

# Analysis of Pesticides in Tomato and Kale on GC/MS/MS with Agilent Bond Elut QuEChERS High Pigment dSPE with Carbon S

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## Abstract

This application note presents the validation of a multiresidue method for the analysis of planar pesticide residues in tomato and kale. The method involves extraction using the Agilent Bond Elut QuEChERS EN extraction kit, followed by cleanup with the Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S, and then GC/MS/MS analysis with the Agilent 7010C triple quadrupole GC/MS System (GC/TQ). Agilent Carbon S is an advanced hybrid carbon sorbent providing efficient and selective matrix pigment removal and significantly reduces the unwanted interaction with targets, especially for sensitive compounds like planar pesticides. The results demonstrate that over 85% of the pesticides were identified with 70 to 130% recoveries, RSD <30%. Compared to traditional graphitized carbon black (GCB) included in other EN pigment dSPE cleanups, Carbon S provided equivalent or better recoveries for these sensitive pesticides.

## Introduction

Natural pigments in fresh fruits and vegetables can be highly abundant, such as chlorophyll and lutein from green vegetables; anthocyanidins and anthocyanins from red, blue, purple, and black fruits; and carotenoids and xanthophylls from orange and yellow fruits and vegetables. These pigments can be easily extracted through an extraction procedure using organic solvent. Without the further removal of pigment co-extractives, the direct injection of highly pigmented sample extract on detection instrumentation, such as GC/TQ, could result in multiple matrix effects, including matrix interferences and accumulated matrix deposition on the detection flow path and MS source, hence decreasing maintenance-free operation uptime. Therefore, it is important to apply improved cleanup to remove pigment co-extractives prior to instrumental analysis.

GCB sorbent has been widely used in sample preparation for efficient pigment removal.<sup>1,2</sup> Especially for the commonly used QuEChERS preparation method in food analysis, GCB has been used in dispersive solid phase extraction (dSPE) kits, recommended for pigment removal. Although GCB has been shown to be efficient in pigment removal, it also causes unwanted analyte loss, especially for compounds with planar structure, such as hexachlorobenzene, chlorothalonil, and pentachloronitrobenzene. Therefore, many QuEChERS dSPE kit formulas were carefully adjusted with a limited amount of GCB sorbent to achieve acceptable target recoveries.

Agilent Carbon S sorbent is an advanced hybrid carbon material with optimized carbon content and pore structure and is used in various dSPE kits as an alternative to GCB. Compared to GCB, the improved sorbent provides

equivalent or better pigment removal from plant-origin sample matrices, and significantly improves sensitive analyte recoveries. As a result, Carbon S sorbent delivers a better balance between analyte recovery and matrix pigment-removal efficiency than traditional GCB sorbent.

This study investigates sample preparation using the High Pigment dSPE kit (EN like) with Carbon S cleanup for the analysis of selected planar pesticides in tomato and kale by GC/MS/MS.

## Experimental

### Solutions and standards

A combined standard spiking solution and a combined internal standard (ISTD) of three deuterated compounds were prepared from Agilent standard mixes (part numbers NPM-619-1, PSM-100-A, PSM-100-AA, PSM-100-AC, PSM-100-G, PSM-100-H, PSM-100-K, and PSM-100-Z). The spiking solution was prepared at 8 µg/mL in acetonitrile (ACN) and the ISTD solution was prepared at 48 µg/mL in ACN.

### Sample preparation

A 10 g sample of homogenized organic tomato or kale was weighed into a 50 mL centrifuge tube (part number 5610-2049) with two ceramic homogenizers (part number 5982-9313). Specified samples were spiked with the standard spiking solution. For each sample, 10 mL of ACN was added and then vortexed. A QuEChERS salt extraction packet for the EN method (part number 5982-5650) was added to each sample. The samples were then placed on a Geno/Grinder (vertical shaking) for 3 minutes and centrifuged at 5,000 rpm for 5 minutes. An aliquot of 1 or 6 mL crude extract was transferred to the High Pigment dSPE with Carbon S, 2 mL (part number 5610-2074) or 15 mL (part number 5610-2076), respectively. The samples were then vortexed for 2 minutes and centrifuged for 5 minutes. Extracts were transferred to 2 mL analysis vials (part numbers 5183-2072 and 5182-0717) for analysis on the 7010C triple quadrupole GC/MS. An outline of this sample preparation procedure is shown in Figure 1.

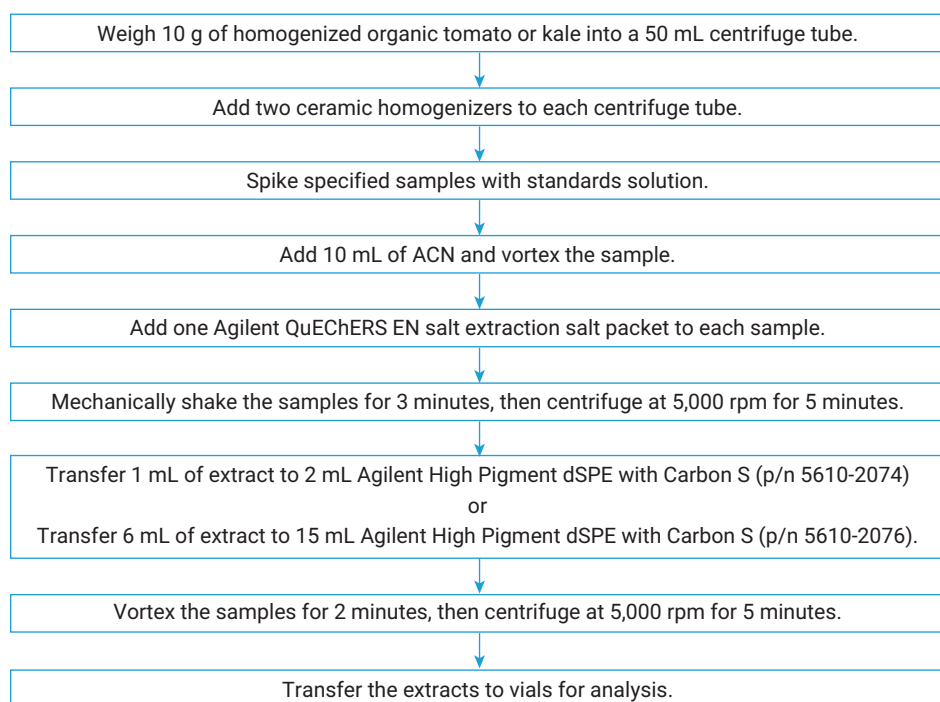


Figure 1. Sample preparation procedure for tomato and kale samples.

## Instrumentation

The study was performed using an Agilent 8890 GC coupled with an Agilent 7010C triple quadrupole GC/MS (Figure 2). The GC system was equipped with an Agilent 7693A automatic liquid sampler (ALS) tower and tray, a multimode inlet (MMI), an electronic pneumatic control (EPC), and an Agilent purged Ultimate union (PUU) for backflush system. Agilent MassHunter Workstation software was used for data acquisition and analysis.

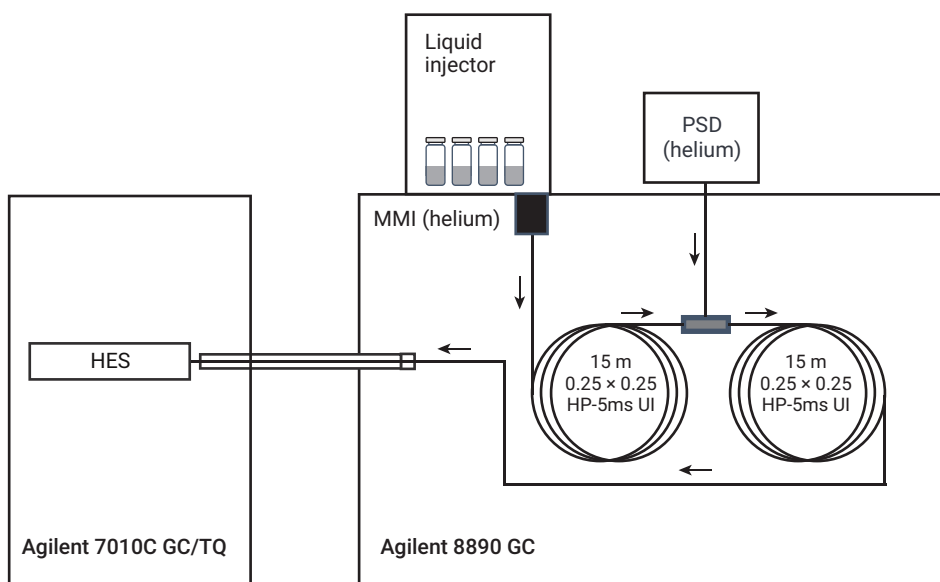
## Instrumental conditions

The GC/TQ instrument conditions were established based on the previously published method using equivalent instruments.<sup>3</sup> Appendix 1 lists the target and ISTD compound multiple reaction monitoring (MRM) parameters. Figure 3 shows an MRM chromatogram of targeted pesticides in an extracted kale sample spiked at 24 ng/g using a EN QuEChERS extraction followed with an EN High Pigment dSPE with Carbon S 2 mL kit cleanup.

## Results and discussion

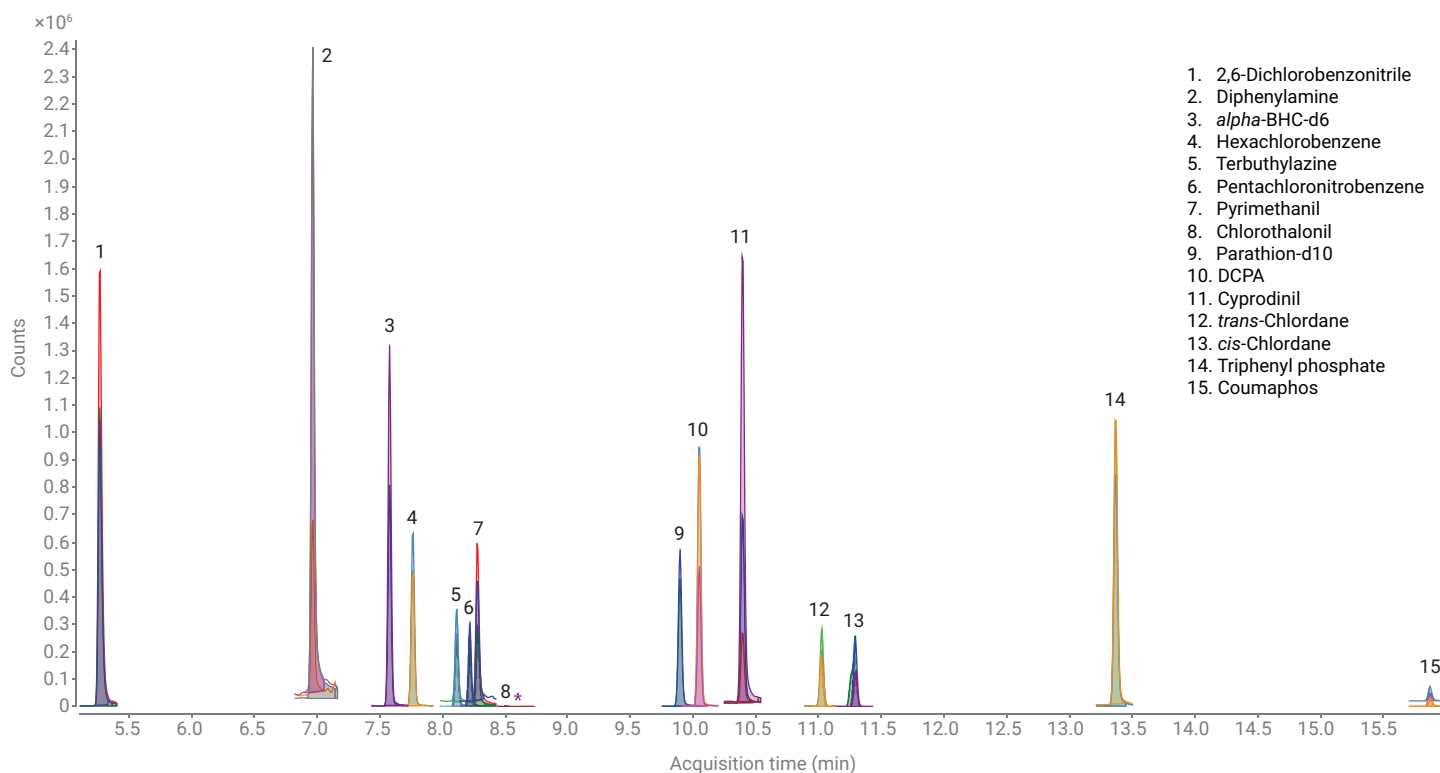
### Carbon S sorbent

Carbon S sorbent is an advanced hybrid carbon material with optimized carbon content and pore structure. The improved sorbent provides equivalent or better pigment removal from plant-origin sample matrices compared to GCB sorbent, and significantly improves recoveries of sensitive targeted analytes. As a result, Carbon S sorbent delivers an excellent balance between analyte recovery and matrix pigment-removal efficiency (Figure 4).

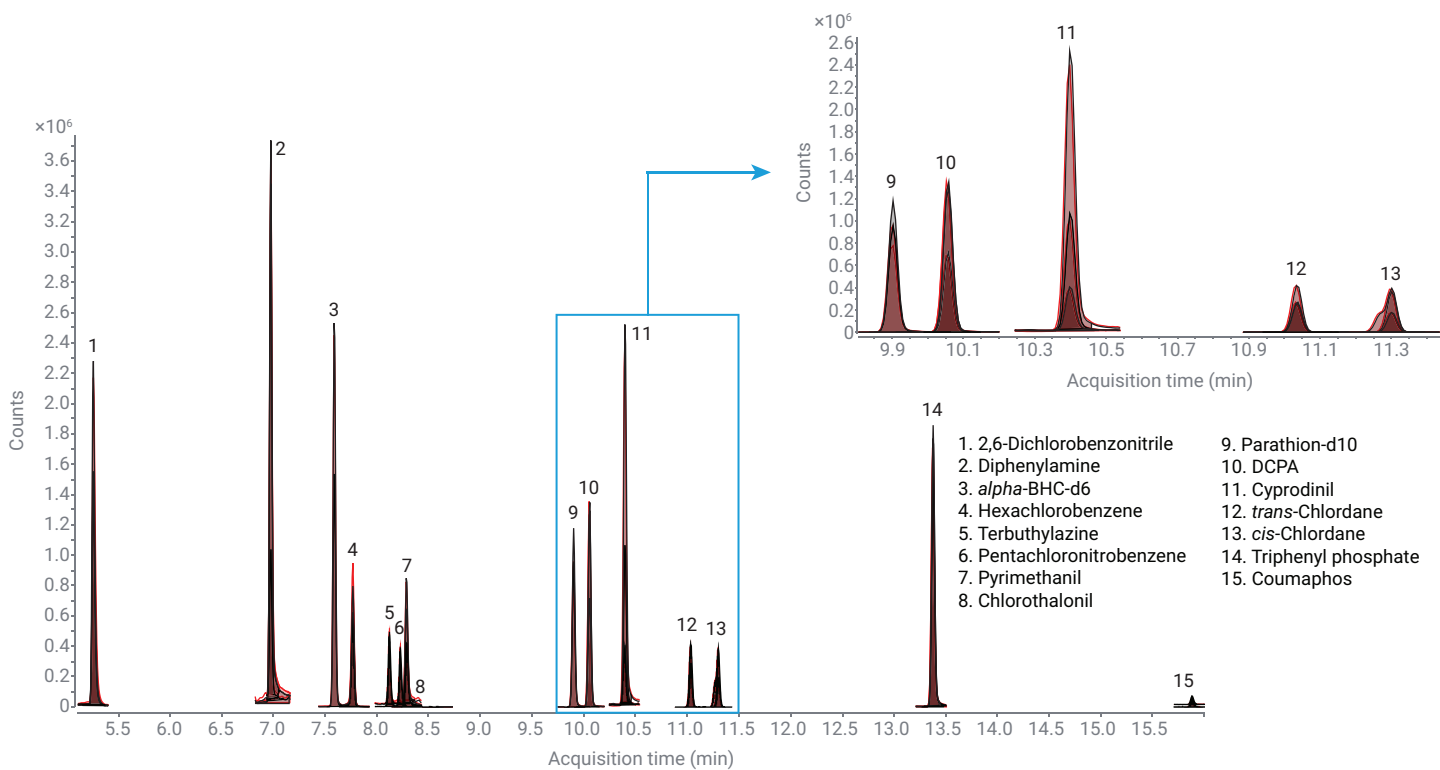


**Figure 2.** The Agilent 7010C triple quadrupole GC/MS (GC/TQ), coupled with an Agilent 8890 GC.





**Figure 3.** MRM chromatogram of planar pesticides in a kale sample spiked at 24 ng/g, using the developed sample preparation method.



**Figure 4.** MRM chromatograms of spiked tomato extract after cleanup with the Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S, 15 mL (black trace), and the Agilent Bond Elut QuEChERS General Fruits and Vegetables dispersive SPE kit, EN method, 15 mL (red trace).

### Sample preparation method performance assessment

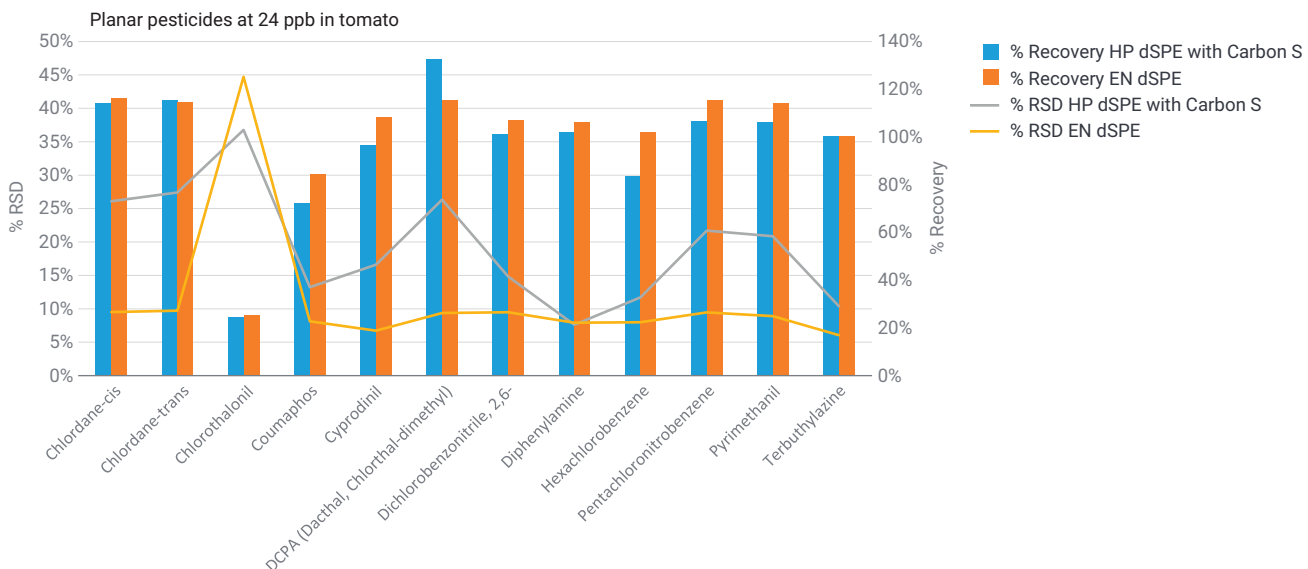
The QuEChERS sample preparation method was evaluated for both tomato and kale using their existing recommended dSPE cleanups alongside the High Pigment dSPE with Carbon S cleanup. The QuEChERS products used in the method performance assessment are shown in Table 1.

Following matrix-matched calibration curve linearity with an  $R^2 > 0.990$  over a calibration range of 0.5 to 50 parts per billion (ppb) (w/v) for all targeted pesticides, the pesticide recoveries were compared between existing recommended dSPE cleanups alongside the High Pigment dSPE with Carbon S cleanup at 24 ppb. Quantitation of the pesticides by matrix-matched calibration determined that 83% of the compounds had recoveries between 70 and 130% at 24 ppb in tomato, and 89% of the compounds had recoveries between 70 and 130% at 24 ppb in kale when cleaned up with the High Pigment

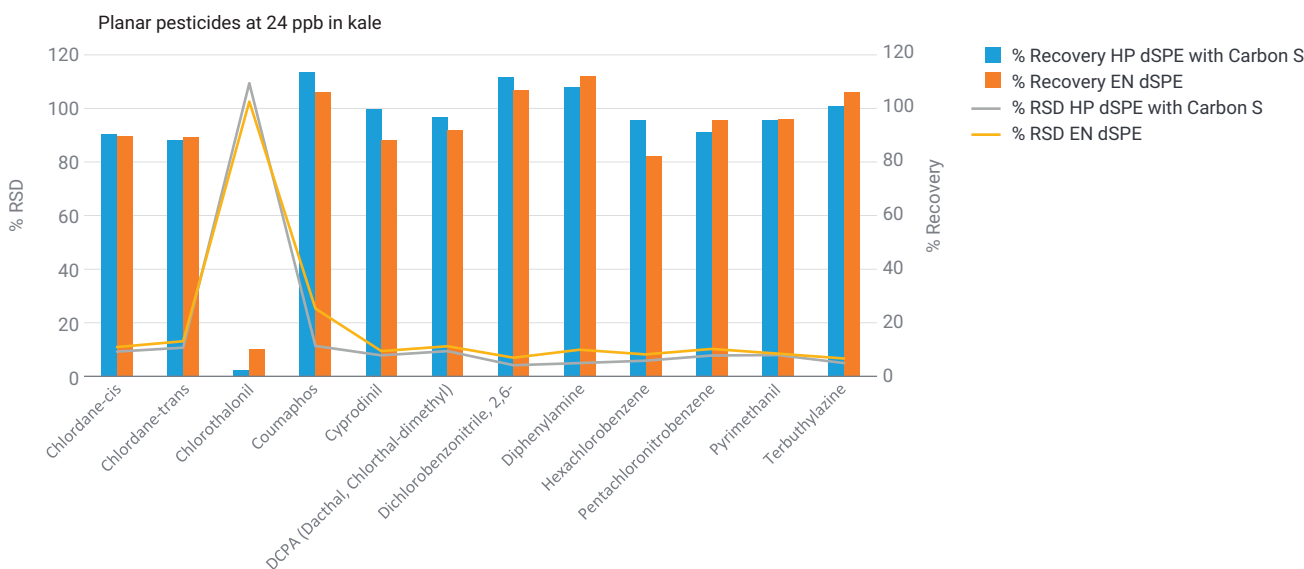
dSPE with Carbon S. When cleaned up with the Highly Pigmented Fruits and Vegetables dSPE, quantitation of the pesticides by matrix-matched calibration determined that 89% of the compounds had recoveries between 70 and 130% at 24 ppb in tomato, and 89% of the compounds had recoveries between 70 and 130% at 24 ppb in kale. Quantitation accuracy and precision ( $n = 6$ ) were also determined to verify the results; 89% of all compounds in tomato and kale with both dSPE cleanup products had RSDs  $< 30\%$ . Figures 5 and 6 provide graphical quantitation data for tomato and kale.

**Table 1.** Agilent QuEChERS products used in the method performance assessment.

Part Number	Product	Matrix
5610-2074	Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S, 2 mL	Tomato and kale
5610-2076	Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S, 15 mL	Tomato and kale
5982-5021	Agilent Bond Elut QuEChERS General Fruits and Vegetables dispersive SPE kit, EN method, 2 mL	Tomato
5982-5056	Agilent Bond Elut QuEChERS General Fruits and Vegetables dispersive SPE kit, EN method, 15 mL	Tomato
5982-5321	Agilent Bond Elut QuEChERS Highly Pigmented Fruits and Vegetables dispersive SPE kit, EN method, 2 mL	Kale
5982-5356	Agilent Bond Elut QuEChERS Highly Pigmented Fruits and Vegetables dispersive SPE kit, EN method, 15 mL	Kale



**Figure 5.** Recovery and RSD (%) comparison of planar pesticides in tomato with the Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S (HP dSPE) and the Agilent Bond Elut QuEChERS General Fruits and Vegetables dispersive SPE kit, EN method (GFV dSPE).



**Figure 6.** Recovery and RSD (%) comparison of planar pesticides in kale with the Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S (HP dSPE) and the Agilent Bond Elut QuEChERS General Fruits and Vegetables dispersive SPE kit, EN method, (GFV dSPE).

## Conclusion

A simple, rapid, and reliable method using extraction with the Agilent Bond Elut QuEChERS EN extraction kit, followed by cleanup with the Agilent Bond Elut QuEChERS High Pigment dispersive SPE kit (EN like) with Carbon S was validated for targeted GC/MS/MS analysis of planar pesticides. The method performance was evaluated based on analyte recovery comparison in tomato and kale between their existing recommended dSPE cleanups alongside the High Pigment dSPE with Carbon S. When comparing to the traditional dSPE cleanup, the EN High Pigment dSPE with Carbon S provides equivalent or better performance on planar pesticides analysis in pigmented fresh matrices than the current recommendations.

## References

1. González-Curbelo, M. Á. *et al.* *Trends In Anal. Chem.* **2015**, 71, 169–185.
2. Varela-Martínez, D. A. *et al.* *Liquid-Phase Extraction Handbooks in Separation Science*, **2020**, Chp 14, 399–437.
3. Andrianova, A. *et al.* *Quantitation of Pesticides in Strawberries at Tolerance Levels Established by the US EPA, Agilent Technologies application note*, publication number 5994-0799EN, **2019**.

## Appendix 1

### MRM parameters of target and ISTD compound MRM parameters

Compound	Target/ISTD	RT (min)	Precursor Ion	MS1 Resolution	Product Ion	MS2 Resolution	CE
2,6-Dichlorobenzonitrile	Target	5.26	173	Wide	100	Wide	25
2,6-Dichlorobenzonitrile	Target	5.26	171	Wide	136.1	Wide	15
2,6-Dichlorobenzonitrile	Target	5.26	171	Wide	100	Wide	25
Diphenylamine	Target	6.97	169	Wide	168.2	Wide	15
Diphenylamine	Target	6.97	168	Wide	167.2	Wide	15
Diphenylamine	Target	6.97	167	Wide	166.2	Wide	20
alpha-BHC-d6	ISTD	7.58	224	Wide	187	Wide	15
alpha-BHC-d6	ISTD	7.58	224	Wide	150	Wide	15
Hexachlorobenzene	Target	7.78	283.8	Wide	248.8	Wide	15
Hexachlorobenzene	Target	7.78	283.8	Wide	213.9	Wide	30
Hexachlorobenzene	Target	7.78	281.8	Wide	211.9	Wide	30
Terbutylazine	Target	8.12	228.9	Wide	173.1	Wide	5
Terbutylazine	Target	8.12	172.9	Wide	172	Wide	5
Terbutylazine	Target	8.12	172.9	Wide	138.1	Wide	5
Pentachloronitrobenzene	Target	8.23	248.8	Wide	213.8	Wide	15
Pentachloronitrobenzene	Target	8.23	176.9	Wide	141.9	Wide	15
Pentachloronitrobenzene	Target	8.23	141.9	Wide	106.9	Wide	30
Pyrimethanil	Target	8.28	198	Wide	183.1	Wide	15
Pyrimethanil	Target	8.28	198	Wide	158.1	Wide	20
Pyrimethanil	Target	8.28	198	Wide	118.1	Wide	35
Chlorothalonil	Target	8.59	265.9	Wide	230.9	Wide	20
Chlorothalonil	Target	8.59	265.9	Wide	168	Wide	30
Chlorothalonil	Target	8.59	265.9	Wide	133	Wide	45
Parathion-d10	ISTD	9.90	301	Wide	115	Wide	15
Parathion-d10	ISTD	9.90	301	Wide	83	Wide	35
DCPA	Target	10.06	331.8	Wide	300.9	Wide	10
DCPA	Target	10.06	300.9	Wide	223	Wide	25
DCPA	Target	10.06	298.9	Wide	221	Wide	25
Cyprodinil	Target	10.39	226.2	Wide	225.3	Wide	10
Cyprodinil	Target	10.39	225.2	Wide	224.3	Wide	10
Cyprodinil	Target	10.39	224.2	Wide	208.2	Wide	20
Chlordane-trans	Target	11.03	374.8	Wide	265.8	Wide	15
Chlordane-trans	Target	11.03	372.8	Wide	265.8	Wide	15
Chlordane-trans	Target	11.03	271.7	Wide	236.9	Wide	15
Chlordane-cis	Target	11.29	372.8	Wide	300.9	Wide	10
Chlordane-cis	Target	11.29	372.8	Wide	265.9	Wide	25
Chlordane-cis	Target	11.29	271.8	Wide	236.9	Wide	15
Triphenyl phosphate	ISTD	13.35	326	Wide	325	Wide	5
Triphenyl phosphate	ISTD	13.35	232.9	Wide	215.1	Wide	10
Triphenyl phosphate	ISTD	13.35	214.9	Wide	168.1	Wide	15
Coumaphos	Target	15.85	361.9	Wide	109	Wide	15
Coumaphos	Target	15.85	225.9	Wide	163.1	Wide	15
Coumaphos	Target	15.85	210	Wide	182	Wide	10

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