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Comparison of Sample Preparation Methods for Pesticide Analysis in Botanical Dietary Supplement Materials

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Abstract

This application note presents a novel streamlined sample preparation method for liquid chromatography/triple quadrupole mass spectrometry (LC/MS/MS) and gas chromatography/triple quadrupole mass spectrometry (GC/MS/MS) multiresidue pesticide (over 440) analysis. This streamlined sample preparation enables analysis in botanical dietary supplement (BDS) materials using the EMR mixed-mode passthrough cleanup with Agilent Captiva EMR with Carbon S cartridges. Various BDS samples are extracted by traditional QuEChERS extraction, followed by appropriate Captiva EMR cartridge cleanup. The selected Captiva EMR cartridges, based on the BDS sample matrix complexity and pigment intensity, include Captiva EMR–GPD for green tea and peppermint tea, Captiva EMR–LPD for barberry root, and Captiva EMR–GPD + EMR–GPF for curcumin complex. The developed method provides a simple and unified sample preparation workflow for both LC/MS/MS and GC/MS/MS pesticide detection. This method demonstrates acceptable performance, i.e., recovery of 70 to 120% and RSDs < 20%, in representative BDS samples for over 82% of the total 447 pesticides analyzed. Compared to the traditional approach that requires multiple sample preparation methods, the newly developed method demonstrates a more one-size-fits-most approach for efficient cleanup. This approach increases the instrument uptime and reduces both consumables and labor resources. The direct comparison of new method versus old method on actual samples analysis demonstrates acceptable equivalence on reporting results.

Introduction

Botanical dietary supplements (BDS) have been used by consumers throughout the world, seeking their positive effects. However, the botanical materials used in these BDS products tend to have a high risk of contamination with pesticide residues during planting, open-air drying, preserving, manufacturing, and storage. Therefore, the detection of pesticide residues in BDS products and raw materials is important to ensure their safety and quality. Validated pesticide analysis methods are needed for analyzing pesticide residues in these BDS matrices.

Due to the necessity of multiclass multiresidue pesticide analysis for BDS products, both LC/MS/MS and GC/MS/MS are used to analyze, quantify, and qualify a wide range of pesticides. GC/MS/MS detection is used primarily for organochlorine, organophosphorus, and pyrethroid pesticide analysis, and LC/MS/MS detection is applied primarily for thermally labile and polar pesticides.[1] Different detection methods place different requirements on preparing samples for instrument detection. In addition, a sample matrix can cause different matrix effects on the two detection techniques, giving two different matrix interferences and tolerances, making it difficult to generate acceptable results. BDS samples are considered a challenge due to their highly anhydrous, complex, and broad variety of features. These challenges from BDS sample matrices and large panel pesticides detection make sample preparation a critical and potential rate-limiting step in the complete workflow.

Various sample preparation techniques have been applied for pesticide analysis in botanicals, including supercritical fluid extraction (SFE)[2], gel permeation chromatography (GPC) or GPC with solid phase extraction (SPE)[3], accelerated solvent extraction (ASE) followed with dispersive SPE (dSPE)[4], and Agilent QuEChERS extraction followed with dSPE or SPE cleanup.[1,5–7] The last sample preparation method in the list is the most widely used method for multiresidue multiclass pesticide analysis. The method starts with standard QuEChERS extraction of 1 g of a homogenized sample by extracting using acidified ACN followed with salt partition using buffered or nonbuffered salts. The crude extract is then either treated by typical dSPE cleanup for LC/MS/MS analysis, or graphite carbon black (GCB)/PSA or GCB/NH$_2$ SPE cleanup for GC/MS/MS analysis. The method provides decent sample extraction efficiency and matrix removal, and delivers acceptable quantitation for a large panel of pesticide analysis by both LC/MS/MS and GC/MS/MS. However, the method requires separate sample preparation on one sample, which doubles the use of sample and preparation time. The dSPE cleanup offers a quick but limited cleanup, making

the analysis on more complex botanicals difficult. The SPE cleanup involves two steps of drying procedure using N$_2$ evaporation, which can be quite time consuming and labor intensive. The use of toxic solvent toluene or methylbenzene may add an additional health risk due to exposure, which is increased by the necessary evaporation steps.

Agilent Captiva EMR with Carbon S cartridges apply mixed-mode passthrough cleanup methodology for fast and efficient sample matrix removal. The Captiva EMR−General Pigmented Dry (EMR−GPD) and EMR−Low Pigmented Dry (EMR−LPD) cartridges are designed for cleanup of complex, dry botanic matrices. These cartridges provide comprehensive matrix removal for many unwanted matrix coextractives such as organic acids and fatty acids, carbohydrate, pigments, lipids and oils, other hydrophobic and hydrophilic interferences. The cartridges deliver the best balance between matrix removal and target recovery for complex dry matrices. For a generally pigmented dry matrix, Captiva EMR−GPD is usually recommended, while for a low pigmented dry matrix, Captiva EMR−LPD is recommended.

QuEChERS extraction followed by EMR mixed-mode passthrough cleanup was demonstrated successfully for pesticide analysis in plant-origin dry matrices.[8–10] In this study, QuEChERS extraction followed by an appropriate Captiva EMR passthrough cleanup was used for the analysis of over 440 pesticides in typical BDS samples, including green tea, black tea, herbal tea, curcumin complex, barberry root, and peppermint tea. The extracted samples were analyzed by both LC/MS/MS and GC/MS/MS detection.

Experimental

Chemicals and reagents

Pesticide standards and internal standards (ISTDs) were either obtained as the standard mix stock solutions from Agilent Technologies (part number 5190-0551), Restek (Bellefonte, PA, USA), or individual stock solutions from AccuStandard (New Haven, CT, USA). ISTDs were either mixed and individual stock solutions from Restek (Bellefonte, PA, USA), or powder from Sigma-Aldrich (St. Louis, MO, USA). HPLC or MS grade solvents were from Honeywell (Muskegon, MI, USA), including acetone, toluene, ethanol (EtOH), acetonitrile (ACN), methanol (MeOH), isopropanol (IPA). Reagent-grade acetic acid glacial (AA), and formic acid were also from Sigma-Aldrich. Anhydrous magnesium sulfate (MgSO$_4$) was from Agilent (part number 5982-0102). The 5M ammonium formate buffer was from Agilent (part number G1946-85021). D-sorbitol, L-(+)-gulonic acid γ-lactone, and shikimic acid were from TCI (Portland, OR, USA).

Equipment and material

The sample preparation products included Bond Elut QuEChERS extraction pouches, AOAC method (part number 5982-6755), Bond Elut QuEChERS extraction pouches, original method (part number 5982-6550), Captiva EMR−General Pigmented Dry (GPD) 6 mL cartridges (part number 5610-2091), Captiva EMR−Low Pigmented Dry (LPD) 6 mL cartridges (part number 5610-2092), and Captiva EMR−General Pigmented Fresh (GPF) 3 mL cartridges (part number 5610-2090). Also included were Bond Elut GCB/PSA, 500/500 mg cartridges (part number 5982-4568), and a typical dSPE kit with PSA, $MgSO_4$, C18, and GCB.

Other equipment and other consumables used included an analytical balance, multitube vortexer, centrifuge, mechanical mixer, pipettes, and repeater, vacuum manifold, polypropylene centrifuge tubes (50 and 15 mL), volumetric flasks, PTFE syringe filter, and an N_2 evaporator.

Instrument methods

Both LC/MS/MS and GC/MS/MS methods were set up on a customer instrument, which were considered as the customer's confidential information. The LC/MS/MS method was for 220 pesticides for analysis, and the GC/MS/MS method was for 227 pesticides for analysis.

Sample preparation

This study mainly focused on the sample preparation methods comparison using the traditional method versus a newly developed method. Traditional methods were adapted from Hayward and Wong's method[1,5], while the newly developed method was based on QuEChERS extraction followed with EMR mixed-mode passthrough cleanup using Captiva EMR with Carbon S cartridges. Traditional methods included two methods to prepare samples for GC/MS/MS detection and LC/MS/MS detection separately, while the new method applied one streamlined method to prepare the sample for both LC/MS/MS and GC/MS/MS detection.

Figure 1 shows the traditional method for GC/MS/MS detection. This method used 1 g of sample for QuEChERS extraction with unbuffered salts (original method). The crude extract was then cleaned by the PSA/GCB SPE conditioning-loading-elution step. The total eluent (~13 mL) was evaporated to ~100 µL, reconstituted in 500 µL of toluene, and dried by $MgSO_4$. The sample was then ready for GC/MS/MS analysis. The entire procedure usually took 6 to 8 hours, depending on the number of samples being processed.

Figure 2 shows the traditional method for LC/MS/MS detection. Similarly, the method starts with a 1 g sample for QuEChERS extraction but with buffered salts (AOAC method).
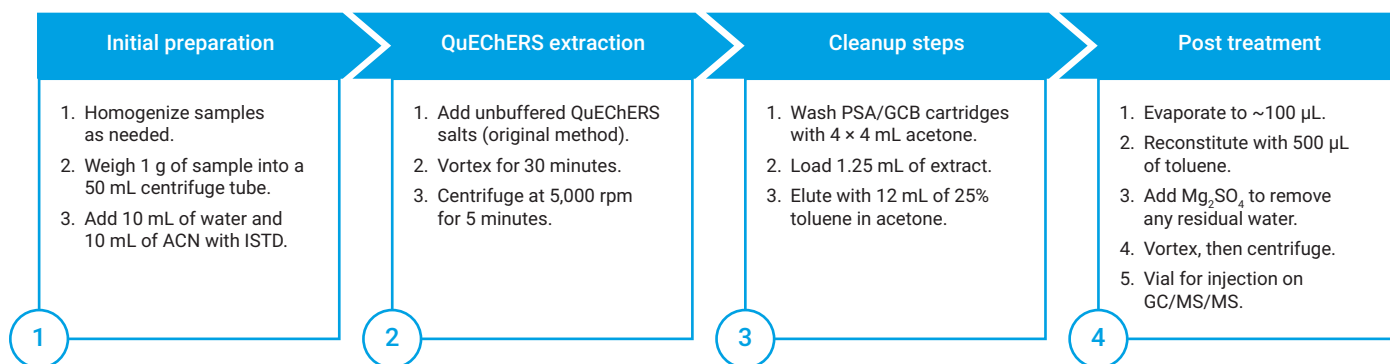
Initial preparation	QuEChERS extraction	Cleanup steps	Post treatment
1. Homogenize samples as needed. 2. Weigh 1 g of sample into a 50 mL centrifuge tube. 3. Add 10 mL of water and 10 mL of ACN with ISTD.	1. Add unbuffered QuEChERS salts (original method). 2. Vortex for 30 minutes. 3. Centrifuge at 5,000 rpm for 5 minutes.	1. Wash PSA/GCB cartridges with 4 × 4 mL acetone. 2. Load 1.25 mL of extract. 3. Elute with 12 mL of 25% toluene in acetone.	1. Evaporate to ~100 µL. 2. Reconstitute with 500 µL of toluene. 3. Add Mg_2SO_4 to remove any residual water. 4. Vortex, then centrifuge. 5. Vial for injection on GC/MS/MS.
1	2	3	4

Figure 1. Traditional sample preparation method for GC/MS/MS detection.

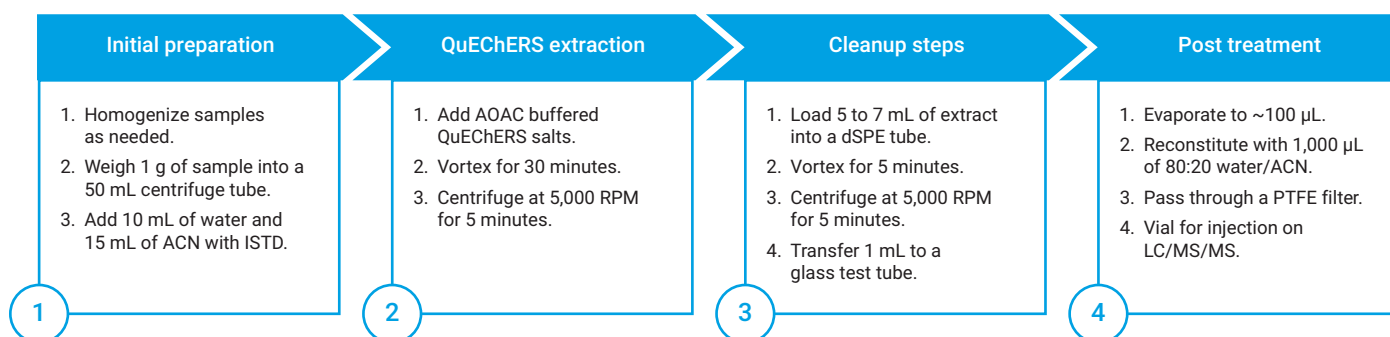| Initial preparation	QuEChERS extraction	Cleanup steps	Post treatment
1. Homogenize samples as needed. 2. Weigh 1 g of sample into a 50 mL centrifuge tube. 3. Add 10 mL of water and 15 mL of ACN with ISTD.	1. Add AOAC buffered QuEChERS salts. 2. Vortex for 30 minutes. 3. Centrifuge at 5,000 RPM for 5 minutes.	1. Load 5 to 7 mL of extract into a dSPE tube. 2. Vortex for 5 minutes. 3. Centrifuge at 5,000 RPM for 5 minutes. 4. Transfer 1 mL to a glass test tube.	1. Evaporate to ~100 µL. 2. Reconstitute with 1,000 µL of 80:20 water/ACN. 3. Pass through a PTFE filter. 4. Vial for injection on LC/MS/MS.
1	2	3	4

Figure 2. Traditional sample preparation method for LC/MS/MS detection.

The crude extraction was simply cleaned by the typical dSPE adding-vortexing-centrifuging step. An aliquot of supernatant (1 mL was dried to ~ 100 µL, reconstituted in 1,000 µL 20:80 ACN/water, and filtered by PTFE syringe filter. The sample was then ready for LC/MS/MS analysis. The entire procedure usually took 3 to 4 hours, depending on the number of samples being processed.

Figure 3 shows the new method for both GC/MS/MS and LC/MS/MS detection. The new method started with 0.5 g for QuEChERS extraction with buffered salts (AOAC method). The crude extract was then mixed with 10% of water with 1% formic acid. The entire mixture was loaded onto the appropriate EMR cartridge, and the eluent was collected completely. An aliquot of 1 mL sample was then applied for GC post-treatment outlined in Figure 1, and an aliquot of 0.5 mL sample was applied for LC post-treatment outlined on Figure 2. Samples were then ready for both LC/MS/MS and GC/MS/MS analysis. The entire procedure usually took 4 to 5 hours, depending on the number of samples being processed.

Less sample preparation time was needed with the new combined method compared to the traditional separate methods. This approach allowed the more efficient use of lab bench and analyst time. The combined method enabled better alignment on data sets generated for both LC/MS/MS and GC/MS/MS detection systems. As a result, the overall sample analysis productivity was improved. As an example, a lab analyst could usually prepare two samples for GC/MS/MS, or four samples for LC/MS/MS, in an 8-hour working day, when using the traditional separate preparation methods. However, with the new method, an analyst was able prepare two samples for both GC/MS/MS and LC/MS/MS

analysis. In comparison, the separate methods yield 2.5 complete datasets per two analysts per day. The use of the new sample preparation method provided a 50% increase on lab productivity. In addition, the misalignment of the datasets from the separate methods was eliminated. The separate data sets added more time required for data processing and QC reviews.

The selection of Captiva EMR with Carbon S cartridges was based on the sample pigment level. Captiva EMR–GPD was used for many pigmented botanical dietary supplement samples, including black tea, green tea, herbal tea, and peppermint tea. The Captiva EMR–LPD was used for the light-pigmented botanical dietary supplement samples such as barberry root. Captiva EMR–GPD + EMR-GPF were used sequentially for the heavily pigmented BDS sample curcumin complex. All cartridges were processed on a SPE manifold at a flow rate set to 1 drop every 3 to 5 seconds.

Method performance evaluation

The new method was evaluated for pesticide recovery and reproducibility, and a large panel pesticide pass rate according to SANTE guidelines.[14] The new method and the traditional method were compared for the matrix impact to critical analytes analysis. BDS samples were prespiked with standard at 50 ng/g in replicates of three, then prepared by the new method. A corresponding matrix blank was prepared and postspiked with a standard at the corresponding level with the consideration of the dilution factor. Recovery was based on a direct targeted response comparison between pre- and postspiked samples.

After the preliminary method validation of the new method, the new method was compared with the traditional method for proficiency test using LGC Axio Proficiency Spices Sample FC308/843. The results were also compared to the actual value and the initially reported value.
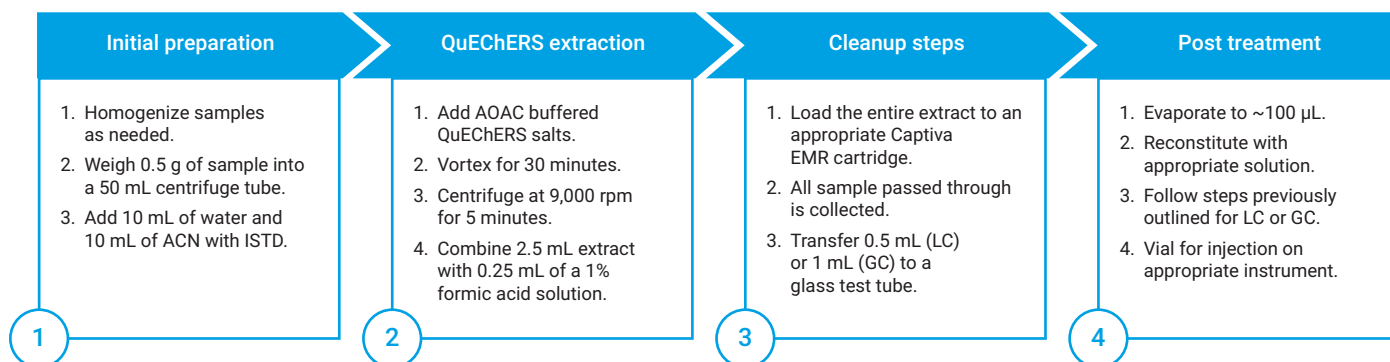
Initial preparation	QuEChERS extraction	Cleanup steps	Post treatment
1. Homogenize samples as needed. 2. Weigh 0.5 g of sample into a 50 mL centrifuge tube. 3. Add 10 mL of water and 10 mL of ACN with ISTD.	1. Add AOAC buffered QuEChERS salts. 2. Vortex for 30 minutes. 3. Centrifuge at 9,000 rpm for 5 minutes. 4. Combine 2.5 mL extract with 0.25 mL of a 1% formic acid solution.	1. Load the entire extract to an appropriate Captiva EMR cartridge. 2. All sample passed through is collected. 3. Transfer 0.5 mL (LC) or 1 mL (GC) to a glass test tube.	1. Evaporate to ~100 µL. 2. Reconstitute with appropriate solution. 3. Follow steps previously outlined for LC or GC. 4. Vial for injection on appropriate instrument.
1	2	3	4

Figure 3. New sample preparation method for both GC/MS/MS and LC/MS/MS detection.

Results and discussion

This study focuses on the comparison of the new method to the traditional method for botanical dietary supplement sample preparation for pesticide analysis by both GC/MS/MS and LC/MS/MS detection. The new method applies a single procedure using QuEChERS extraction followed with Captiva EMR passthrough cleanup for both detections. The traditional method uses two separate procedures, including QuEChERS extraction plus dSPE cleanup for LC/MS/MS detection, and QuEChERS extraction plus SPE cleanup for GC/MS/MS detection.

New method versus traditional method comparison on workflow

The new method based on traditional QuEChERS extraction followed with Captiva EMR passthrough cleanup provides a simpler, faster, and more cost-effective sample preparation for both LC/MS/MS and GC/MS/MS analysis. The EMR passthrough cleanup provides an easy, mixed mode chemical filtration, where the unwanted matrix co-extractives are removed efficiently and selectively, but the targeted pesticides are passed through for analysis. The Captiva EMR cartridge does not require the use of solvent for preconditioning. Sample crude extract can be directly loaded on the EMR cartridge for cleanup, which saves time and labor. It increases the sample volume recovery from ~ 50% to > 90%, providing sufficient sample volume for various post treatments required by different detections. The previous study demonstrates the high efficiency of complex dry botanical matrix removal, improvement on pesticide overall quantitation results, and higher pass rate for large panel pesticide analysis.[8–10] These features were confirmed in this study, and thus made the method qualified to support both LC/MS/MS and GC/MS/MS analysis. The method does not require the use of toluene, which means only 10 mL of organic solvent is used per sample.

The traditional method involves the two separate sample preparation procedures, which means using more sample, analyst time and labor, solvent, and consumables. Both procedures start with QuEChERS extraction but followed with different cleanup. The procedure for LC/MS/MS was relatively simple and easy because the following sample cleanup is dSPE. However, it still required many steps that took time and effort, such as multiple sample transfers, centrifuging, and capping and uncapping of dSPE tubes. Sample volume recovery for dSPE cleanup was only ~ 50%, which limits certain post treatments such as concentrating. The cleanup only provided limited matrix removal, which can support LC/MS/MS analysis but is unqualified for GC/MS/MS analysis. Therefore, a separate cleanup with more intense matrix cleaning must be used for GC/MS/MS analysis. This procedure requires the use of 10 mL organic solvent.

The GC/MS/MS procedure applied the PSA/GCB SPE conditioning-loading-eluting cleanup procedure, which was a much more time-consuming and labor-intensive procedure. The use of a PSA/GCB cartridge for cleanup provided intense matrix cleanup, but also caused sensitive pesticide loss, especially the planar compounds. Therefore, the elution with a solvent mixture of toluene and acetone was necessary to recover the retained pesticides on the cartridge. The SPE cartridge also required using solvent for preconditioning. After the SPE procedure, the entire eluent (> 13 mL) was then dried for concentrating and solvent switch, which was an even more time-consuming step for such a large volume sample drying. The entire procedure required the use of 38 mL of organic solvent. Together with the solvent used in the procedure for LC/MS/MS, the traditional method required a total of 48 mL of organic solvent per sample. It took approximately double the time for an analyst to prepare the same number of samples compared to the novel single preparation method for both LC/MS/MS and GC/MS/MS detection. Table 1 shows the comparison of new method and traditional method for consumable and solvent used, and time needed.

Table 1. Comparison of the new method versus the traditional method on the required consumables, solvents, and time to prepare two levels of spiked matrix samples and a 5-point matrix-matched calibration curve for each sample analysis.

Procedure		New Method	Traditional Method
		One Extraction Required	Two Extractions Required
Consumables per Sample	Extraction	Salt pouch (7), 50 mL tube (7)	Salt pouch (14), ceramic homogenizers (14), 50 mL tube (14)
	Cleanup	Agilent Captiva EMR cartridges (10), mixing or collection tube (10)	dSPE tube (8), SPE cartridge (8), collection tube (16)
Organic Solvent per Sample		~ 70 mL	~ 85 mL
Time per Sample		~ 5 to 6 hours	~ 12 hours (spread over two days/analysts)

New method performance assessment

The new method was evaluated for multiresidue pesticide recovery and reproducibility, and large panel overall pass rate. The SANTE/11312/2021 guideline was referred to for method performance assessment.[11]

1. Pesticide recovery in a botanical dietary supplement matrix (BDS)

Pesticide recovery in a BDS matrix was evaluated by prespiking standards in four different BDS matrices at the 50 ng/g level, including green tea extract, curcumin complex, barberry root extract, and peppermint tea. Samples were prepared by the new method and evaluated for critical pesticide recovery. Figure 4 shows the representative pesticide recovery in four typical BDS sample matrices, which demonstrates that acceptable pesticide recovery was obtained in all four BDS matrices using the new sample preparation method.
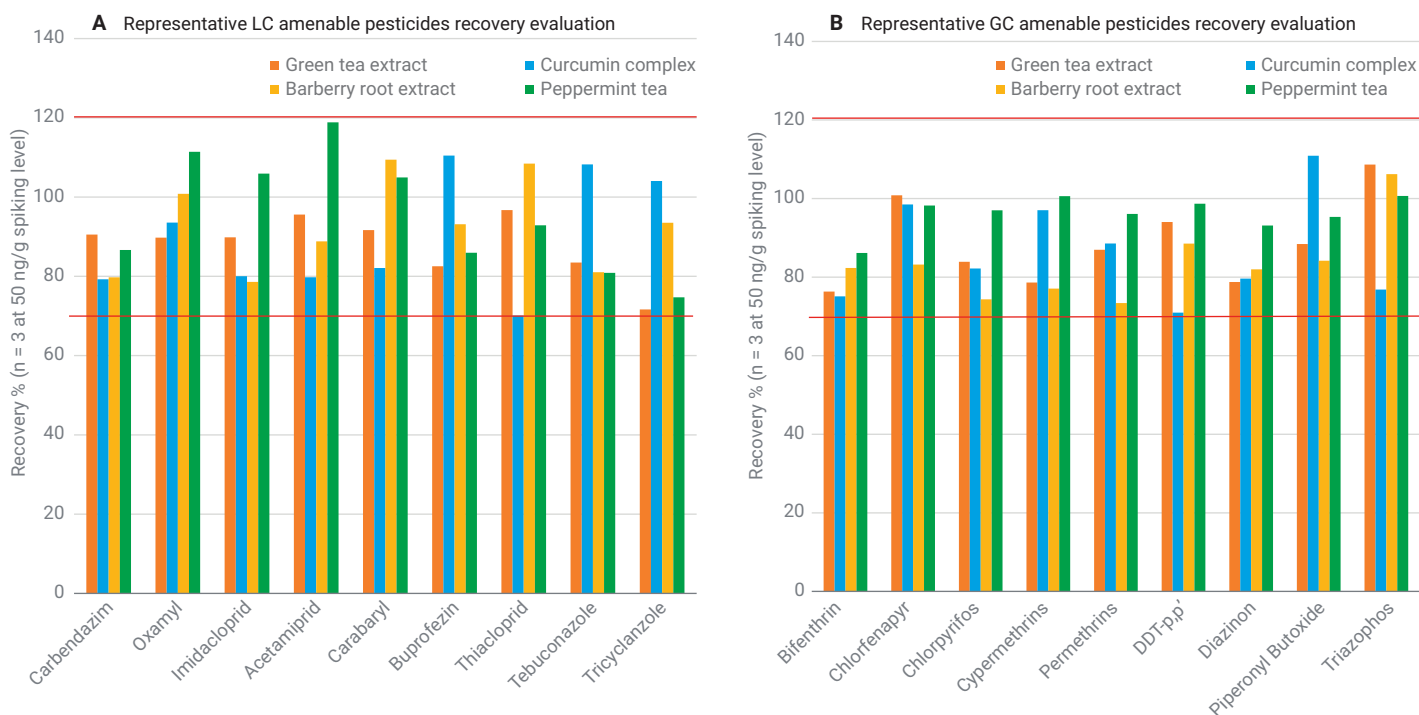

Figure 4. Representative pesticide recovery in BDS sample matrices, green tea extract, curcumin complex, barberry root extract, and peppermint tea. (A) Representative LC amenable pesticides, and (B) representative GC amenable pesticides in four BDS matrices.

The new method also provided a cleaner sample matrix that reduced the matrix impact on the pesticide analysis. One example was azinphos-ethyl in saffron, shown in Figure 5. When preparing the saffron sample using the traditional GC method with PSA/GCB SPE cleanup, the matrix blank showed a significant coeluting interference that caused a false positive of the target in this matrix. When preparing the sample using the new method with Captiva EMR–GPD, the interference still showed up but with much lower abundance, which allowed the interference peak to shift slightly early. In the spiked matrix, the interference peak was separated from the target, and the later peak had matched retention times with the neat reference standard. This result resolved the false positive issue when preparing with the traditional method and provided the more accurate analysis of this target in saffron matrix.

2. Large panel pesticide analysis

Large panel pesticide (> 440) analysis was evaluated in black tea and herbal tea matrices. Three replicates of black tea and herbal tea samples were spiked at 50 ng/g, prepared using the new sample preparation method, and evaluated for recovery and RSDs. The pesticide recovery statistical distribution is shown in Figure 6, and the standard spiked black tea chromatograms are shown in Figure 7. Overall, the new method generated 70 to 120% recovery for > 86% of pesticides in black tea and > 82% of pesticides in herbal tea, which were considered acceptable for such a big panel pesticide analysis and such challenging samples. Method reproducibility performance was excellent, with 97% of pesticides delivering < 20% of method RSD.
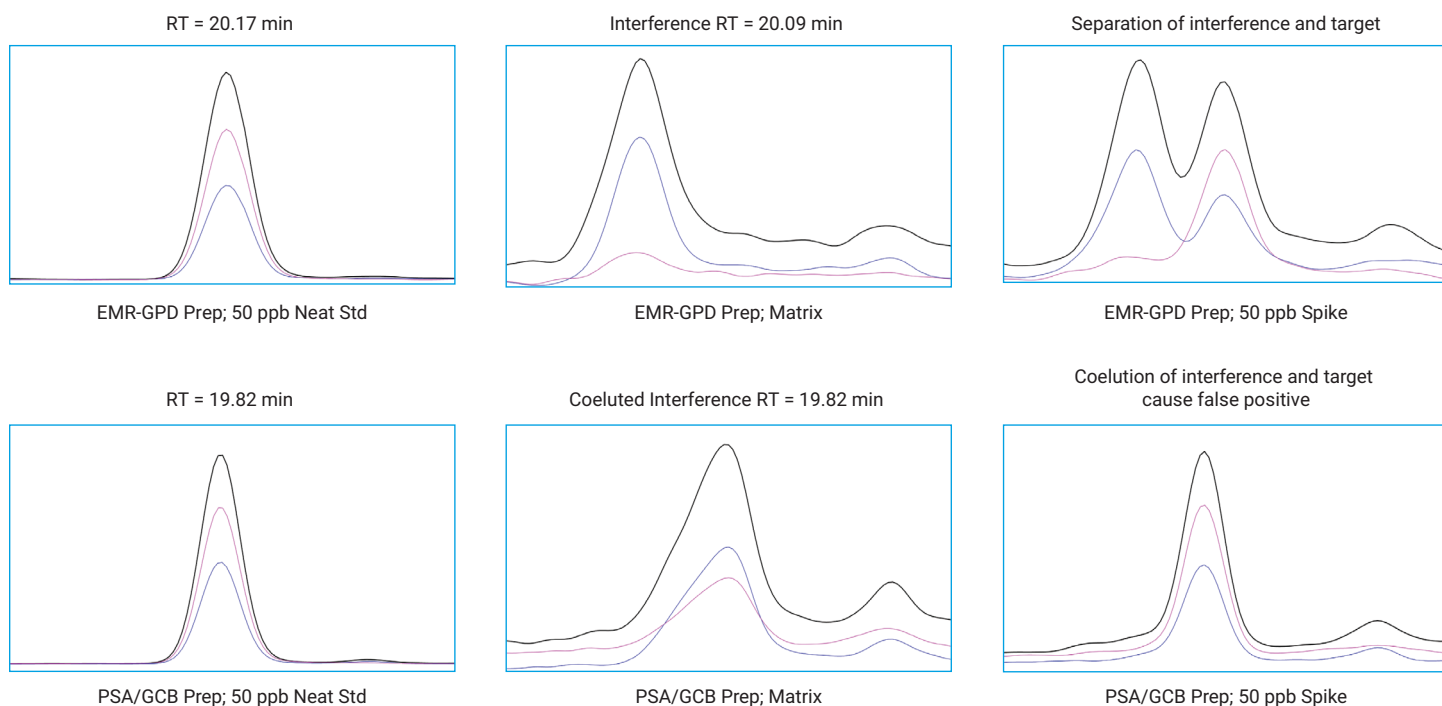

Figure 5. Azinphos-ethyl in saffron comparison between traditional GC PSA/GCB SPE cleanup (bottom) and Captiva EMR–GPD cleanup (top).

A Black tea

- 7% for 40 to 70%
- 1% for < 40%
- 3% for >120%
- 3% for NR
- 86% for 70 to 120%

B Herbal tea

- 5% for 40 to 70%
- 2% for < 40%
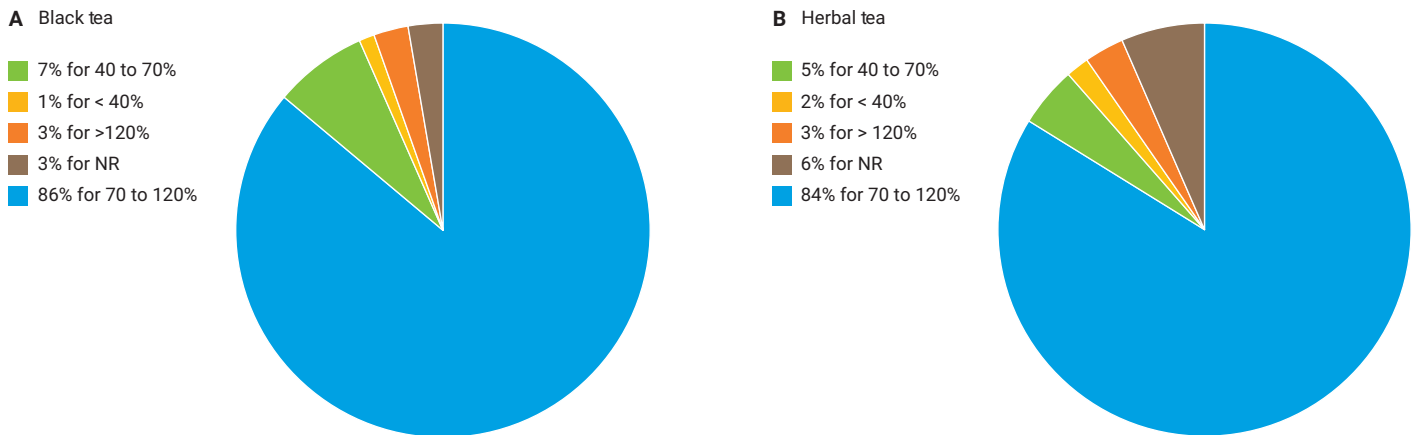- 3% for > 120%
- 6% for NR
- 84% for 70 to 120%

Figure 6. Large panel pesticide (447 total) recovery in black tea (A) and herbal tea (B) matrix distribution using the new sample preparation method.

A GC/MS/MS chromatogram, 50 ng/g spiking in black tea

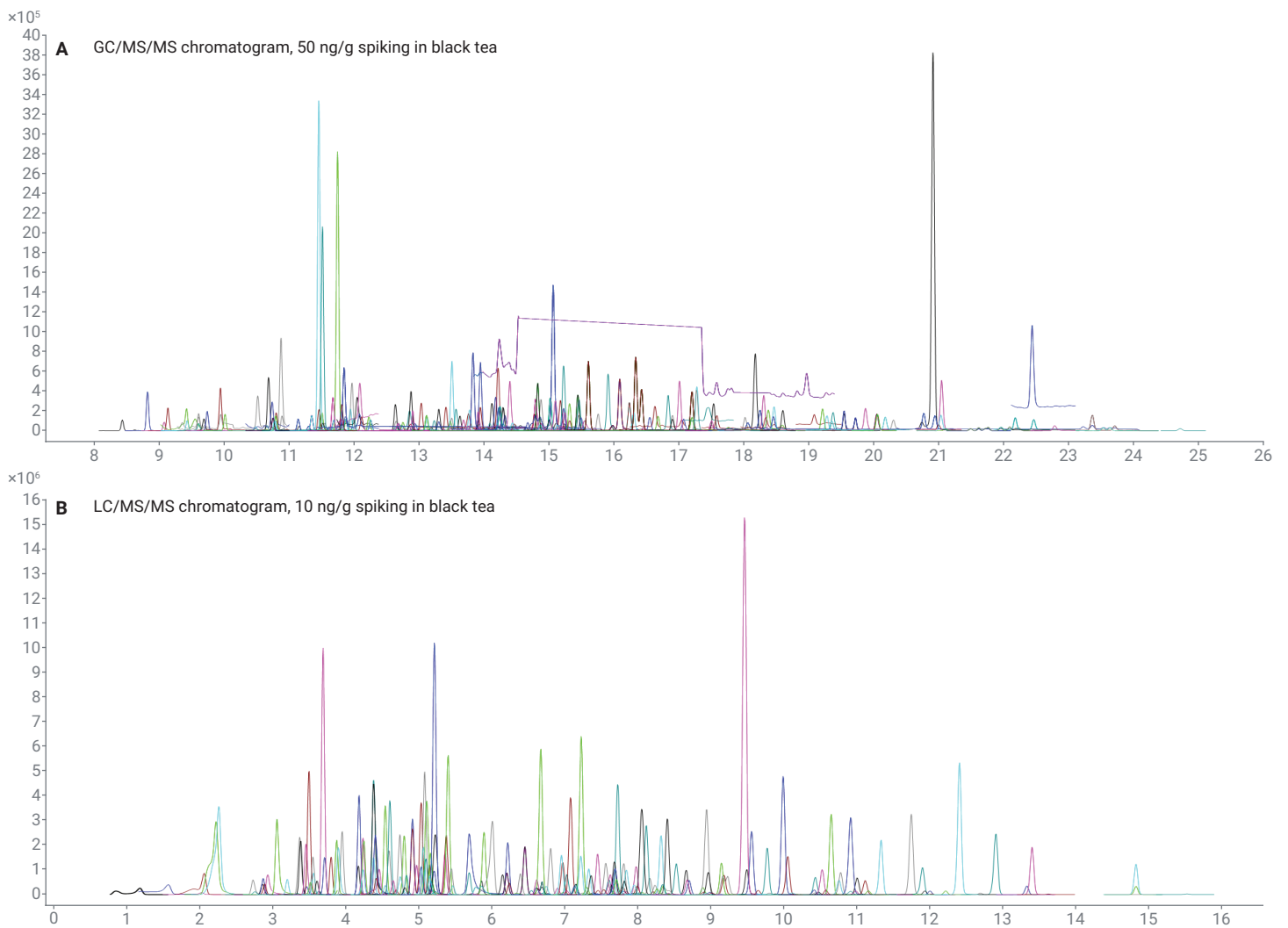B LC/MS/MS chromatogram, 10 ng/g spiking in black tea

Figure 7. Black tea sample chromatograms with 50 ng/g GC-amenable pesticides and 10 ng/g LC-amenable pesticides standard spiking. Sample was prepared using the QuEChERS extraction followed with Captiva EMR−GPD cleanup. (A) GC/MS/MS MRM chromatogram and (B) LC/MS/MS MRM chromatogram.

Method comparison for proficiency test

With the method confirmation on the preliminary evaluation and comparison, the stricter evaluation was the participation in the proficiency testing program. In proficiency testing, the new and traditional methods were applied side by side for preparing a complicated proficiency sample for the pesticide quantitative detection in the sample. As a correlation test between the traditional and new methods, one of the most complex and demanding proficiency samples were chosen in this assessment. Figure 8 shows a picture taken during the EMR−GPD cleanup, where the initial orange sample extract being cleaned and yielding a clear liquid being collected.
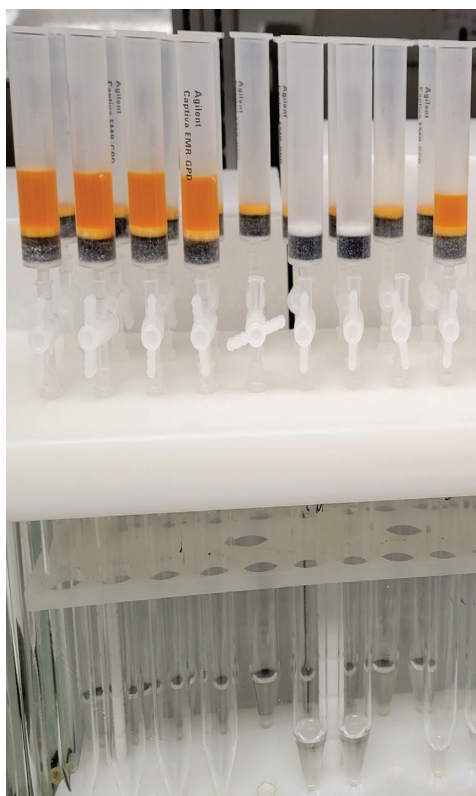

Figure 8. Proficiency sample test. Samples were extracted by QuEChERS extraction, followed with Captiva EMR−GPD cleanup.

Table 2 shows the reported results from the same sample but prepared using the traditional separate methods vs the new combined method. The proficiency sample actual value, the reported value, and the accuracy by each method are compared. The difference between the two reported values using a different method is included. In addition, given the age of proficiency sample (over two years), the original report value is included as well. Upon analyzing the reported results, the following conclusions can be drawn.

1. All of the analytes were detected within the acceptable reporting range when using the new sample preparation method. The reported values for the detectable analytes are comparable between the two different preparation methods, with < 15% difference, except for Triazophos.

2. Several targets, including diazinon, imazalil, and malathion, showed lower report values from both methods than the original report value, indicating the targets degradation or loss during > 2-year sample storage.

3. Targets with > 10% differences on the report values between the two methods were first related to the less matrix effect that reduced false positive or negative detection, such as acetamiprid, cypermethrins, imidacloprid, and triazophos. Another reason was related to slightly higher target loss during sample cleanup on the EMR−GPD cartridge, such as bifenthrin, cyhalothrin, and permethrins.

The proficiency test that confirmed the acceptable equivalent results were delivered using the new sample preparation method for practical sample analysis.

Table 2. Reported results for proficiency sample test and comparison.

Reported Analytes	Actual Value	Acceptance Range	New Method		Traditional Separate Method		Difference%	Original Report Value	Assigned Value
			Report	Accuracy%	Report	Accuracy%			
Acetamiprid	49	21 to 63	46.2	−5.7	56.6	15.5	10.1	43	42
Bifenthrin	68	29 to 86.9	50.0	−26.4	64.0	−5.9	12.2	58.8	57.9
Carabaryl	48	17.8 to 61.2	45.9	−4.3	55.5	15.7	9.5	41	39.5
Carbofuran	66	24 to 130	51.1	−22.6	46.4	−29.7	4.8	DNR	77
Chlorpyrifos	20	17.6 to 52.7	33.0	64.8	30.3	51.5	4.2	35.3	35.2
Cyhalothrin	299	136.8 to 410.3	252.0	−15.7	310.3	3.8	10.4	DNR	273.5
Cypermethrins	116	None given	122.6	5.7	152.5	31.4	10.9	126.45	116
Diazinon	132	41 to 144	68.9	−47.8	58.4	−55.8	8.3	91	92.5
Imazalil	498	180.9 to 576.1	196.3	−60.6	233.9	−53.0	8.7	404.2	378.5
Imidacloprid	58	29.2 to 87.4	58.7	1.1	68.7	18.4	7.9	58.6	58.3
Malathion	46	14.8 to 44.3	19.0	−58.7	21.5	−53.2	6.3	33.2	29.5
Oxamyl	46	24.1 to 72.2	54.0	17.4	61.3	33.4	6.3	49.2	48.1
Parathion-ethyl	108	38.4 to 163.6	84.7	−21.6	89.2	−17.4	2.6	DNR	101
Permethrins	89	31.6 to 108.6	60.1	−32.4	79.2	−11.0	13.7	74.2	70.1
Propoxur	108	47.8 to 143.3	113.0	4.7	115.5	7.0	1.1	102.1	95.5
Thiacloprid	93	42 to 126	99.3	6.7	105.4	13.4	3.0	95.2	84
Triazophos	61	37.8 to 113.4	68.6	12.4	93.9	54.0	15.6	73.2	75.6

* Samples tested on the new method were stored for 2 years, which risked possible degradation of some pesticides such as diazinon, imazalil, and malathion.

Conclusion

A simple, rapid, and reliable method using Agilent Bond Elut QuEChERS extraction followed by EMR mixed-mode passthrough cleanup using Agilent Captiva EMR with Carbon S cartridges was developed. The results of this method were verified for over 440 pesticides in botanical dietary supplement extracts and products by LC/MS/MS and GC/MS/MS. The EMR mixed-mode passthrough cleanup method provided a convenient and simplified cleanup method after sample extraction for selective and efficient matrix removal in BDS matrices and acceptable quantitation recovery and reproducibility in large panel pesticide quantitation. The detailed proficiency test confirmed the acceptable method performance for practical sample analysis.

The ability to streamline sample preparation into a single method allows for a reduction in the total amount of sample preparation consumables and reduces the preparation time. The reduced organic solvent, especially the toxic solvent used per sample, made the entire procedure greener while being more people and environmentally friendly. Also, having one sample to be prepped in a single day allows for much greater traceability regarding shared analytes between LC and GC analyses. This single sample preparation also helps simplify the results and documentation. Consolidating sample preparation documentation into a single packet, as opposed to two packets, minimizes time spent by reviewing staff.

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