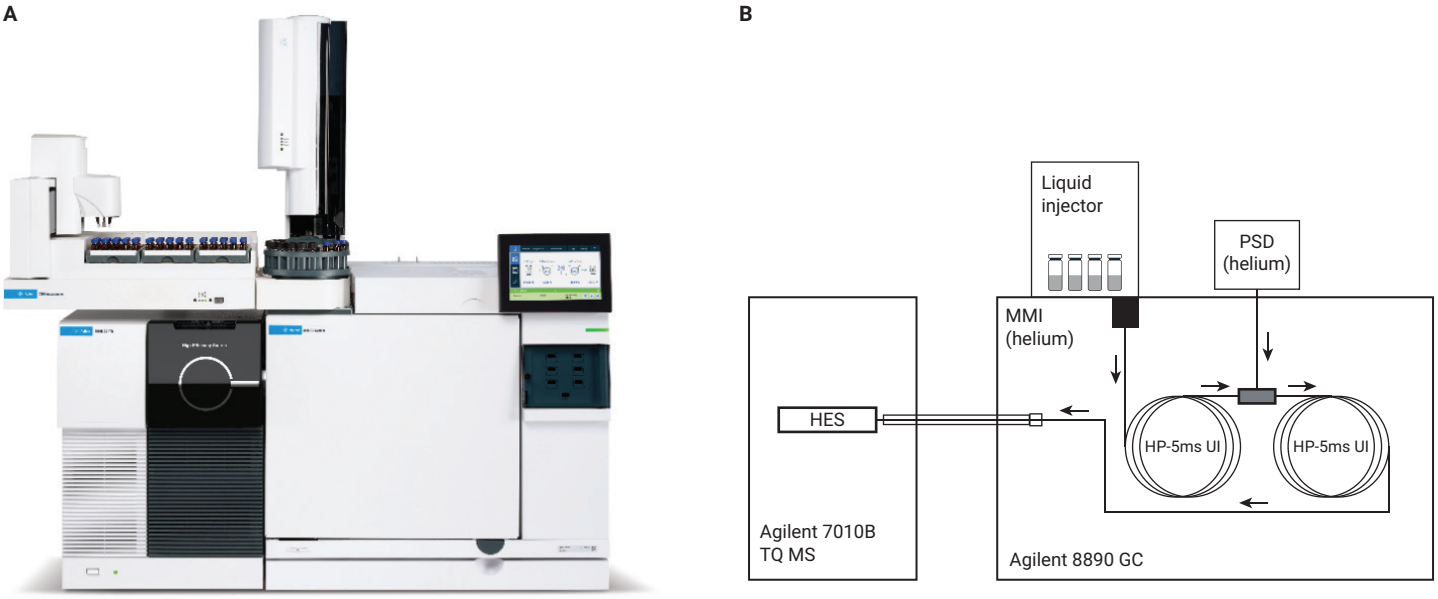

Figure 1. The Agilent 8890/7010B GC/TQ system (A) and system configuration (B).

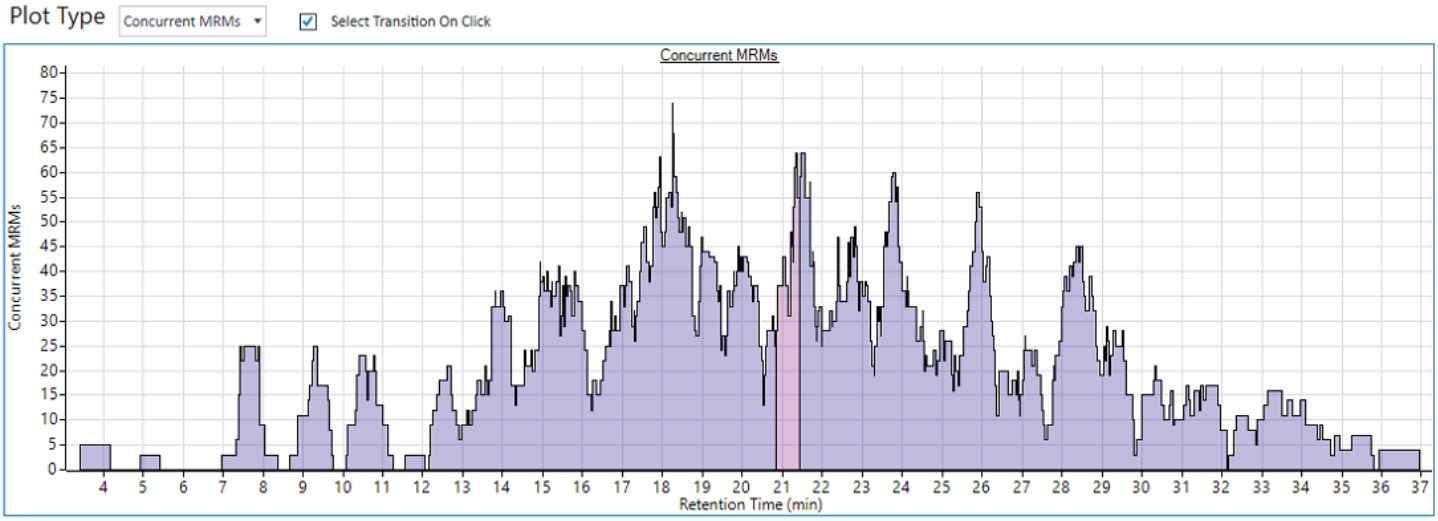

Figure 2. The distribution of 1,233 MRM transitions with up to 74 concurrent MRMs monitored during the analysis enables efficient dwell time distribution.

The JetClean self-cleaning ion source in Clean Only mode is used to clean the ion-source. It was performed after every 50 samples to clean the ion source; detailed specifications are presented in Table 1.

Table 1. Agilent 8890 GC/7010B GC/TQ conditions for pesticide analysis.

GC	
Agilent 8890 GC (220 V oven) with fast oven, auto injector, and tray	
Inlet	Multimode Inlet (MMI)
Mode	Splitless
Purge Flow to Split Vent	50 mL/min at 0.75 min
Septum Purge Flow	3 mL/min
Septum Purge Flow Mode	Standard
Injection Volume	1 µL
Injection Type	Fast inject
L1 Airgap	0.2 µL
Gas Saver	On at 30 mL/min after 3 min
Inlet Temperature	280 °C, Hot Splitless Injection mode
Post-run Inlet Temperature	280 °C
Carrier Gas	Helium
Inlet Liner	Ultra Inert, splitless, single taper, glass wool
Inlet Liner Part Number	5190-2293
Oven	
Initial Oven Temperature	60 °C
Initial Oven Hold	1 min
Ramp Rate 1	40 °C/min
Final Temp 1	120 °C
Final Hold 1	0 min
Ramp Rate 2	5 °C/min
Final Temp 2	310 °C
Final Hold 2	0 min
Total Run Time	40.5 min
Post Run Time	5 min
Equilibration Time	1 min
Column	
Type	Agilent J&W HP-5ms Ultra Inert (19091S-431UI) x2
Length	15 m
Diameter	0.25 mm
Film Thickness	0.25 µm
Control Mode	Constant flow
Flow	1.0 mL/min (column 1) 1.2 mL/min (column 2)
Inlet Connection	Multimode inlet – column 1 PSD – column 2
Outlet Connection	PSD – column 1 MSD – column 2
Backflush	
Inlet Pressure	2 psi
PSD Pressure	50.0 psi
Timing	5 min duration during postrun
Oven Temperature	310 °C
MSD	
Model	Agilent 7010B GC/TQ
Source	High Efficiency Source (HES)
Vacuum Pump	Performance turbo
Tune File	Atunes.eihs
Solvent Delay	3 min
Quad Temperature (MS1 and MS2)	150 °C
Source Temperature	280 °C
Mode	dMRM
He Quench Gas	4 mL/min
N_2 Collision Gas	1.5 mL/min
MRM Statistics	
Total MRMs (dMRM mode)	1233
Minimum Dwell Time	4.57 ms
Minimum Cycle Time	98.7 ms
Maximum Concurrent MRMs	74
Cycles per Second	2.5
EM Voltage Gain Mode	20
Agilent JetClean Self-Cleaning Ion Source	
Mode	Clean Only
Hydrogen Flow	0.67 mL/min
Emission	40 µA
Source Temperature	280 °C
Duration Time	3 min
Stabilization Duration	10 min

Sample preparation

Sample preparation involved the following products and equipment:

- Agilent Bond Elut QuEChERS EN extraction kit (part number 5982-5650CH)
- Agilent Captiva Enhanced Matrix Removal—General Pigmented Dry cartridge (EMR-GPD, part number 5610-2091)
- Agilent QuEChERS Universal dispersive SPE kit (part number 5982-0028)
- Agilent Vac Elut 20 manifold (part number 12234105)
- Centrifuge
- Vortexer

Figure 3 displays a workflow diagram for sample preparation. This process involved two primary stages: initial sample extraction using the traditional QuEChERS method, followed by cleanup using the Captiva enhanced matrix removal (EMR) pass-through for dried tea and dispersive solid phase extraction (dSPE) Universal for black pepper.

In the first step, samples were extracted using the EN 15662 method. Two grams of homogenized black pepper or dried tea were weighed into a 50 mL centrifuge tube, followed by the addition of 10 mL of deionized water to the sample. The mixture was vortexed and allowed to stand for 30 minutes before extraction with 10 mL of ACN. The partitioning process used the traditional Agilent Bond Elut QuEChERS EN extraction kit.

During the cleanup process, a two-step dilution approach was used to enhance cleaning efficiency and reduce the matrix content in the final solution. The first dilution step was carried out before the cleanup process to ensure that there was no overload of cleanup material for background matrices such as black pepper and dried tea. The supernatant of the two sample matrices is diluted 4 and 8 times, respectively, for black pepper and dried tea matrices.

For black pepper, 1 mL of the diluted solution was cleaned using the Agilent QuEChERS Universal dispersive SPE kit. The solution was then diluted 2.5 times and analyte protectants (APs) were added before injection into the GC/TQ system.

For dried tea matrix, the diluted solution was mixed with 20% deionized water, and 2 mL of the solution was passed through a Captiva EMR-GPD cleanup cartridge. The eluent was dried with anhydrous magnesium sulfate, then diluted 1.25 times and APs were added before injection into the GC/TQ system.

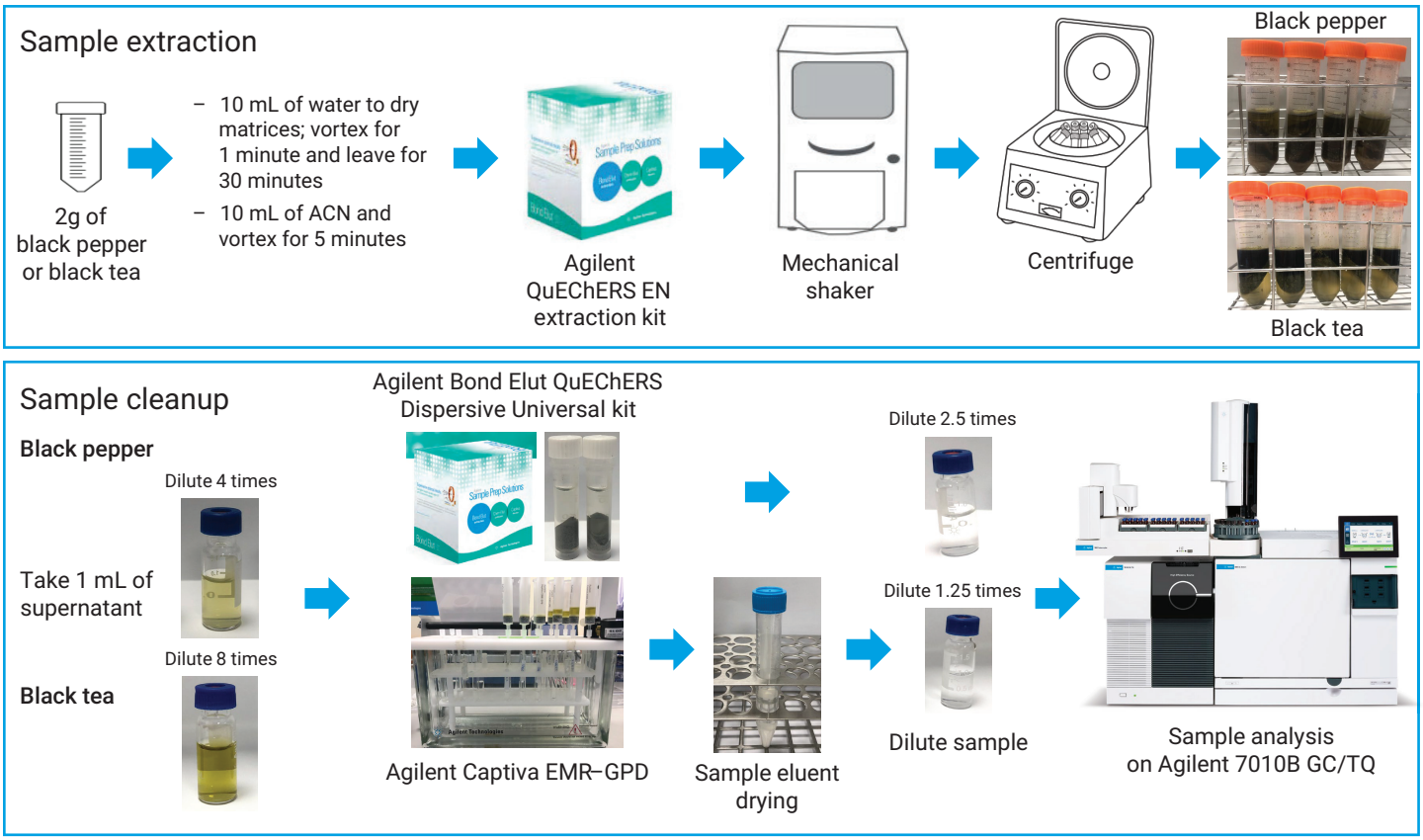

Figure 3. Sample preparation flowchart including Agilent QuEChERS extraction, followed by Agilent Captiva EMR pass-through (black tea) or dSPE (black pepper) cleanup.

Analyte protectants

All samples had APs added to them, making the APs stock solution account for 5% of the injected sample volume. The composition of the stock solution of APs includes 3-Ethoxy-1,2-propanediol (7 mg/mL); sorbitol (5 mg/mL); D-(–)gluconic acid-δ-lactone (1.25 mg/mL); and shikimic acid (5 mg/mL), all prepared in methanol. When incorporating the APs, it is advised to include an ACN/isopropanol mixture in one of the syringe wash solvents at a ratio of 1:1 (v/v) to avoid syringe plunger stickiness.

Matrix matched calibration

Matrix-matched calibration curves were prepared by postspiking the intermediate standard solution into a matrix blank. Preparation of matrix-matched calibration levels was identical to solvent standard preparation, except by using a matrix blank instead of an acetonitrile solvent blank. In this study, six levels of concentration were used to build the matrix-matched calibration curves, including 0.1, 0.2, 0.5, 1, 2, and 5 µg/L in matrix blank solution.

Evaluating the robustness of GC-TQ

To evaluate the robustness of the 7010B GC/TQ, samples were injected in a back-to-back and nonstop manner, as follows:

- The total number of injections into the system included 905 samples, including the process of evaluating sample processing methods
- After completing the method validation process, blank matrix samples were continuously injected into the system
- A QC sample (5 µg/L) in matrix solution was used to evaluate the stability of the device after every fifth injection of blank matrix solution

Results and discussion

In this application note, a two-step dilution approach, including pre- and post cleanup, is employed for pesticide analysis in complex matrices. Due to the large dilution factor, it is essential to have a high sensitivity and robust analytical system. The equipment's performance and the sample processing method were evaluated based on factors such as instrument sensitivity, the linearity of the calibration curve, method sensitivity (limit of quantitation, LOQ), recovery rates (accuracy), and precision (repeatability and reproducibility) in accordance with SANTE guidelines.[4]

Sensitivity of instrument

A standard solution of 284 pesticide compounds at a concentration of 0.1 µg/L in a matrix blank solution for both black pepper and dried tea matrices was used to assess the sensitivity and response of the equipment, with the method's limit of quantitation set to 10 µg/kg. This was performed following the sample preparation procedure outlined in Figure 3. The results indicated that all compounds exhibited a signal-to-noise ratio of peak greater than 10 at a concentration of 0.1 µg/L. Figure 4 presents the chromatograms of pesticide compounds with low sensitivity on GC, showing early, mid-, and late elution times in the analysis cycle, along with low dwell times. For instance, pesticides such as EPTC, Zoxamide, and Deltamethrin demonstrated low sensitivity on GC; however, the peak shapes were well-defined and unaffected by matrix components. Similarly, the compound Simeconazole (RT 18.2 minutes) with a dwell time of approximately 4 ms, showed consistent results. These findings confirm that the Agilent 7010B GC/TQ exhibits excellent sensitivity, making it suitable for complex matrices such as black pepper and dried tea, and demonstrates effective background noise reduction due to its specially designed mass analyzer and collision cell with quenching gas.

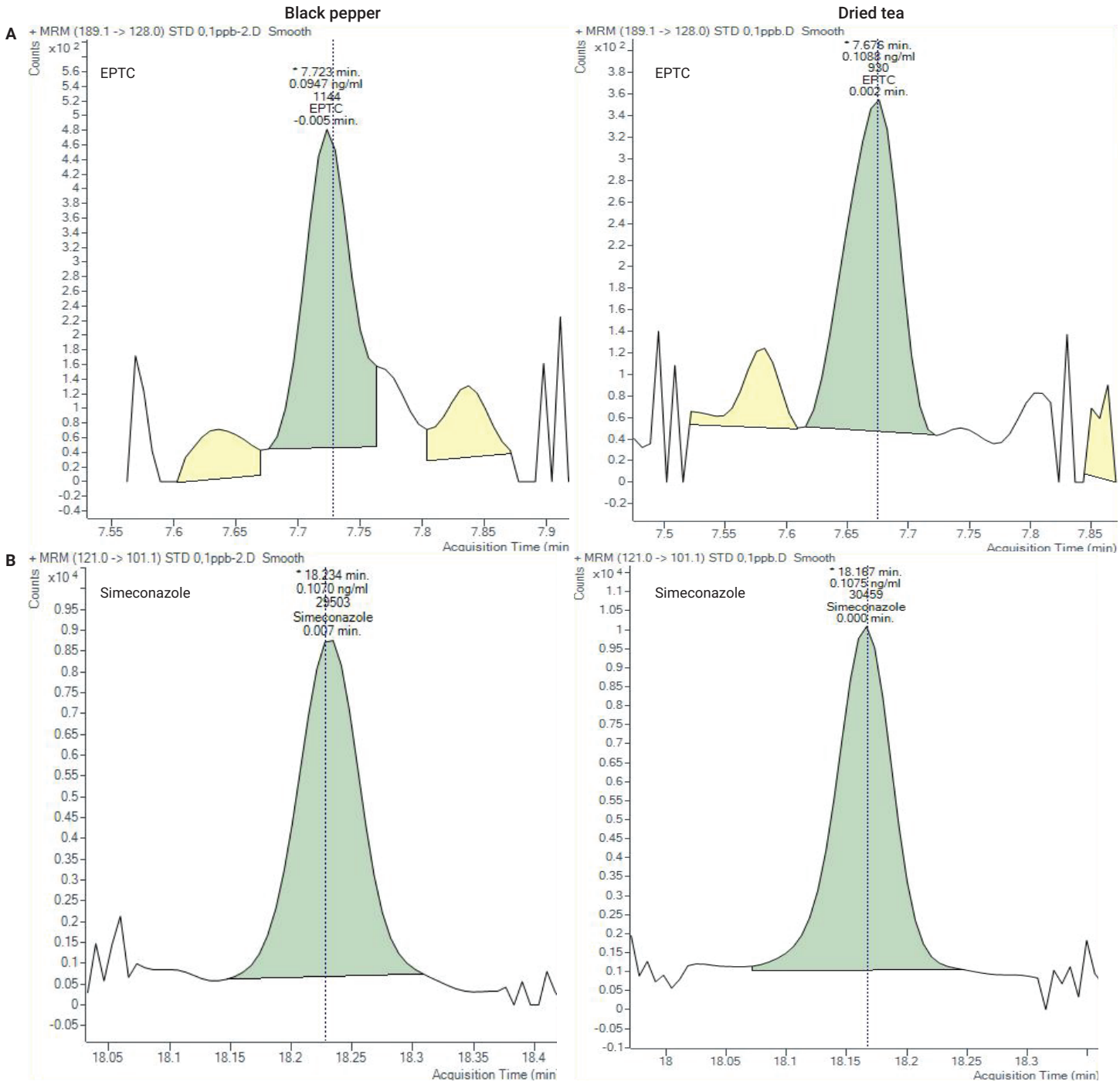

Figure 4. MRM chromatograms for (A) EPTC, (B) Simeconazole, (C) Zoxamide, and (D) Deltamethrin at 0.1 µg/L in black pepper and dried tea extract, analyzed with the Agilent 7010B GC/TQ (continued on next page).

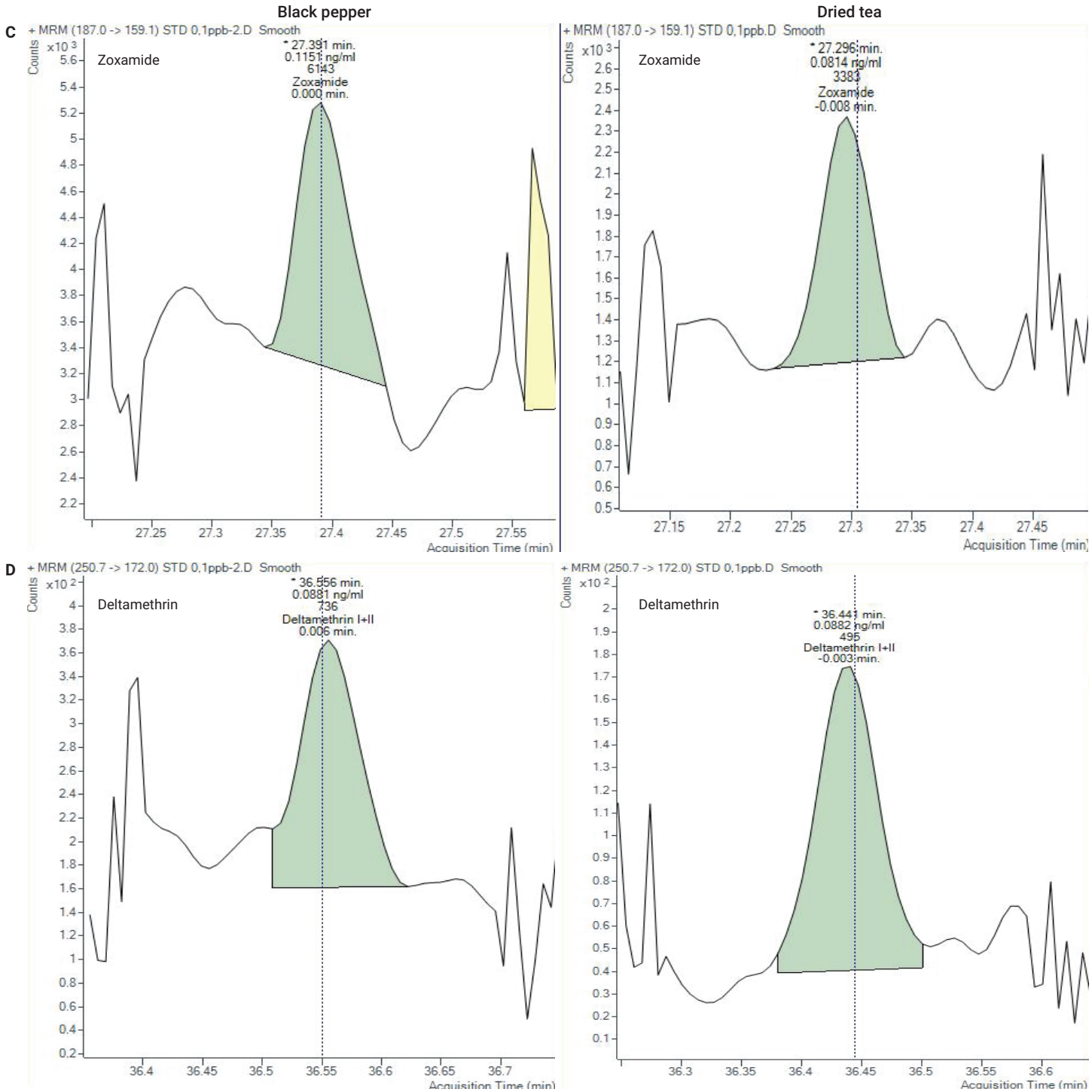

Figure 4. MRM chromatograms for (A) EPTC, (B) Simeconazole, (C) Zoxamide, and (D) Deltamethrin at 0.1 µg/L in black pepper and dried tea extract, analyzed with the Agilent 7010B GC/TQ.

Calibration

The linearity of the calibration curve for all targets was evaluated using matrix-matched standards within a range of 0.1 to 5 µg/L. All 284 targets met the calibration curve linearity criterion with an R^2 value of ≥ 0.99 (As shown in Figures 5A and 5B). Furthermore, the accuracy of the regression equation was assessed by comparing the theoretical and calculated concentrations across all calibration levels. The results demonstrated that the quantitative accuracy of each calibrator was within ± 20%. These accuracy levels confirm that the 7010B GC/TQ complies with the SANTE/11312/2021 requirements for pesticide analysis.

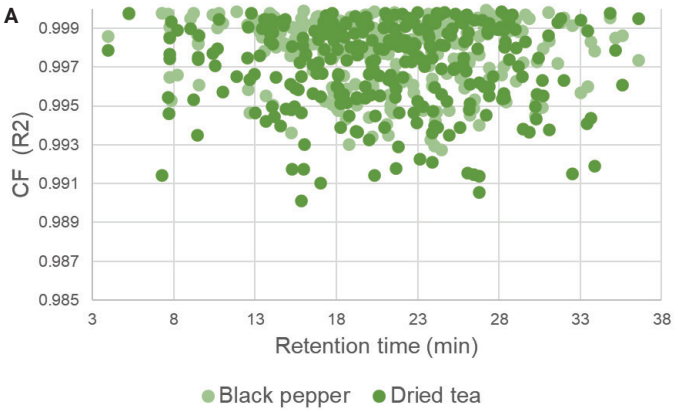

Figure 5A. Method performance evaluation in terms of the calibration curve.

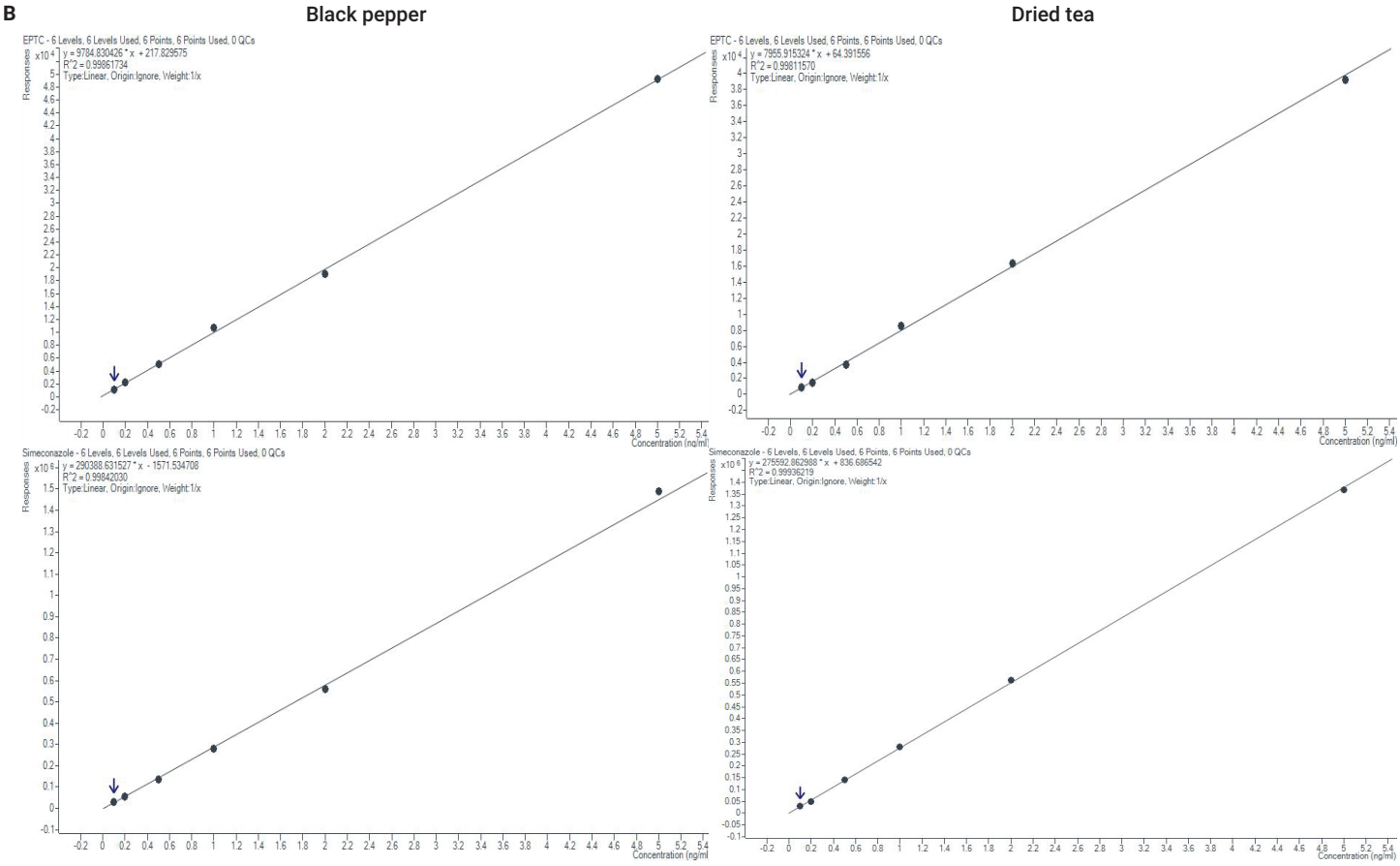

Figure 5B. Calibration curve of EPTC, Simeconazole, Zoxamide, and Deltamethrin for black pepper and dried tea (continued on next page).

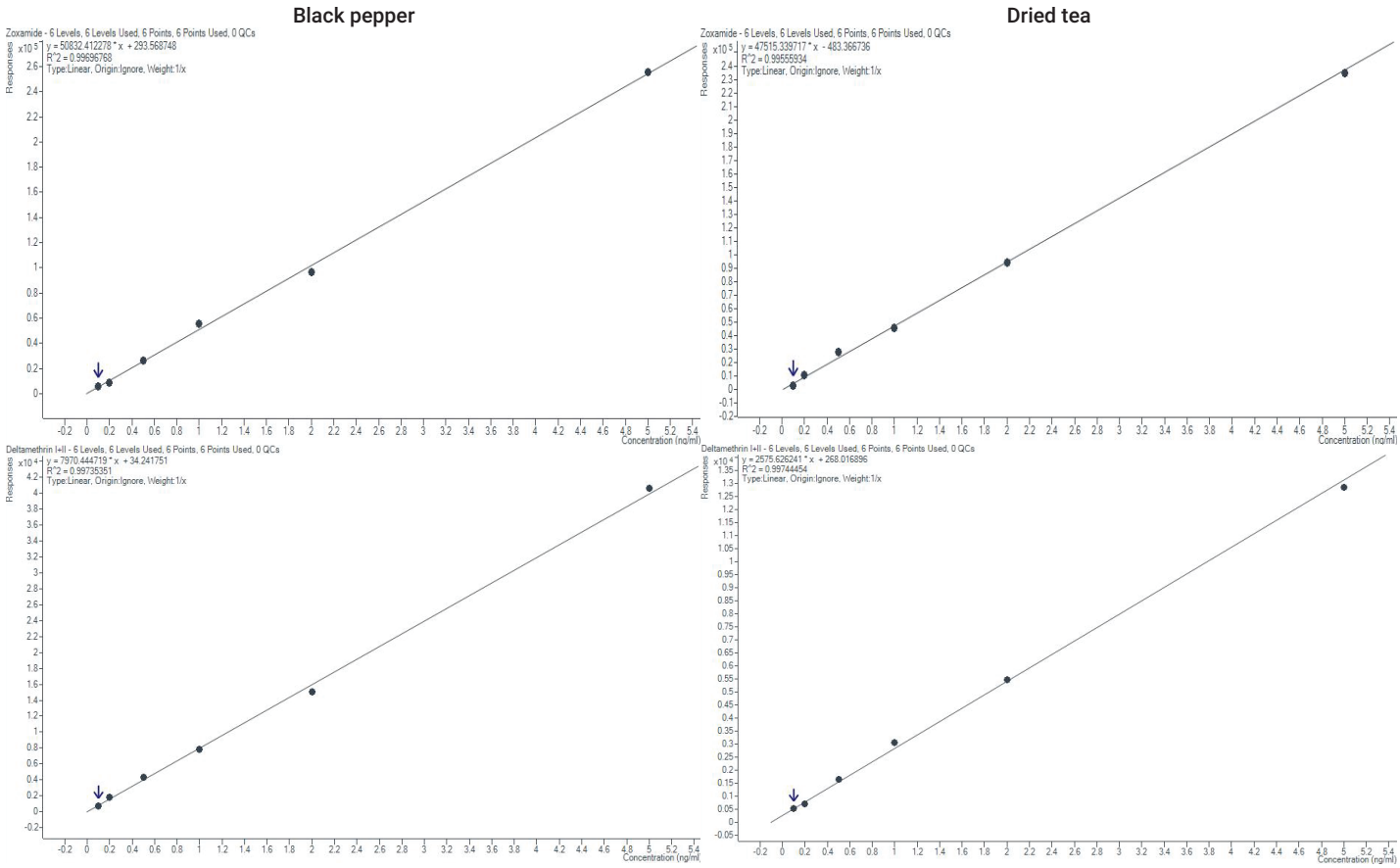

Figure 5B. Calibration curve of EPTC, Simeconazole, Zoxamide, and Deltamethrin for black pepper and dried tea.

Method accuracy and precision

Accuracy: In the analysis of pesticide residues in food matrices, target recovery is a crucial indicator of the sample preparation method and instrument performance. According to EU regulations, the maximum residue limits (MRL) for pesticides in pepper and tea matrices range from 10 to 50 µg/kg. A general default MRL of 10 µg/kg applies where a pesticide is not specifically mentioned.[2] Based on the guidelines from SANTE, the pesticide analysis method must have a sensitivity that meets the EU's MRL regulations, with the Limit of Quantification (LOQ) value being less than or equal to the MRL.[4] In this application note, the method's sensitivity is demonstrated by setting a common LOQ threshold for all compounds at 10 µg/kg. To evaluate target recovery, prespiked samples were prepared at two concentration levels: 10 µg/kg (LOQ) and 50 µg/kg (5 LOQ). The SANTE guidelines state that average recovery should be between 30 and 140%, provided it is consistent (RSD ≤ 20%).[4] More stringent criteria set an acceptable recovery range between 40 and 120%, with RSD ≤ 20%. Figures 6A and 6B illustrate the mean recovery based on 12 technical replicates (n = 12) of prespiked samples for each concentration in both matrices.

Regarding black pepper, most compounds exhibit good recovery rates at both the prespiked LOQ and 5 LOQ levels. Specifically, 269 and 274 pesticides (about 95% of the total compounds) achieve recovery efficiencies between 70 and 120% at the LOQ and 5 LOQ levels, respectively. When the recovery efficiency criteria are broadened to 40–120% with an RSD% of less than 20, 275 and 278 pesticides (over 97% of the pesticide list) meet the criteria at the LOQ and 5 LOQ levels, respectively. Some pesticides with planar structures are adsorbed by GCB, resulting in recovery efficiencies below 40%. Additionally, a few compounds found in blank samples at high concentrations cannot be evaluated.

For dried tea samples, a similar trend is observed. With recovery efficiency criteria set between 70 and 120%, 244 and 246 pesticides (accounting for 86% of the target list) meet the requirements at the LOQ and 5 LOQ levels, respectively. There are 18 pesticides with recovery efficiencies ranging from 40 to less than 70% at the LOQ level, and this number decreases to 16 at the 5 LOQ level. Additionally, 22 compounds show recovery efficiencies of less than 40%, or are found in the matrix at high concentrations.

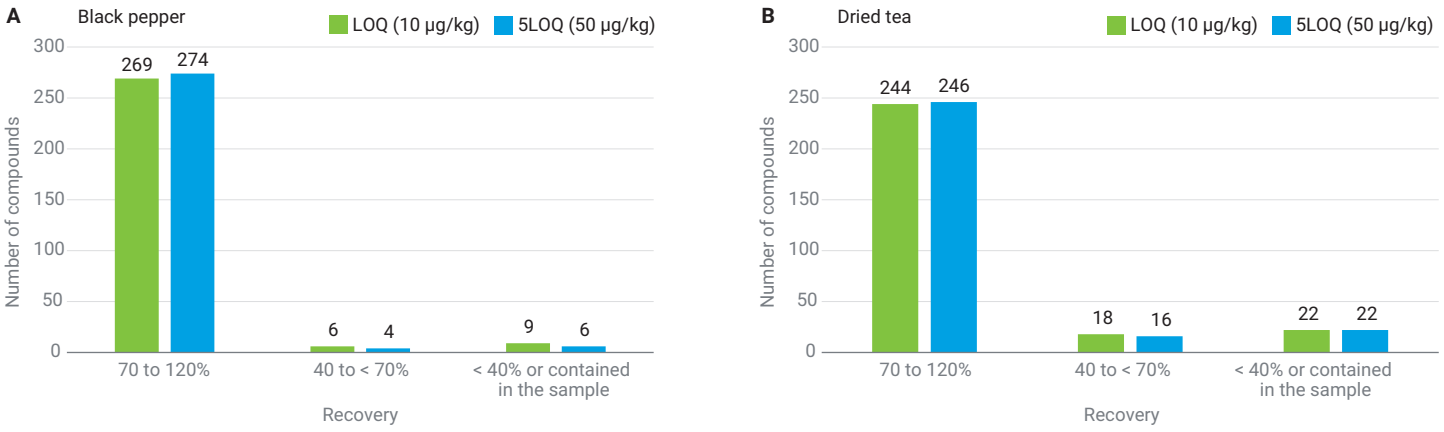

Figure 6. Prespiked QC (10 µg/kg, 50 µg/kg) recovery distribution of all 284 targets in black pepper (A) and dried tea (B).

Repeatability (RSDr): Method precision was assessed by examining the intrabatch recovery repeatability using six technical replicates at prespiked LOQ and 5 LOQ levels. Figure 7 shows the fluctuation in recovery of all pesticide compounds through %RSD values. Overall, it is clear that %RSD is less than 20% for all pesticides in both matrices. At the LOQ level, most pesticide compounds have %RSD values between 3 and less than 15% for both sample matrices. Additionally, at the 5 LOQ level, the repeatability of sample processing improves, with %RSD values ranging from 2 to 7%. From the above results, the sample preparation method is beneficial for both matrices and meets the SANTE criteria.

Reproducibility (RSD_{wR}): The reproducibility of the analytical method for pesticides, which demonstrated satisfactory recovery performance and repeatability in line with SANTE guidelines, was evaluated at two different concentration levels. To determine $\%RSD_{wR}$, recoveries were calculated from 12 replicates of prespiked quality controls across two batches. These batches were prepared by two separate lab scientists using different lots of sample matrices on different days.

Generally, similar results were obtained for the reproducibility of the sample preparation method. Specifically, the $\%RSD_{wR}$ ranged from 7 to 12% at the LOQ level and from 4 to 8% at the 5 LOQ level for most compounds in both matrices (as shown in Figure 7). This indicates that the method performs very well and meets the SANTE guidelines.

Considering the results, including linearity, recovery, repeatability, and reproducibility, it is evident that this method is highly suitable for analyzing a wide range of pesticides in a complex matrix. It consistently delivers reliable quantitative results, making it ideal for routine day-to-day analyses.

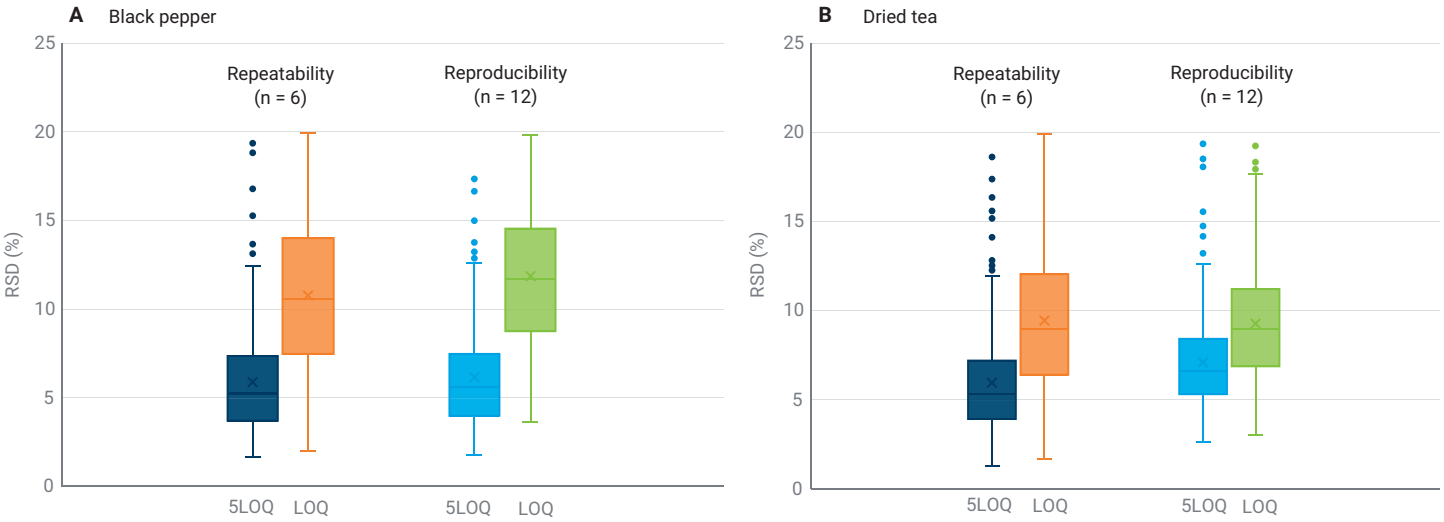

Figure 7. Method performance evaluation in terms of repeatability (n = 6), and reproducibility (n = 12) in (A) black pepper and (B) dried tea.

Robustness of instrument: In addition to sensitivity, the GC/TQ also requires robustness when analyzing complex sample matrices, which is a mandatory requirement in high sample-volume labs and production environments. In this application note, the robustness of the 7010B GC/TQ system with JetClean is evaluated through continuous injection analysis of over 900 injections over nearly 30 days. The results are shown in Figures 8 and 9.

From Figure 8, the repeller of the HES source is only minimally contaminated after 905 injections. This indicates that the Agilent JetClean ion source cleaning feature using H_2 gas is highly effective. Furthermore, Figure 8C shows the condition of other ion source components (extractor, post extractor (PE) 1, 2, ion focus, and entrance lens), which remain relatively clean. There are a few contaminants on post extractor 2 as it is designed to reverse and neutralize trapped ions back onto PE1.

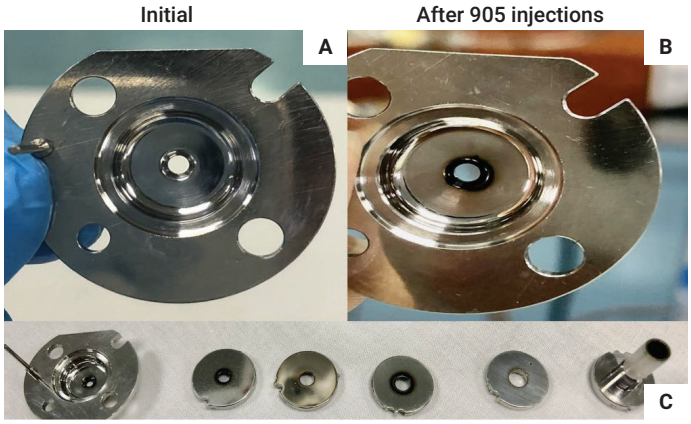

Figure 8. Repeller before (A) and after (B) 905 injections of black pepper and dried tea matrix samples; component parts of HES source when disassembled (C).

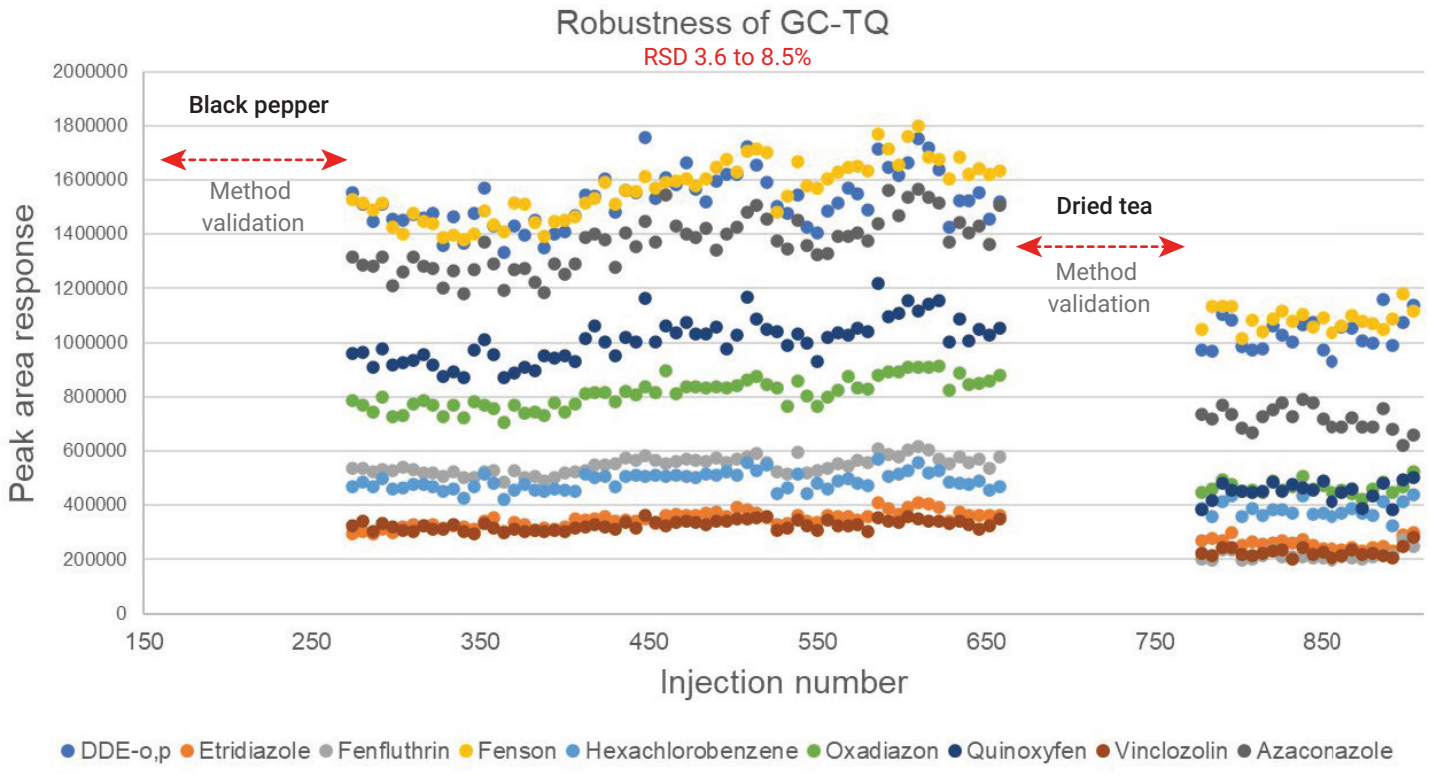

Figure 9. Stability of MRM peak areas for pesticide compounds in the QC sample (5 µg/L) over 900 injections.

Regarding the stability of the instrument sensitivity, the repeatability results through the %RSD values of the QC sample on each matrix show that the device maintains very good sensitivity (Table 2 and Figure 9).

Specifically, Figure 9 shows raw peak areas for each analyte, plotted as a function of injection number for every fifth injection. The repeatability of the monitored pesticide compounds is very good, with %RSD values ranging from 3.6 to 8.5%. The %RSD values range from 2.96 to 7.74% when data normalization is performed, based on the internal standard signal. The analytes of interest exhibit < 10 %RSD in both cases, including measuring raw peak area responses and IS-corrected responses.

Table 2. Signal response statistics represented by raw peak area and internal standard (IS) corrected peak area ratio.

Analyte	Raw Peak Area %RSD		IS Corrected Peak Area Ratio (%RSD)	
	Black Pepper	Dried Tea	Black Pepper	Dried Tea
DDE-o,p	6.53	5.88	3.49	5.24
Etridiazole	8.07	7.93	5.13	7.74
Fenfluthrin	5.58	8.46	3.12	6.72
Fenson	6.76	3.60	4.07	2.96
Hexachlorobenzene	6.45	7.76	3.99	6.27
Oxadiazon	6.68	4.96	3.97	4.23
Quinoxyfen	7.88	7.72	4.85	6.78
Vinclozolin	5.25	8.02	3.68	7.49
Azaconazole	7.15	6.09	3.88	5.89

Conclusion

This application note describes an approach for the analysis of multipesticides in complex and distinctive matrices, including black pepper and dried tea using the Agilent 8890 GC/7010B GC/TQ. The comprehensive solution successfully addresses the challenges encountered when analyzing multipesticides in difficult matrices such as black pepper and dried tea. The high sensitivity of the 7010B GC/TQ enables the application of deep dilution methods. Additionally, the use of backflush technology combined with the Agilent JetClean self-cleaning ion source ensures system stability and robustness, enhancing the operational efficiency of testing laboratories and reducing equipment downtime during maintenance.

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Appendix

Table 3. The list of target pesticide compounds and their recoveries at prespiked 10 and 50 µg/kg (n = 12) in black pepper and dried tea matrices.

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
1	2,4-D-methyl ester	12.98	23.28 ± 3.2	89.51 ± 14.86	19.66 ± 1.65	78.7 ± 8.38
2	8-Hydroxyquinoline	7.84	23.84 ± 4.63	D	21.95 ± 2.58	D
3	Acetochlor	18.03	108.3 ± 13.21	93.87 ± 7.65	107.14 ± 12.15	90.97 ± 6.5
4	Acibenzolar-S-methyl	18.18	58.87 ± 6.44	D	87.14 ± 7.75	23.44 ± 17.41
5	Aclonifen	24.93	94.36 ± 12.95	83.27 ± 7.22	92.25 ± 9.18	74.81 ± 4.15
6	Ametryn	18.45	79.27 ± 11.43	81.21 ± 10.77	89.12 ± 8.43	79.43 ± 7.77
7	Aminocarb	15.65	83.51 ± 6.87	96.68 ± 9.86	85.1 ± 5.14	92.03 ± 3.52
8	Anthracene	16.05	96.2 ± 10.17	D	87.01 ± 10.15	D
9	Atraton	14.89	99.23 ± 13.02	93.58 ± 11.55	100.78 ± 8.9	87.83 ± 8.15
10	Atrazine	15.28	89.16 ± 9.73	90.93 ± 13.01	97.16 ± 6.4	91 ± 7.15
11	Azaconazole	23.86	91.33 ± 7.26	82.01 ± 8.06	95.56 ± 3.65	82.3 ± 4.62
12	Azinphos-ethyl	30.62	101.29 ± 17.76	D	107.4 ± 11.81	70.36 ± 3.68
13	Beflubutamid	21.69	95.68 ± 12.24	102.54 ± 8.47	90.85 ± 5.71	100.71 ± 6.24
14	Benalaxyl	25.97	81.37 ± 14.11	95.66 ± 10.05	93.04 ± 10.2	104.46 ± 7.44
15	Benfluralin	13.98	93.07 ± 10.81	97.96 ± 5.52	99.7 ± 4.3	102.63 ± 7.16
16	Benodanil	25.22	90.82 ± 7.6	92.41 ± 5.7	97.62 ± 5.18	94.18 ± 8.63
17	Benoxacor	17.19	97.84 ± 13.18	100.73 ± 10.5	110.41 ± 6.06	96.02 ± 6.09
18	Benthiocarb	19.53	85.11 ± 10.27	94.38 ± 6.52	90.6 ± 3.46	90.8 ± 5.42
19	Bifenthrin	28.32	94.18 ± 10.71	96.53 ± 8.41	91.79 ± 3.36	85.41 ± 7.3
20	Bioresmethrin	27.30	84.69 ± 9.43	99.34 ± 10.95	73.05 ± 4.24	85.55 ± 5.9
21	Biphenyl	8.18	102.59 ± 88.74	D	90.46 ± 11.81	70.13 ± 7.05
22	Boscalid	33.43	88.27 ± 15.36	78.93 ± 4.16	90.48 ± 6.39	67.45 ± 3.02
23	Bromacil	19.24	100.34 ± 14.33	119.76 ± 8.42	92.68 ± 8.06	96.28 ± 5.72
24	Bromocyclen	17.01	86.78 ± 14.21	79.31 ± 7.15	97.27 ± 6.02	79.57 ± 5.74
25	Bromophos-ethyl	22.22	94.34 ± 9.14	42.33 ± 4.11	93.83 ± 4.4	45.93 ± 4.48
26	Bromopropylate	28.10	88.96 ± 9.58	86.65 ± 12.35	94.32 ± 4.11	93.54 ± 3.01
27	Bromuconazole I	27.90	91.65 ± 7.16	98.91 ± 7.41	93.82 ± 4.59	92.52 ± 6.81
28	Bromuconazole II	28.78	84.78 ± 9.89	99.34 ± 8.77	87.79 ± 4.96	88.32 ± 6.26
29	Bupirimate	24.00	104.52 ± 16.74	106.64 ± 9.61	98.14 ± 6.61	102.32 ± 9.34
30	Buprofezin (Z-isomer)	23.82	93.94 ± 14.44	100.39 ± 9.08	89.87 ± 8.89	90.37 ± 9.04
31	Butachlor	22.69	88.68 ± 16.49	104.5 ± 12.58	103.43 ± 6.92	103.55 ± 7.98
32	Butafenacil	32.50	98.2 ± 6.72	112 ± 7.78	103.09 ± 4.05	113.04 ± 8.47
33	Butamifos	22.99	105.03 ± 10.81	104.38 ± 8.21	95.15 ± 6.46	101.11 ± 8.37
34	Butralin	20.62	100.14 ± 13.69	96.16 ± 8.55	101.61 ± 9.99	100.02 ± 7.55
35	Butylate	8.98	93.69 ± 5.02	93.43 ± 8.11	96.57 ± 2.24	97.55 ± 3.74
36	Cadusafos	14.03	86.71 ± 8.88	89.37 ± 8.58	91.71 ± 3.22	102.3 ± 3.5
37	Carbophenothion	25.87	93.49 ± 15.15	91.72 ± 13.37	96.35 ± 10.56	86.42 ± 6.28
38	Carboxin	23.65	74.24 ± 12.48	96.47 ± 10.91	82.55 ± 6.57	90.3 ± 6.19
39	Carfentrazone-ethyl	26.09	105.48 ± 12.6	103.16 ± 8.56	104.16 ± 6.9	111.67 ± 7.03
40	Chlorbenside	21.78	83.7 ± 7.06	44.72 ± 4.44	86.12 ± 1.77	43.29 ± 1.57

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
41	Chlorbufam	15.22	92.05 ± 17.23	106.78 ± 9.95	99.77 ± 9.76	93.19 ± 11.23
42	Chlordimeform	13.40	73.31 ± 6.49	78.33 ± 6.05	77.58 ± 2.66	80.24 ± 5.15
43	Chlorethoxyfos	12.73	107.96 ± 8.95	96.15 ± 6.38	101.99 ± 4.29	97.97 ± 3.41
44	Chlorfenapyr	24.45	86.76 ± 17.16	M.D	101.64 ± 9.74	M.D
45	Chlorfenson	22.84	98.11 ± 6.3	95.64 ± 5.31	96.86 ± 5.77	92.54 ± 6.63
46	Chlorfenvinphos	21.54	90.94 ± 13.88	96.52 ± 8.55	94.04 ± 5.82	96.89 ± 5.36
47	Chlormephos	9.17	95.47 ± 5	96.66 ± 4.24	94.97 ± 2.31	104.28 ± 4.26
48	Chlorobenzilate	24.62	85.29 ± 4.06	102.31 ± 6.35	93.06 ± 3.77	102.53 ± 4.96
49	Chloroneb	10.51	88.23 ± 5.15	93 ± 5.36	93.9 ± 3.52	95.41 ± 4.95
50	Chloropropylate	24.62	85.61 ± 7.07	99.76 ± 4.52	93.72 ± 4.29	100.86 ± 4.05
51	Chlorpropham	13.29	83.19 ± 7.64	106.28 ± 17.08	89.61 ± 2.52	78.53 ± 11.28
52	Chlorpyrifos-methyl	18.07	99.37 ± 12.75	82.13 ± 5.67	97.35 ± 4.69	71.32 ± 3.91
53	Chlorthiophos	25.29	88.5 ± 8.98	62.24 ± 7.56	89.93 ± 3.05	48.91 ± 4.46
54	Clodinafop-propargyl	26.43	90.5 ± 12.73	95.32 ± 11.14	98.14 ± 11.35	106.24 ± 5.79
55	Cloquintocet-mexyl	28.35	94.82 ± 11.67	D	88.02 ± 3.99	22.94 ± 5.14
56	Crimidine	10.66	80.12 ± 9.53	76.83 ± 7.04	93.16 ± 5.36	81.71 ± 6.6
57	Cyanofenphos	26.05	98.71 ± 9.53	113.45 ± 6.57	96.31 ± 6.97	95.48 ± 6.71
58	Cyanophos	15.81	94.15 ± 9.86	96.85 ± 7.73	97.2 ± 3.98	101.05 ± 7.05
59	Cycloate	12.94	96.33 ± 5.85	86.7 ± 4.89	96.4 ± 3.11	91.11 ± 4.48
60	Cyenopyrafen	28.97	79.35 ± 8.61	95.33 ± 15.55	73.02 ± 2.88	87.41 ± 10.95
61	Cyflufenamid	24.40	94.65 ± 13.53	98.51 ± 8.86	98.21 ± 5.16	107 ± 8.43
62	Cyfluthrin I-IV	33.00	77.19 ± 9.66	114.3 ± 8.37	90.85 ± 3.63	118.1 ± 3.82
63	Cyhalofop-butyl	29.84	88.78 ± 7.08	118.36 ± 7.16	95.49 ± 3.15	118.85 ± 4.07
64	Cyhalothrin (Lambda)	30.39	85.94 ± 10.24	126.01 ± 20.33	85.91 ± 9.12	110.27 ± 5.15
65	Cypermethrin I-IV	33.63	86.6 ± 10.05	M.D	94.85 ± 4.77	M.D
66	Cyprazine	17.75	90.12 ± 10.86	100.66 ± 5.05	98.13 ± 3.48	97.54 ± 7.51
67	Cyproconazole	24.18	81.22 ± 8.79	106.02 ± 8.12	89.15 ± 4.43	104.52 ± 5.81
68	Cyprodinil	20.89	84.35 ± 8.66	63.12 ± 8.37	87.04 ± 3.14	48.7 ± 5.8
69	DCPA	20.13	86.75 ± 8.15	90.66 ± 8.58	98.25 ± 5.17	97.76 ± 7.22
70	DDD-o,p'	23.70	97.03 ± 10.05	85.4 ± 5.5	97.81 ± 6.88	84.79 ± 6.43
71	DDE-o,p'	22.22	93.18 ± 5.43	76.42 ± 3.81	94.47 ± 2.59	73.34 ± 4.15
72	DDT-o,p'	25.02	92.81 ± 7.16	74.3 ± 4.78	95.79 ± 3.62	71.82 ± 3.94
73	Deltamethrin I+II	36.55	84.91 ± 9.01	87.7 ± 11.98	91.7 ± 5.17	87.77 ± 7.68
74	Demeton-O	12.55	85.36 ± 12.82	88.82 ± 7.15	90.3 ± 4.54	97.84 ± 6.78
75	Desmetryn	17.61	90.19 ± 11.41	102.8 ± 9.02	94.88 ± 5.13	98.36 ± 7.64
76	Diallate I+II	14.15	97.54 ± 10.24	94.76 ± 10.43	97.09 ± 5.12	97.63 ± 6.24
77	Dichlofenthion	17.74	93.55 ± 8.28	82.67 ± 7.4	96.25 ± 3.5	83.6 ± 5.21
78	Dichlormid	7.74	109.91 ± 8.38	96.34 ± 15.6	101.36 ± 8.63	113.18 ± 3.99
79	Dichlorobenzamide, 2,6-	13.64	80.94 ± 7.41	95.74 ± 7.19	84.14 ± 9.01	85.84 ± 10.2
80	Dichlorobenzonitrile, 2,6-	7.63	108.37 ± 4.67	100.59 ± 3.05	111.85 ± 2.61	104.01 ± 4.26
81	Dichlorobenzophenone, 4,4'-	19.98	90.53 ± 5.89	76.58 ± 2.45	92.04 ± 2.11	75.91 ± 4.17
82	Dichlorophenol, 2,4-	5.20	38.03 ± 5.87	47.73 ± 2.49	53.53 ± 1.56	53.46 ± 3.4
83	Diclobutrazol	23.77	76.2 ± 8.34	100.95 ± 12.31	92 ± 7.36	96.32 ± 11.08
84	Diclofop-methyl	26.93	90.52 ± 10.59	106.26 ± 8.66	94.36 ± 5.2	93.8 ± 6.94
85	Dicofol, o, p'-	18.85	93.93 ± 6.28	79.73 ± 5.29	96.6 ± 2.92	102.83 ± 5.05

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
86	Diethofencarb	19.83	100.6 ± 11.13	87.81 ± 8.63	98.86 ± 4.83	93.66 ± 8.63
87	Diflufenican	27.07	78.06 ± 9.36	D	89.6 ± 6.3	D
88	Dimefox	3.94	99.87 ± 8.13	84.34 ± 6.01	95.67 ± 5.06	86.28 ± 4.96
89	Dimepiperate	21.55	93.27 ± 10.06	96.9 ± 10.92	93.05 ± 5.65	95.56 ± 6.59
90	Dimethachlor	17.75	106.24 ± 9.74	115.48 ± 4.31	98.51 ± 5.68	101.59 ± 7.54
91	Dimethenamid-P	17.79	99.22 ± 6.4	97.12 ± 9.87	100.74 ± 3.95	96.24 ± 7.59
92	Dimethipin	15.25	85.27 ± 14.65	95.09 ± 16.81	91.88 ± 9.75	102.87 ± 10.46
93	Dimethoate	14.84	102.57 ± 8.54	84.1 ± 10.14	107.89 ± 3.84	109.35 ± 7.31
94	Dimetilan	18.61	83.95 ± 16.26	79.13 ± 9.77	93.9 ± 14.08	89.27 ± 6.58
95	Dimoxystrobin	28.17	100.37 ± 9.26	110.61 ± 10.65	98.9 ± 3.09	111.7 ± 3.59
96	Diniconazole	24.79	76.61 ± 6.85	81.23 ± 7.94	83.09 ± 5.97	75.05 ± 3.82
97	Dioxabenzofos	13.65	94.91 ± 11.26	106.98 ± 8.08	100.84 ± 8.4	106.86 ± 12.76
98	Diphenamid	20.64	83.13 ± 14.12	103.66 ± 8.29	93.07 ± 3.84	99.66 ± 4.53
99	Diphenylamine	12.67	94.57 ± 7.77	107.25 ± 11.62	106.58 ± 2.53	99.18 ± 6.06
100	Dipropetryn	19.57	86.35 ± 12.99	94.9 ± 10.49	93.68 ± 5.69	98.07 ± 6.12
101	Disulfoton sulfone	22.50	69.79 ± 8.43	92.34 ± 8.92	70.28 ± 6.02	109.12 ± 7.97
102	Disulfoton-sulfoxide	7.26	97.13 ± 3.53	101.85 ± 3.18	96.21 ± 2.05	105.75 ± 3.92
103	Ditalimfos	22.71	26.28 ± 4.92	49.55 ± 18.88	34.67 ± 3.64	40.48 ± 2.82
104	Diuron	21.32	99.22 ± 13.64	90.82 ± 18.49	89.29 ± 7.67	89.14 ± 8.81
105	Edifenphos	26.02	80.13 ± 10.06	94.52 ± 9.67	78.69 ± 2.85	95.75 ± 5.83
106	EPN	28.13	87.51 ± 10.18	110.14 ± 10.42	99.62 ± 8.41	98.49 ± 7.93
107	Epoxiconazole	27.39	93.82 ± 7.59	87.83 ± 8.66	97.36 ± 5.86	81.4 ± 3.63
108	EPTC	7.73	96.21 ± 14.59	109.11 ± 14.77	97.96 ± 7.78	98.28 ± 10.46
109	Esfenvalerate	35.54	76.31 ± 4.73	92.53 ± 8.8	84.87 ± 3.12	91.69 ± 5.29
110	Etaconazole I (a)	24.83	92.96 ± 7.91	88.44 ± 6.02	97.86 ± 3.89	100.59 ± 9.44
111	Ethalfluralin	13.54	95.37 ± 10.64	97.34 ± 10.84	99.35 ± 7.05	106.5 ± 7.08
112	Ethion	25.18	92.45 ± 14.05	103.05 ± 8.08	94.32 ± 4.47	99.79 ± 6.29
113	Ethofumesate, 2-keto-	17.75	90.25 ± 16.78	97.57 ± 11.84	94.2 ± 8.85	106.27 ± 6.47
114	Ethofumesate	19.30	84.61 ± 9.69	95.74 ± 8.94	96.92 ± 12.02	100.58 ± 8.61
115	Ethylan	24.36	102.52 ± 7.35	90.81 ± 7.09	97.01 ± 4.33	85.14 ± 5.77
116	Etoxazole	28.60	101.61 ± 15.42	96.07 ± 10.28	101.8 ± 12.52	108.99 ± 9.52
117	Etridiazole	9.48	98.01 ± 7.88	99.57 ± 5.78	103.44 ± 5.23	93.4 ± 3.66
118	Fenamiphos	22.99	96.95 ± 18.65	70.15 ± 6.51	88.66 ± 14.76	87.61 ± 11.57
119	Fenarimol	30.33	106.73 ± 9.29	118.34 ± 5.38	101.61 ± 5.77	118.32 ± 4.73
120	Fenclorim	14.28	90.03 ± 7.19	34.26 ± 2.55	88.97 ± 3.19	24.89 ± 1.73
121	Fenfluthrin	17.56	93.2 ± 9.01	90.87 ± 6.96	97.83 ± 3.88	89.99 ± 7.05
122	Fenhexamid	26.17	23.78 ± 4.71	62.3 ± 31.76	26.87 ± 2.22	36.48 ± 3.84
123	Fenitrothion	19.15	88.85 ± 7.72	96.72 ± 8.98	92.65 ± 4.50	95.52 ± 4.51
124	Fenoxaprop-ethyl	31.05	88.79 ± 10.68	D	97.66 ± 4.67	19.21 ± 3.47
125	Fenpropimorph	19.95	84.15 ± 7.14	75.22 ± 3.93	83.03 ± 4.69	64.26 ± 2.99
126	Fenson	20.30	88.91 ± 6.43	94.41 ± 3.92	95.28 ± 3.5	97.79 ± 3.83
127	Fenvalerate I+II	35.16	114.33 ± 12.07	102.35 ± 5.61	111 ± 4.41	103.34 ± 3.75
128	Fipronil sulfide	21.39	90.54 ± 15.03	95.01 ± 12.67	96.8 ± 6.59	104.74 ± 16.29
129	Fipronil sulfone	24.02	81.22 ± 9.48	101.13 ± 12.46	97.98 ± 5.99	109.47 ± 6.97
130	Fipronil	21.65	82.27 ± 15.92	96.19 ± 17.63	96.91 ± 5.59	113.86 ± 7.39

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
131	Fluacrypyrim	25.82	98.78 ± 9.98	113.01 ± 11.22	94.48 ± 5.24	116.87 ± 4.95
132	Fluazifop-butyl	24.45	84.76 ± 6.73	94.54 ± 13.11	93.16 ± 4	101.39 ± 8.6
133	Fluchloralin	16.53	95.42 ± 12.39	91.25 ± 8.41	97.16 ± 3.97	102.11 ± 4.05
134	Flucythrinate I+II	33.89	107.62 ± 16.51	109.32 ± 9.54	94.48 ± 10.69	111.43 ± 6.64
135	Fludioxonil	23.41	88.18 ± 10.07	87.6 ± 8.14	89.03 ± 5.15	78.81 ± 5.94
136	Flufenacet	20.20	103 ± 8.56	94.32 ± 6.36	98.08 ± 2.78	104.17 ± 5.8
137	Flumetralin	22.74	97.43 ± 8.24	91.8 ± 8.25	90.05 ± 2.12	98.03 ± 4.68
138	Fluotrimazole	27.38	97.1 ± 7.9	91.91 ± 10.75	97.28 ± 4.53	103.85 ± 7.97
139	Fluquinconazole	31.95	81.46 ± 5.65	105.87 ± 6.74	89.94 ± 2.88	101.46 ± 6.84
140	Flusilazole	23.87	105.99 ± 13.58	92.33 ± 11.93	97.63 ± 5.92	103.16 ± 5.22
141	Flutolanil	23.13	85.75 ± 5.07	105.44 ± 15.52	89.77 ± 3.88	108.14 ± 6.62
142	Flutriafol	22.73	96.81 ± 5.55	99.67 ± 6.65	97.96 ± 2.91	103.38 ± 4.72
143	Fonofos	15.91	92.93 ± 9.09	93.72 ± 8.12	98.38 ± 4.59	91.98 ± 5.77
144	Formothion	17.25	68.33 ± 6.29	85.88 ± 46.03	74.18 ± 4.55	73.17 ± 7.63
145	Furalaxyl	21.77	96.4 ± 8.58	105.7 ± 8.89	99.84 ± 4.57	106.98 ± 7.06
146	Furametpyr	29.19	89.19 ± 5.27	112.87 ± 5.74	89.56 ± 3.51	113.9 ± 2.96
147	Halfenprox	33.45	84.8 ± 12.94	79.64 ± 4.23	105.34 ± 5.34	78.57 ± 6.27
148	Haloxyfop-methyl	22.34	81.02 ± 10.85	101.05 ± 8.56	101.25 ± 6.16	103.13 ± 12.83
149	Heptachlor endo-epoxide	21.24	86.68 ± 13.74	81.19 ± 8.2	95.32 ± 6.68	87.39 ± 6.05
150	Heptenophos	11.85	90.73 ± 4.24	101.12 ± 4.18	93.16 ± 2.66	104.16 ± 3.42
151	Hexachlorobenzene	14.52	68.94 ± 4.52	39.56 ± 2.24	67.69 ± 2.22	35.94 ± 10.52
152	Hexazinone	26.67	85.15 ± 5.56	87.34 ± 4.54	92.27 ± 3.53	93.35 ± 4.97
153	Hydroprene	17.70	95.7 ± 15.5	D	87.35 ± 7.45	75.49 ± 4.7
154	Iodofenphos	23.04	90.51 ± 9.82	49.05 ± 7.23	87.95 ± 5.92	48.3 ± 4.86
155	Ipconazole	30.12	108.44 ± 12.53	87.07 ± 9.78	97.67 ± 5.11	98.41 ± 5.88
156	Iprobenfos	17.11	89.34 ± 10.81	106.57 ± 5.71	97.44 ± 4.18	101 ± 4.09
157	Isazofos	16.86	100.86 ± 15.92	104.41 ± 10.07	98.73 ± 6.08	110.93 ± 4.8
158	Isobenzan	20.17	99.53 ± 12.51	71.82 ± 7.54	98.11 ± 7.37	83.54 ± 8.47
159	Isocarbophos	20.22	77.8 ± 10.86	97.78 ± 5.83	89.14 ± 3.98	105.7 ± 6.72
160	Isodrin	20.63	90.88 ± 10.24	62.1 ± 7.81	91.44 ± 4.91	70.58 ± 4.56
161	Isofenphos oxon	20.29	100.67 ± 9.36	94.27 ± 7.01	85.54 ± 3.29	99.07 ± 6.33
162	Isofenphos	21.55	79.59 ± 9.68	97.71 ± 8.45	93.38 ± 6.18	97.18 ± 4.51
163	Isofenphos-methyl	20.97	95.27 ± 9.11	103.91 ± 5.81	95.33 ± 4.67	101.43 ± 5.88
164	Isopropalin	20.93	94.59 ± 7.24	85.31 ± 7.18	100.79 ± 3.35	86.83 ± 5.49
165	Isoprothiolane	23.24	103.67 ± 9.05	105.16 ± 8.6	95.47 ± 4.28	111.91 ± 5.16
166	Isopyrazam	31.02	96.37 ± 10.06	113.08 ± 7.64	95.86 ± 3.39	119.98 ± 8.09
167	isoxadifen-ethyl	25.78	99.79 ± 11.65	94.55 ± 9.49	97.99 ± 5.89	111.98 ± 7.41
168	Kresoxim-methyl	24.07	92.25 ± 15.98	99.06 ± 7.85	97.12 ± 6.65	107.74 ± 7.51
169	Lactofen	30.41	101.15 ± 12.33	102.38 ± 10.26	98.61 ± 5.16	113.99 ± 6.5
170	Leptophos	29.46	83.1 ± 13.12	35.93 ± 45.38	83.25 ± 4.66	13.28 ± 6.22
171	Malathion	19.63	97.17 ± 8.71	106.59 ± 11.95	95.92 ± 7.14	105.9 ± 4.87
172	Mefenpyr-diethyl	27.64	87.79 ± 7.68	104.76 ± 7.88	97.09 ± 3.08	111.18 ± 5
173	Mepanipyrim	22.59	104.55 ± 15.54	25.56 ± 7.92	94.83 ± 3.77	29.54 ± 5.98
174	Mephosfolan	21.49	83.19 ± 11.88	104.23 ± 9.31	85.12 ± 7.18	95.41 ± 6.78
175	Metalaxyl	18.61	103.27 ± 15.24	82.22 ± 9.65	98.71 ± 6.29	95.54 ± 8.36

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
176	Metazachlor	21.08	91.16 ± 11.84	97.41 ± 17.46	92.48 ± 5.33	99.34 ± 5.56
177	Methacrifos	10.40	95.75 ± 5.82	109.54 ± 4.65	97.25 ± 4.18	104.06 ± 7.39
178	Methidathion	22.09	100.96 ± 8.18	101.58 ± 4.89	96.85 ± 2.79	99.4 ± 3.94
179	Methoprotryne	23.90	96.99 ± 10.59	106.97 ± 12.73	97.7 ± 8.90	105.28 ± 10.53
180	Metolachlor	19.77	95.33 ± 6.82	91.98 ± 4.68	99.12 ± 3.47	98.02 ± 4.1
181	Metribuzin	17.80	101.93 ± 12.24	103.03 ± 7.6	97.15 ± 6.8	93.2 ± 4.57
182	Mirex	29.61	82.46 ± 6.57	45.38 ± 3.06	85.21 ± 3.82	45.95 ± 2.59
183	Molinate	11.00	83.44 ± 13.08	81.77 ± 5.16	93.05 ± 3.90	77.25 ± 5.05
184	Myclobutanil	23.72	98.86 ± 11.26	101.65 ± 10.74	97.74 ± 4.88	98.67 ± 9.19
185	Napropamide	22.94	77.93 ± 10.42	87.13 ± 10.98	89.02 ± 8.09	91.62 ± 8.67
186	Nitrapyrin	9.43	92.86 ± 10.14	97.28 ± 7.02	97.28 ± 6.60	96.38 ± 5.14
187	Nitrofen	24.15	90.46 ± 13.16	83.17 ± 4.55	98.04 ± 7.73	81.31 ± 6.06
188	Nitrothal-isopropyl	20.34	93.27 ± 7.5	89.7 ± 4.48	96.55 ± 5.97	86.96 ± 5.53
189	Norflurazon	26.19	86.93 ± 13.05	93.84 ± 9.18	90.47 ± 5.25	80.44 ± 7.01
190	Norflurazon-Desmethyl	25.60	84.29 ± 8.26	D	84.64 ± 3.27	D
191	Nuarimol	26.76	82.66 ± 10.79	103.28 ± 5.63	93.81 ± 5.27	104.68 ± 7.86
192	Ofurace	25.78	104.07 ± 11.81	99.87 ± 6.99	95.01 ± 6.5	104.56 ± 6.87
193	Oxadiazon	23.66	102.08 ± 5.76	97.66 ± 8.64	96.35 ± 3.29	101.65 ± 5.39
194	Oxadixyl	25.11	94.63 ± 7.41	102.9 ± 10.26	96.93 ± 4.37	104.64 ± 6.29
195	Oxyfluorfen	23.88	80.11 ± 14.3	80.92 ± 11.25	104.92 ± 13.89	87.41 ± 12.38
196	Paclobutrazol	22.27	86.89 ± 9.51	97.62 ± 7.01	92.1 ± 4.99	98.58 ± 7.81
197	Parathion	19.99	82.82 ± 15.92	93.5 ± 12.07	102.77 ± 6.77	101.93 ± 6.95
198	Parathion-methyl	18.07	93 ± 13.08	89.31 ± 8.44	98.13 ± 6.42	75.88 ± 3.57
199	Pebulate	9.55	89.06 ± 17.48	96.4 ± 8.84	101.78 ± 9.07	92.4 ± 5.95
200	Penconazole	21.20	88.13 ± 10.77	95.39 ± 7.89	94.36 ± 4.54	90.59 ± 6.71
201	Pendimethalin	21.17	81.81 ± 16.13	84.75 ± 16.3	103.49 ± 11.48	79.11 ± 7.61
202	Pentachloroaniline	17.28	74.19 ± 13.21	28.51 ± 37	92.17 ± 11.87	22.77 ± 11.57
203	Pentachloroanisole	14.74	84.38 ± 7.31	55.92 ± 2.68	89.18 ± 2.64	45.96 ± 2.69
204	Pentachlorobenzene	10.78	79.11 ± 5.16	32.3 ± 3.76	82.08 ± 2.66	26.54 ± 2.31
205	Pentachloronitrobenzene	15.72	83.47 ± 10.76	41.43 ± 5.52	89.93 ± 3.88	44.21 ± 3.84
206	Pentachlorophenol	15.51	5.88 ± 5.26	D	7.42 ± 1.49	D
207	Pentachlorothioanisole	19.19	73.98 ± 9.8	D	74.21 ± 3.51	D
208	Pentanochlor	19.24	87.92 ± 6.24	96.3 ± 6.54	89.39 ± 2.07	98.09 ± 4.64
209	Permethrin, (1R)-*cis*-	31.60	98.72 ± 18.83	118.08 ± 5.89	100.26 ± 8.6	105.63 ± 9.66
210	Phenkapton	28.39	98.63 ± 13.59	44.56 ± 10.45	93.68 ± 12.89	48.91 ± 7.53
211	Phenthoate	21.65	90.79 ± 15.55	100.19 ± 11.82	93.22 ± 11.74	102.26 ± 7.44
212	Phorate sulfone	19.74	79.66 ± 12.49	102.76 ± 12.39	95.15 ± 7.08	103.19 ± 9.81
213	Phorate	14.05	89.45 ± 12.5	96.01 ± 12.10	90.34 ± 7.05	114.31 ± 10.12
214	Phosalone	29.38	85.37 ± 12.67	95.76 ± 12.98	85.68 ± 5.81	85.29 ± 5.57
215	Phthalide	7.70	100.41 ± 11.8	M.D	112.11 ± 6.04	M.D
216	Picolinafen	28.26	85.28 ± 14.19	5.92 ± 6.35	98.45 ± 10.34	3.44 ± 2.15
217	Picoxystrobin	23.07	95 ± 7.64	107.36 ± 8.34	93.17 ± 2.99	112.86 ± 5.73
218	Piperonyl butoxide	27.21	82.79 ± 10.51	104.84 ± 14.48	86.47 ± 6.41	94.81 ± 7.76
219	Piperophos	28.33	96.34 ± 11.99	100.69 ± 14.45	100.51 ± 7.26	109.41 ± 11.02
220	Pirimicarb	17.36	98.94 ± 9.12	101.22 ± 9.7	99.21 ± 5.78	96.74 ± 8.57

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
221	Pirimiphos-ethyl	20.89	95.47 ± 12.66	88.7 ± 10.32	95.16 ± 6.91	87.08 ± 7.33
222	Pirimiphos-methyl	19.29	97.27 ± 12.37	96.34 ± 7.71	91.38 ± 5.31	94.57 ± 6.49
223	Plifenate	18.10	97.41 ± 10.76	100.63 ± 7.52	101.31 ± 8.03	98.84 ± 7.86
224	Pretilachlor	23.44	88.16 ± 8.28	106.15 ± 6.99	91.04 ± 4.97	104.9 ± 5.45
225	Procymidone	21.81	106.08 ± 15.42	106.43 ± 8.16	101.85 ± 6.7	102.01 ± 10.58
226	Profenofos	23.29	92.98 ± 11.76	92.64 ± 11.48	97.95 ± 5.77	83.82 ± 6.11
227	Profluralin	16.03	77.78 ± 13.39	101.37 ± 12.12	105.29 ± 11.04	92.24 ± 7.62
228	Prometon	15.15	88.9 ± 14.72	91.58 ± 4.52	96.37 ± 12.16	93.99 ± 4.85
229	Prometryn	18.61	88.97 ± 11.36	89.51 ± 7.74	93.02 ± 5.82	89.3 ± 3.82
230	Propachlor	12.51	94.35 ± 12.04	84.64 ± 8.06	97.36 ± 3.46	100.55 ± 5.74
231	Propanil	17.71	83.95 ± 12.6	86.52 ± 8.75	84.34 ± 3.41	83.74 ± 6.41
232	Propaphos	22.23	93.61 ± 7.47	96.93 ± 4.57	95.37 ± 4.58	100.54 ± 4.22
233	Propazine	15.46	86.19 ± 9.51	91.17 ± 12.52	94.17 ± 4.85	98.27 ± 5.82
234	Propetamphos	15.92	98.78 ± 16.38	80.17 ± 10.12	95.81 ± 6.25	85.15 ± 5.71
235	Propham	9.45	91.75 ± 13.52	101.14 ± 15.03	93.36 ± 3.68	96.69 ± 4.09
236	Propiconazole I+II	26.16	89.29 ± 10.76	89.37 ± 6.74	106.99 ± 5.86	100.45 ± 7.67
237	Propisochlor	18.56	77.25 ± 12	95.35 ± 13.9	95.66 ± 6.19	99.32 ± 10.17
238	Propyzamide	15.96	95.87 ± 7.24	93.58 ± 5.3	96.23 ± 3.25	93.6 ± 3.77
239	Prosulfocarb	18.75	85.57 ± 11.68	82.66 ± 7.56	103.51 ± 6.96	91.7 ± 10.05
240	Pyrazophos	30.68	93.08 ± 12.46	D	90.39 ± 8.53	44.84 ± 32.57
241	Pyridaben	31.80	65.26 ± 8.45	119.51 ± 6.76	88.03 ± 3.33	112.81 ± 3.53
242	Pyrifenox I	21.31	83.63 ± 15.61	94.13 ± 9.12	83.06 ± 9.35	87.89 ± 5.78
243	Pyrifenox II	22.29	94.04 ± 13.31	90.97 ± 12.05	93.03 ± 7.17	81.79 ± 8.35
244	Pyrimethanil	16.12	89.06 ± 8.75	67.66 ± 9.04	91.48 ± 1.62	60.05 ± 5.08
245	Pyrimidifen	34.82	81.48 ± 8.21	19.21 ± 23.07	80.68 ± 3.01	11.75 ± 9.47
246	Quinalphos	21.61	38.11 ± 32.62	51.49 ± 30.3	83.42 ± 6.51	77.54 ± 6.24
247	Quinoclamine	19.27	50.26 ± 6.15	D	50.28 ± 3.57	D
248	Quinoxyfen	26.02	80.29 ± 7.92	D	86.56 ± 6.76	27.48 ± 2.07
249	Resmethrin	27.29	87.49 ± 13.72	100.81 ± 10.69	73.59 ± 3.55	83.26 ± 4.94
250	Sebuthylazine	17.02	86.81 ± 13.82	108.37 ± 13.29	91.95 ± 9.11	94.73 ± 7.90
251	Secbumeton	16.61	86.38 ± 8.84	99.02 ± 9.66	97.71 ± 4.68	95.39 ± 4.87
252	Simeconazole	18.23	83.30 ± 5.85	77.92 ± 2.65	91.68 ± 4.28	83.13 ± 3.78
253	Simetryn	18.24	77.26 ± 10.82	74.45 ± 7.62	90.65 ± 9.71	73.83 ± 5.28
254	Sulfotep	14.06	99.66 ± 13.82	94.07 ± 16.28	96.7 ± 6.01	107.48 ± 7.07
255	Tebuconazole	26.75	93.36 ± 6.89	86.43 ± 7.11	89.16 ± 3.78	94.95 ± 6.29
256	Tebufenpyrad	28.62	76.46 ± 14.12	100.35 ± 10.6	89.22 ± 8.23	109.2 ± 5.6
257	Tebupirimfos	17.13	91.72 ± 13.35	110.42 ± 7.55	100.91 ± 7.27	96.06 ± 8.84
258	Tebutam	14.05	83.66 ± 10.92	95.71 ± 10.57	96.58 ± 3.21	105.33 ± 6.54
259	Tefluthrin	16.85	99.39 ± 3.61	82.85 ± 3.93	98.94 ± 4.3	86.29 ± 5.28
260	Terbacil	16.55	95.46 ± 11.97	102.42 ± 9.05	100.82 ± 4.64	97.58 ± 5.73
261	Terbucarb	18.12	86.14 ± 14.62	99.23 ± 9.24	100.39 ± 10.28	95.81 ± 5.25
262	Terbufos sulfone	21.21	90.80 ± 9.12	96.62 ± 5.71	95.87 ± 3.99	92.67 ± 3.91
263	Terbufos	15.82	99.04 ± 14.54	83.41 ± 7.63	98.57 ± 5.64	105.06 ± 6.87
264	Terbuthylazine	15.84	92.93 ± 11.25	93.5 ± 5.68	97.22 ± 7.53	91.67 ± 8.67
265	Terbuthylazine-desethyl	13.86	79.63 ± 6.96	106.15 ± 8.39	92.19 ± 2.53	101.06 ± 7.66

Order	Compound	RT (min)	Recovery			
			LOQ (10 µg/kg)		5 LOQ (50 µg/kg)	
			Black Pepper	Dried Tea	Black Pepper	Dried Tea
266	Terbutryn	19.07	101.55 ± 8.47	85.91 ± 6.97	98.72 ± 3.85	91.19 ± 3.86
267	Tetraconazole	20.35	83.23 ± 10.24	86.45 ± 13.65	99.79 ± 4.87	103.97 ± 9.53
268	Tetradifon	29.02	97.07 ± 7.42	95.35 ± 9.56	93.05 ± 4.37	97.93 ± 8.31
269	Tetramethrin I+II	28.29	83.8 ± 9.45	104.25 ± 7.05	83.62 ± 4.76	109.45 ± 5.36
270	Tetrasul	25.30	79.02 ± 7.56	D	80.26 ± 4.19	25.27 ± 2.84
271	Thenylchlor	26.77	97.83 ± 9.11	111.71 ± 5.72	93.17 ± 3.56	112.17 ± 5.86
272	Thiometon	14.54	74.11 ± 14.16	105.7 ± 8.35	93.27 ± 3.61	83.41 ± 5.87
273	Tolclofos-methyl	18.24	96.19 ± 13.05	83.51 ± 8.41	101.38 ± 8.07	79.89 ± 6.99
274	Transfluthrin	18.35	94.17 ± 11.17	89.03 ± 7.21	97.91 ± 6.74	81.66 ± 5.17
275	Triadimefon	20.08	100.61 ± 16.58	94.62 ± 31.74	96.57 ± 6.42	99.93 ± 9.28
276	Triallate	16.79	93.56 ± 10.52	90.63 ± 8.38	96.94 ± 2.54	85.47 ± 3.77
277	Triazophos	25.65	86.98 ± 11.94	105.22 ± 11.06	96.29 ± 6.61	91.93 ± 7.99
278	Trichlorophenol, 2,4,6-	7.70	D	D	D	D
279	Triclosan	22.02	59.67 ± 8.76	80.43 ± 8.5	65.17 ± 7.23	84.3 ± 10.65
280	Tridiphane	18.57	92.23 ± 17.27	112.14 ± 10.71	100.11 ± 17.37	98.99 ± 7.38
281	Trifloxystrobin	26.49	97.12 ± 13.13	94.64 ± 8.92	96.01 ± 7.01	109.81 ± 6.58
282	Trifluralin	13.90	106.04 ± 9.04	99.43 ± 10.53	103.47 ± 3.03	100.84 ± 6.07
283	Vinclozolin	18.08	92.83 ± 17.93	99.39 ± 11.13	103.72 ± 8.30	98.21 ± 7.25
284	Zoxamide	27.39	94.71 ± 10.94	98.15 ± 6.13	91.66 ± 5.26	95.72 ± 4.56

M.D = Positive in-sample spiked
D = Detection but lower than lowest-level calibration

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