

# Quantitative Analysis of Pesticides in Celery and Grape

Using the Agilent Bond Elut QuEChERS Universal dispersive SPE Kit with Carbon S cleanup by LC/MS/MS

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## Abstract

This application note evaluates the application of the Agilent Bond Elut QuEChERS Universal dispersive SPE kit with Carbon S for the analysis of 45 representative pesticides in grape and celery by LC/MS/MS. Both common formats of Universal dSPE (2 and 15 mL) were assessed and compared between the Bond Elut QuEChERS Universal dSPE kits with either Carbon S or graphite carbon black (GCB). The two Universal dSPE cleanup methods were compared based on target recovery and reproducibility. Compared to the traditional Universal dSPE with GCB (U-dSPE with GCB), the novel Universal dSPE with Carbon S (U-dSPE with Carbon S) provided better recoveries and RSDs on planar pesticides, and equivalent performance on nonplanar pesticides.

## Introduction

Natural pigment ingredients in fresh fruits and vegetables can be highly abundant, and easily extracted through an extraction procedure using organic solvent. Without the further removal of pigment co-extractives, the direct injection of a highly pigmented sample extract on a detection instrument such as LC/MS/MS or GC/MS/MS could result in multiple matrix effects, including matrix ion suppression on LC/MS/MS, matrix interferences on GC/MS/MS, accumulated matrix deposition on the detection flow path and MS source, and so on. Therefore, it is important to apply further cleanup to remove pigment coextractives before instrument analysis.

GCB, as the most absorbent sorbent for pigment removal, has been commonly adopted in standard QuEChERS dispersive kits in food analysis. However, given the high efficiency of pigment removal, GCB sorbent can also cause unwanted analyte loss, especially for compounds with planar structure, such as thiabendazole, cyprodinil, and so on. Therefore, standard QuEChERS dispersive kit formulas were carefully optimized to have a limited amount of GCB sorbent. Among various dSPE kits, Universal dSPE has widely been accepted as a generic dSPE cleanup for many fresh produces. The universal formula for this dSPE kit includes the blending of primary secondary amine (PSA), end-capping C18 (EC-C18), GCB, and  $\text{MgSO}_4$ . This universal formula provides the convenience of easy selection for various fruit and vegetable matrices, improving sample preparation methods and product consistency in food-testing labs.

Agilent 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 to GCB sorbent, but significantly improves the recovery of sensitive analytes. As a result, Carbon S sorbent delivers a better balance between analyte recovery and matrix pigment removal efficiency. This application note investigates sample preparation using U-dSPE with Carbon S for the analysis of 45 common pesticides in general pigmented matrices of celery and grape by LC/MS/MS.

## Experimental

### Chemicals and reagents

All reagents and solvents used in sample preparation were HPLC or analytical grade, and the reagent and solvents used in the LC/MS analysis were LC/MS grade. Acetonitrile (ACN) and methanol (MeOH) were from Honeywell (Muskegon, MI, USA). Formic acid (FA), acetate acid, and ammonium formate were obtained from Anpel (Shanghai, China). Ammonium fluoride was obtained from Sigma-Aldrich. All pesticide standards at 1,000  $\mu\text{g}/\text{mL}$  in acetonitrile, were purchased from Alta (Tianjin, China) and stored at  $-20\text{ }^\circ\text{C}$ .

### Equipment and consumables

- Eppendorf 5810R centrifuge (Hamburg, Germany)
- SPEX SamplePrep 2010 Geno/Grinder (Metuchen, NJ, USA)
- Agilent Bond Elut QuEChERS extraction kit, AOAC 2007.01, with ceramic homogenizers (part number 5982-5755CH)
- Agilent Bond Elut QuEChERS Universal dispersive SPE kit, 2 mL, 50 mg PSA, 50 mg C18, 7.5 mg GCB, 150 mg  $\text{MgSO}_4$  (part number 5982-0028)
- Agilent Bond Elut QuEChERS Universal dispersive SPE kit, 15 mL, 400 mg PSA, 400 mg C18, 45 mg GCB, 1,200 mg  $\text{MgSO}_4$  (part number 5982-0029)
- Agilent Bond Elut QuEChERS Universal dispersive SPE kit, 2 mL, with Carbon S, 50 mg PSA, 50 mg C18, 7.5 mg Carbon S, 150 mg  $\text{MgSO}_4$  (part number 5610-2058)
- Agilent Bond Elut QuEChERS Universal dispersive SPE kit, 15 mL, with Carbon S, 400 mg PSA, 400 mg C18, 45 mg Carbon S, 1,200 mg  $\text{MgSO}_4$  (part number 5610-2060)

### Instrument conditions

LC/MS/MS detection was performed on an Agilent 1290 Infinity II LC system, including the Agilent 1290 Infinity II high-speed pump (G7120A), the Agilent 1290 Infinity II multisampler (G7167B), and the Agilent 1290 Infinity II multicolumn thermostat (G7116B), coupled with an Agilent triple quadrupole LC/MS (G6470A) with an Agilent Jet Stream Electrospray ion source. Agilent MassHunter Workstation software was used for data acquisition and analysis. Table 1 lists the LC/MS/MS method conditions. The MRM transitions and settings are listed in Table 2.

## Sample preparation

The sample preparation included sample extraction with the buffered QuEChERS protocol using the Agilent Bond Elut QuEChERS AOAC extraction kit and dSPE cleanup using Bond Elut QuEChERS Universal dispersive SPE kits. Homogenized grape and celery, 15 g, were weighted into 50 mL polypropylene tubes and extracted with 15 mL of ACN with 1% acetate acid. After addition of the AOAC extraction kit, the samples were shaken vigorously for 5 minutes using a Geno/Grinder at 1,000 rpm. Tubes were then centrifuged at 4,000 rpm for 5 minutes at 10 °C.

For the 15 mL Universal dSPE, an 8 mL aliquot of the upper ACN layer was transferred to a dSPE tube, and for the 2 mL Universal dSPE, 1 mL of supernatant was transferred. The tubes were capped and shaken for 1 minute and centrifuged again for 5 minutes at (a) 4,000 rpm for 15 mL tubes on a regular centrifuge, or (b) 10,000 rpm for 2 mL tubes on a microcentrifuge. From the upper layer, 200 µL was transferred and mixed with 800 µL of water for LC/MS/MS analysis.

**Table 1.** LC/MS/MS method conditions.

| LC/MS/MS Parameter                              | Setting   |                |                    |
|---|---|----------------|--------------------|
| Column  | Agilent InfinityLab Poroshell 120 EC-C18, 2.1 × 100 mm, 2.7 µm column (p/n 695775-902)  |                |                    |
| Column Temperature                              | 40 °C   |                |                    |
| Autosampler Temperature                         | 10 °C   |                |                    |
| Injection Volume                                | 2 µL  |                |                    |
| Mobile Phase                                    | A) Water containing 4.5 mM ammonium formate, 0.5 mM ammonium fluoride, and 0.1% formic acid<br>B) Methanol containing 4.5 mM ammonium formate, 0.5 mM ammonium fluoride, and 0.1% formic acid |                |                    |
| Gradient  | Time (min)  | %A             | Flow rate (mL/min) |
|   | 0   | 98             | 0.4                |
|   | 0.5   | 98             |                    |
|   | 3   | 80             |                    |
|   | 16  | 0              |                    |
|   | 18  | 0              |                    |
|   | 18.1  | 98             |                    |
|   | 20  | 98             |                    |
| Stop Time                                       | 20 min  |                |                    |
| <b>Source Parameters</b>                        |   |                |                    |
| Gas Temperature                                 | 250 °C  |                |                    |
| Gas Flow  | 10 L/min  |                |                    |
| Nebulizer                                       | 40 psi  |                |                    |
| Sheath Gas Temperature                          | 350 °C  |                |                    |
| Sheath Gas Flow                                 | 11 L/min  |                |                    |
| Capillary Voltage                               | +3,500  |                |                    |
| Nozzle Voltage                                  | +300  |                |                    |
| <b>Time Segments</b>                            |   |                |                    |
| <b>Agilent 1290 Infinity II High-Speed Pump</b> |   |                |                    |
| Start Time (min)                                | Scan Type   | Diverter Valve | Delta EMV (+)      |
| 0   | DMRM  | To waste       | 0                  |
| 1.2   | DMRM  | To MS          | 400                |
| 19  | DMRM  | To waste       | 0                  |

**Table 2.** MRM conditions for the pesticides.

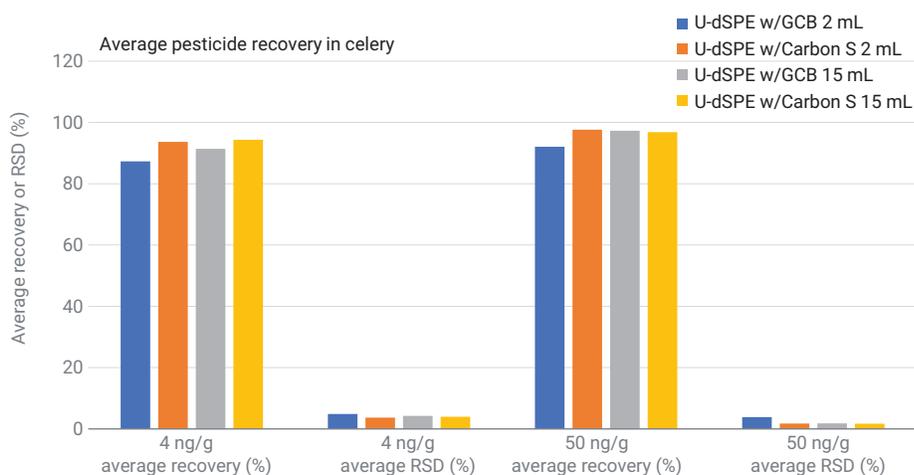
| Compound Name       | Precursor Ion  | Product Ion    | Retention Time (min) | Fragmentor | Collision Energy | Cell Accelerator Voltage |
|---------------------|----------------|----------------|----------------------|------------|------------------|--------------------------|
| 3-Hydroxycarbofuran | 238.1          | 220<br>163.1   | 6.2                  | 80         | 5<br>10          | 4                        |
| Acephate            | 183.9          | 143<br>49      | 2.72                 | 70         | 2<br>20          | 3                        |
| Acetamiprid         | 223            | 126.1<br>90.1  | 6.24                 | 80         | 18<br>35         | 4                        |
| Aldicarb            | 208            | 116<br>89.1    | 7.31                 | 65         | 6<br>10          | 4                        |
| Aldicarb-sulfone    | 223.1          | 86.1<br>148    | 3.89                 | 80         | 8<br>1           | 4                        |
| Aldicarb-sulfoxide  | 207.1          | 131.9<br>89.1  | 3.61                 | 65         | 2<br>10          | 4                        |
| Buprofezin          | 306.1          | 201.2<br>116   | 14.04                | 105        | 9<br>15          | 4                        |
| Cadusafos           | 271.1          | 159<br>97      | 13.35                | 90         | 8<br>40          | 4                        |
| Carbaryl            | 202            | 145<br>127.1   | 9.07                 | 65         | 2<br>28          | 3                        |
| Carbendazim         | 192.1          | 160.1<br>65.2  | 4.72                 | 105        | 16<br>52         | 3                        |
| Carbofuran          | 222.1          | 165.1<br>123.1 | 8.62                 | 80         | 6<br>20          | 4                        |
| Chlorantraniliprole | 483.9          | 452.9<br>286   | 10.67                | 105        | 16<br>12         | 5                        |
| Chlordimeform       | 197.1          | 117<br>89      | 5.08                 | 110        | 25<br>64         | 3                        |
| Chlorpyrifos        | 351.9<br>349.9 | 199.9<br>97    | 14.38                | 100        | 15<br>36         | 4                        |
| Coumaphos           | 363            | 289.1<br>226.9 | 12.86                | 120        | 22<br>28         | 4                        |
| Cymoxanil           | 199            | 128.1<br>111.1 | 6.55                 | 50         | 6<br>15          | 3                        |
| Diazinon            | 305.1          | 169<br>97.1    | 12.9                 | 105        | 26<br>36         | 4                        |
| Dichlorvos          | 220.9          | 109<br>95.1    | 8.3                  | 100        | 12<br>32         | 4                        |
| Diflubenzuron       | 311            | 158<br>141     | 12.36                | 80         | 18<br>46         | 4                        |
| Dimethoate          | 230            | 199<br>125     | 5.94                 | 70         | 4<br>24          | 4                        |
| Ethoprophos         | 243            | 173.1<br>97    | 12.02                | 90         | 12<br>30         | 4                        |
| Fenazaquin          | 307.2          | 161.1<br>57.1  | 15.1                 | 105        | 12<br>25         | 4                        |
| Fonofos             | 247.0          | 137.0<br>109.0 | 12.76                | 80         | 5<br>15          | 4                        |
| Forchlorfenuron     | 248.1          | 129<br>92.9    | 10.23                | 110        | 16<br>40         | 4                        |
| Isazofos isotope    | 316            | 122<br>96.9    | 11.72                | 85         | 34<br>46         | 4                        |
| Isofenphos-methyl   | 332.1          | 273<br>231     | 12.61                | 80         | 0<br>8           | 4                        |
| Metalaxyl           | 280.1          | 220<br>192     | 10.15                | 95         | 10<br>20         | 4                        |
| Methamidophos       | 142            | 125<br>94.1    | 1.98                 | 85         | 10<br>12         | 3                        |

| Compound Name      | Precursor Ion | Product Ion            | Retention Time (min) | Fragmentor | Collision Energy | Cell Accelerator Voltage |
|--------------------|---------------|------------------------|----------------------|------------|------------------|--------------------------|
| Methomyl           | 162.9         | 106.1<br>88.1          | 4.33                 | 50         | 6<br>4           | 3                        |
| Omethoate          | 214           | 183<br>125             | 3.23                 | 80         | 6<br>20          | 4                        |
| Paclobutrazol      | 294.1         | 125<br>70.1            | 11.41                | 115        | 44<br>18         | 4                        |
| Phorate            | 261           | 75.1<br>47             | 13.04                | 60         | 6<br>35          | 4                        |
| Phorate sulfone    | 293.0         | 171<br>143             | 9.82                 | 80         | 6<br>15          | 4                        |
| Phorate sulfoxide  | 277.0         | 199<br>171             | 9.63                 | 80         | 5<br>12          | 4                        |
| Phosalone          | 368           | 182<br>111.1           | 13.11                | 70         | 10<br>45         | 4                        |
| Phoxim             | 299.06        | 129.1<br>125.1         | 13.01                | 70         | 12<br>8          | 4                        |
| Prochloraz         | 376           | 308<br>70.1            | 13.04                | 70         | 4<br>24          | 4                        |
| Pyridaben          | 365.1         | 309.1<br>147.1         | 15.19                | 85         | 8<br>25          | 4                        |
| Tebufenozide       | 353           | 297.2<br>133.1         | 12.44                | 95         | 5<br>15          | 4                        |
| Terbufos-sulfone   | 321.04        | 171<br>97              | 10.86                | 80         | 5<br>48          | 4                        |
| Terbufos-sulfoxide | 305.1         | 186.9<br>96.9          | 10.89                | 50         | 10<br>50         | 4                        |
| Thiabendazole      | 202           | 175.1<br>131.1<br>65.1 | 5.48                 | 151        | 22<br>30<br>46   | 4                        |
| Thidiazuron        | 221           | 127.9<br>101.9         | 8.64                 | 107        | 12<br>14         | 4                        |
| Triadimefon        | 294.1         | 197<br>69.1            | 11.57                | 111        | 6<br>14          | 4                        |
| Triazophos         | 314.1         | 119.1<br>92            | 11.79                | 111        | 42<br>50         | 4                        |

## Results and discussion

### Celery results

Four Universal dSPE kits were investigated based on celery matrix including traditional U-dSPE with GCB (2 and 15 mL), and U-dSPE with Carbon S (2 and 15 mL). The recoveries and RSDs were compared using two levels of prespiked QCs, 4 and 50 ng/g in celery, in replicates of five. Figure 1 shows the statistical data of the comparison. Overall, the U-dSPE with Carbon S delivered equivalent performance to the current U-dSPE with GCB, with over 80% average recovery and  $\leq 10\%$  RSD for all 45 pesticides.

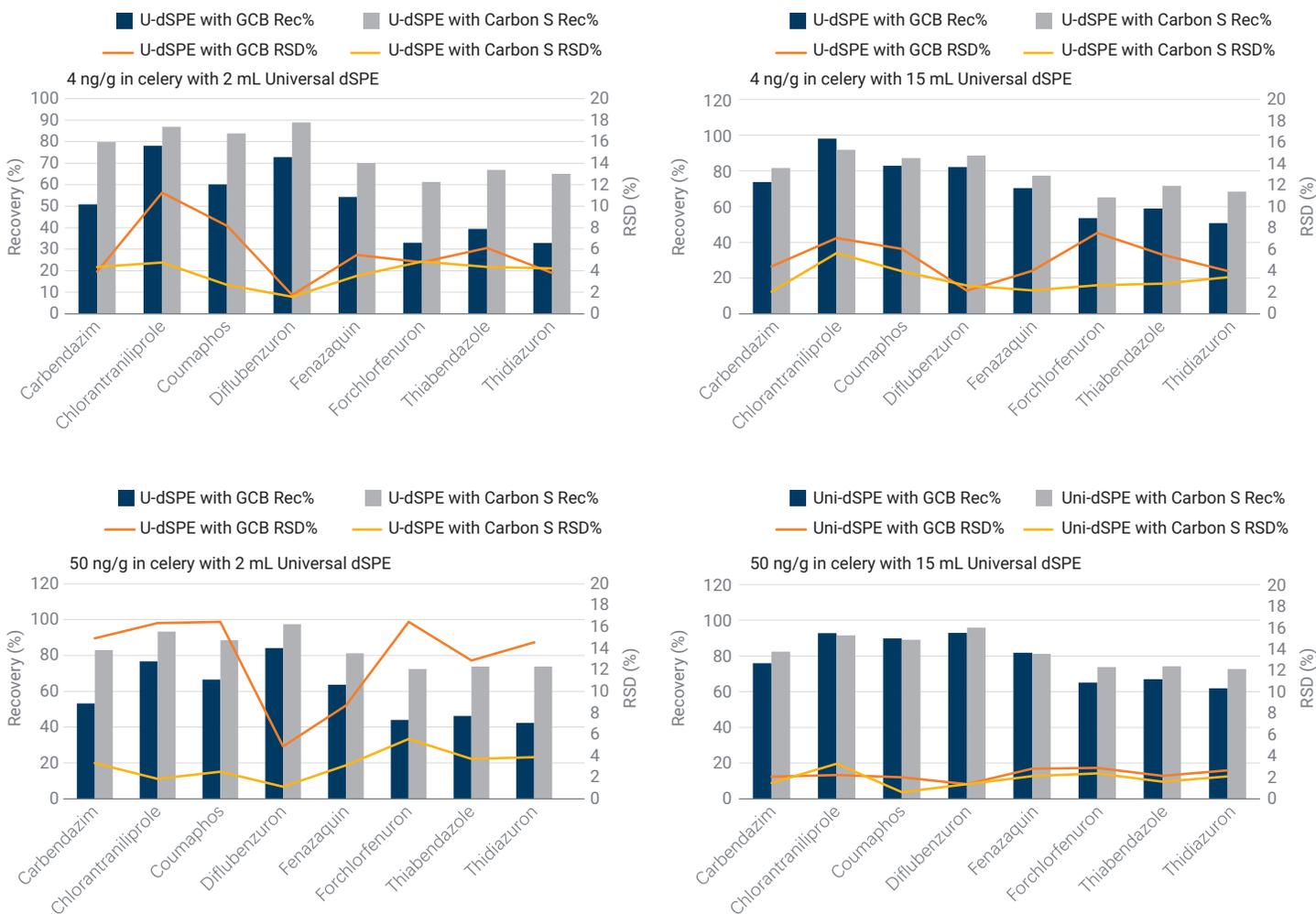


**Figure 1.** Comparison of Agilent Bond Elut QuEChERS Universal dispersive SPE kits with either Carbon S or GCB (2 and 15 mL) on average recoveries and RSDs of pesticides in celery (n = 5).

The only difference in these two types of Universal dSPE is the sorbent used for pigment removal: Carbon S or GCB. The recoveries of planar pesticides were specifically studied for comparison. For the eight planar pesticides in the target group, as shown in Figure 2, the U-dSPE with Carbon S delivered better recoveries

and reproducibility than the U-dSPE with GCB. The results clearly demonstrate that the use of Carbon S sorbent instead of GCB in the dSPE can improve sensitive planar pesticide recovery. In addition, the recovery differences between two types of Universal dSPE were more significant in the 2 mL kit rather than the 15 mL

kit. This can be explained by a relatively higher ratio of GCB used in the 2 mL kit formula than 15 mL kit formula. The formula ratio differences between 2 and 15 mL Universal dSPE kits amplified the disadvantage of GCB-caused planar pesticide loss in the U-dSPE with GCB.

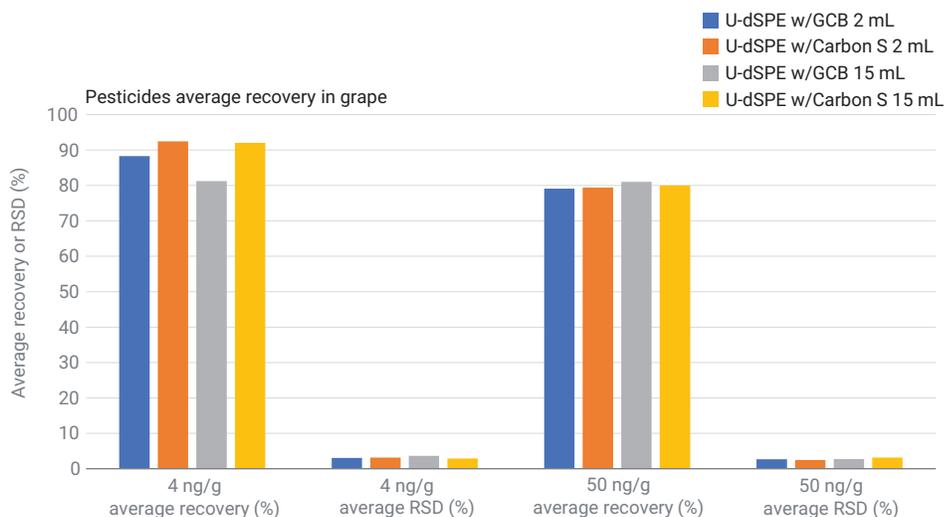


**Figure 2.** Performance comparison of the Agilent Bond Elut QuEChERS Universal dispersive SPE kits with either GCB or Carbon S (2 and 15 mL) on planar pesticides in celery (n = 5).

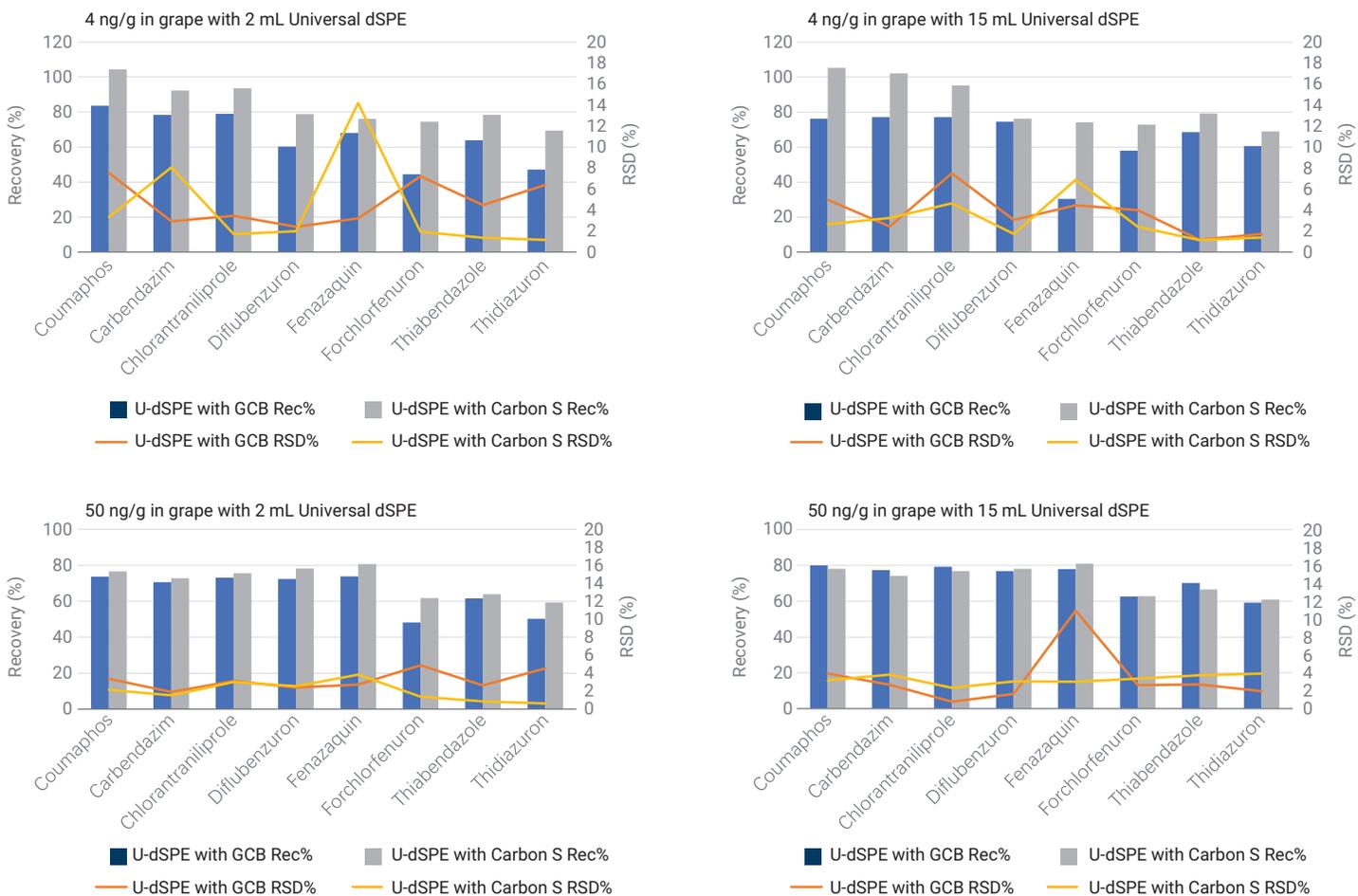
## Grape results

Similarly, four Universal dSPE kits were investigated in grape matrix. The statistical data for the average recoveries and RSDs are shown in Figure 3. Generally, the U-dSPE with Carbon S performed slightly better than the U-dSPE with GCB at 4 ng/g spiking level and equivalent at 50 ng/g spiking level.

For planar pesticides, the U-dSPE with Carbon S delivered much better recoveries, especially at low spiking levels because the planar pesticides were more sensitive with GCB at low levels. In comparison, the U-dSPE with Carbon S delivered consistent and excellent recoveries for planar pesticides at both low and high spiking levels.



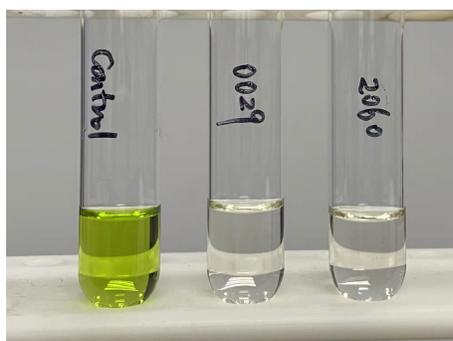
**Figure 3.** Comparison of the Agilent Bond Elut QuEChERS Universal dispersive SPE kits with either GCB or Carbon S (2 and 15 mL) on average recoveries and RSDs for pesticides in grape (n = 5).



**Figure 4.** Performance comparison of the Agilent Bond Elut QuEChERS Universal dispersive SPE kits with GCB or Carbon S (2 and 15 mL) on planar pesticides in grape (n = 5).

### Matrix pigment removal

The results using the U-dSPE with Carbon S demonstrate superior recoveries for planar pesticides compared to those using the U-dSPE with GCB. However, it was questioned whether there would be a compromise on pigment removal. Figure 5 shows the supernatant of celery samples after dSPE cleanups using the U-dSPE with GCB (middle) and U-dSPE with Carbon S (right). Visually, both samples are colorless and transparent, which indicates the equivalent pigment removal efficiency using the Universal dSPE kits with either Carbon S or GCB.



**Figure 5.** Supernatant of celery samples from Agilent Bond Elut QuEChERS AOAC extraction (left), followed with dSPE cleanup using the Agilent Bond Elut QuEChERS Universal dispersive SPE kits with either GCB (middle) or Carbon S (right).

### Method validation

The quantitative method was validated based on calibration curve linearity and dynamic range, and analyte accuracy and precision at both low and high spiking levels using the novel U-dSPE with Carbon S, 15 mL. The quantitation results are shown in Tables 3 and 4 for celery and grape, respectively.

Eight or more calibration standards were used to generate calibration curves over the dynamic range from 1 to 100 ng/g. Linear regression fit and 1/x weighting were used. Excellent calibration curve linearity was demonstrated with correlation coefficients ( $R^2$ ) >0.997 for all of targets. Acceptable target accuracy >75% for nonplanar pesticides and >60% for planar pesticides was achieved. Method reproducibility was demonstrated with <10% RSDs for 99% of the data.

**Table 3.** Method quantitation results for 45 pesticides in celery using the Agilent Bond Elut QuEChERS U-dSPE with Carbon S, 15 mL.

| Target              | CF R <sup>2</sup> | Calibration Range (ng/g) | QC with 15 mL Carbon S dSPE Kit |         |              |         |
|---------------------|-------------------|--------------------------|---------------------------------|---------|--------------|---------|
|                     |                   |                          | 4 ng/g                          |         | 50 ng/g      |         |
|                     |                   |                          | Accuracy (%)                    | RSD (%) | Accuracy (%) | RSD (%) |
| 3-Hydroxycarbofuran | 0.9999            | 1 to 100                 | 100                             | 5.2     | 101          | 1.7     |
| Acephate            | 0.9998            | 0.5 to 100               | 93                              | 1.6     | 93           | 1.1     |
| Acetamiprid         | 0.9999            | 0.5 to 100               | 98                              | 2.6     | 101          | 1.1     |
| Aldicarb            | 0.9989            | 0.5 to 100               | 92                              | 4.5     | 100          | 1.8     |
| Aldicarb-sulfone    | 0.9995            | 1 to 100                 | 98                              | 5.6     | 100          | 1.5     |
| Aldicarb-sulfoxide  | 0.9997            | 0.5 to 100               | 96                              | 3.4     | 97           | 1.2     |
| Buprofezin          | 0.9997            | 0.5 to 100               | 100                             | 3.2     | 101          | 0.7     |
| Cadusafos           | 0.9999            | 0.5 to 100               | 95                              | 2.9     | 101          | 0.9     |
| Carbaryl            | 0.9999            | 0.5 to 100               | 100                             | 3.0     | 101          | 2.4     |
| Carbendazim         | 0.9997            | 1 to 100                 | 82                              | 2.1     | 82           | 1.5     |
| Carbofuran          | 1.0000            | 0.5 to 100               | 101                             | 2.3     | 102          | 1.0     |
| Chlorantraniliprole | 0.9992            | 0.5 to 100               | 92                              | 5.6     | 92           | 3.3     |
| Chlordimeform       | 0.9995            | 0.5 to 100               | 82                              | 4.6     | 89           | 2.4     |
| Chlorpyrifos        | 0.9998            | 0.5 to 100               | 96                              | 3.2     | 99           | 1.9     |
| Coumaphos           | 0.9999            | 0.5 to 100               | 87                              | 4.0     | 89           | 0.6     |
| Cymoxanil           | 0.9998            | 0.5 to 100               | 101                             | 2.1     | 101          | 2.0     |
| Diazinon            | 0.9999            | 1 to 100                 | 100                             | 4.0     | 101          | 1.3     |
| Dichlorvos          | 0.9974            | 4 to 100                 | 99                              | 13.9    | 109          | 3.0     |
| Diflubenzuron       | 0.9995            | 0.5 to 100               | 89                              | 2.6     | 96           | 1.4     |
| Dimethoate          | 0.9999            | 0.5 to 100               | 96                              | 0.8     | 100          | 1.3     |
| Ethoprophos         | 0.9999            | 0.5 to 100               | 100                             | 5.7     | 100          | 1.0     |
| Fenazaquin          | 0.9998            | 0.5 to 100               | 77                              | 2.2     | 81           | 2.1     |

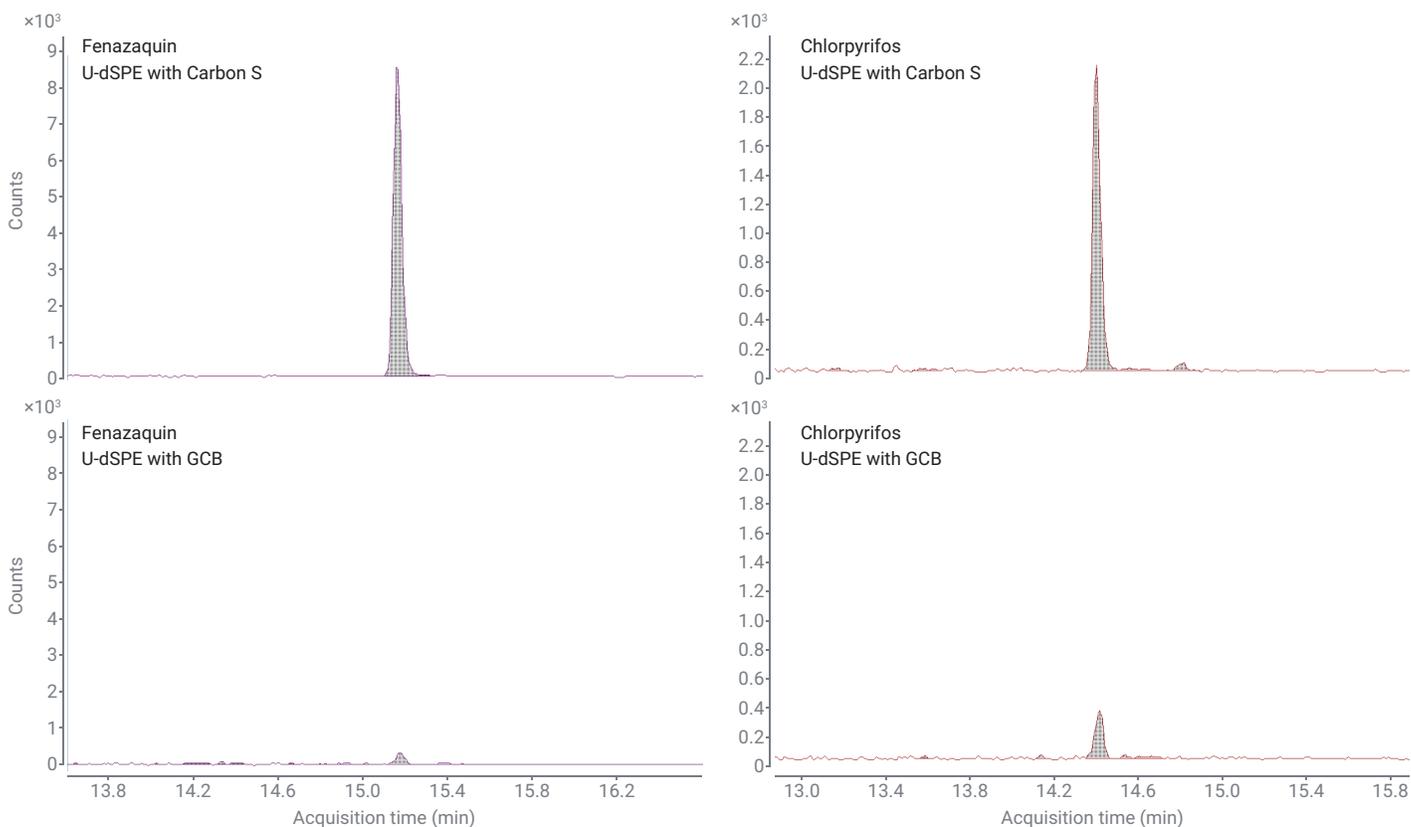
| Target             | CF R <sup>2</sup> | Calibration Range (ng/g) | QC with 15 mL Carbon S dSPE Kit |         |              |         |
|--------------------|-------------------|--------------------------|---------------------------------|---------|--------------|---------|
|                    |                   |                          | 4 ng/g                          |         | 50 ng/g      |         |
|                    |                   |                          | Accuracy (%)                    | RSD (%) | Accuracy (%) | RSD (%) |
| Fonofos            | 0.9997            | 2 to 100                 | 90                              | 9.1     | 98           | 1.9     |
| Forchlorfenuron    | 0.9999            | 0.5 to 100               | 65                              | 2.6     | 74           | 2.4     |
| Isazofos isotope   | 0.9999            | 0.5 to 100               | 100                             | 2.2     | 98           | 2.0     |
| Isofenphos-methyl  | 0.9990            | 1 to 100                 | 99                              | 9.4     | 100          | 3.4     |
| Metalaxyl          | 0.9997            | 0.5 to 100               | 100                             | 1.4     | 102          | 1.8     |
| Methamidophos      | 0.9997            | 0.5 to 100               | 89                              | 1.3     | 88           | 1.7     |
| Methomyl           | 0.9998            | 0.5 to 100               | 99                              | 3.4     | 100          | 0.8     |
| Omethoate          | 0.9995            | 0.5 to 100               | 93                              | 2.6     | 95           | 2.0     |
| Paclobutrazol      | 0.9999            | 0.5 to 100               | 97                              | 3.4     | 100          | 0.9     |
| Phorate sulfone    | 0.9997            | 0.5 to 100               | 94                              | 7.6     | 101          | 2.0     |
| Phorate sulfoxide  | 0.9998            | 0.5 to 100               | 114                             | 2.8     | 111          | 2.3     |
| Phorate            | 0.9991            | 1 to 100                 | 102                             | 2.7     | 100          | 1.1     |
| Phosalone          | 0.9993            | 1 to 100                 | 91                              | 9.2     | 102          | 1.7     |
| Phoxim             | 0.9999            | 0.5 to 100               | 103                             | 1.1     | 102          | 0.9     |
| Prochloraz         | 0.9997            | 0.5 to 100               | 99                              | 2.6     | 98           | 1.5     |
| Pyridaben          | 0.9999            | 0.5 to 100               | 99                              | 2.4     | 102          | 1.8     |
| Tebufenozide       | 0.9997            | 0.5 to 100               | 104                             | 3.7     | 101          | 2.4     |
| Terbufos-sulfone   | 0.9997            | 1 to 100                 | 102                             | 6.0     | 103          | 2.4     |
| Terbufos-sulfoxide | 0.9999            | 0.5 to 100               | 101                             | 3.0     | 103          | 1.1     |
| Thiabendazole      | 0.9999            | 0.5 to 100               | 71                              | 2.8     | 74           | 1.6     |
| Thidiazuron        | 0.9997            | 0.5 to 100               | 68                              | 3.4     | 73           | 2.1     |
| Triadimefon        | 1.0000            | 1 to 100                 | 98                              | 7.6     | 101          | 1.7     |
| Triazophos         | 0.9998            | 0.5 to 100               | 96                              | 3.1     | 99           | 1.1     |

**Table 4.** Method quantitation results for 45 pesticides in grape using the Agilent Bond Elut QuEChERS U-dSPE kit with Carbon S, 15 mL.

| Targets             | CF R <sup>2</sup> | Calibration Range (ng/g) | QC with 15 mL Carbon S dSPE Kit |         |              |         |
|---------------------|-------------------|--------------------------|---------------------------------|---------|--------------|---------|
|                     |                   |                          | 4 ng/g                          |         | 50 ng/g      |         |
|                     |                   |                          | Accuracy (%)                    | RSD (%) | Accuracy (%) | RSD (%) |
| 3-Hydroxycarbofuran | 0.9995            | 1 to 100                 | 99                              | 2.6     | 78           | 3.1     |
| Acephate            | 0.9995            | 0.5 to 100               | 93                              | 1.4     | 76           | 3.6     |
| Acetamiprid         | 0.9999            | 0.5 to 100               | 96                              | 1.7     | 80           | 3.5     |
| Aldicarb            | 0.9998            | 1 to 100                 | 89                              | 3.5     | 81           | 3.5     |
| Aldicarb-sulfone    | 0.9998            | 0.5-100                  | 106                             | 4.0     | 81           | 2.7     |
| Aldicarb-sulfoxide  | 0.9997            | 0.5 to 100               | 95                              | 2.4     | 79           | 3.7     |
| Buprofezin          | 0.9997            | 0.5 to 100               | 91                              | 2.2     | 83           | 2.3     |
| Cadusafos           | 0.9995            | 0.5 to 100               | 93                              | 1.9     | 82           | 3.0     |
| Carbaryl            | 0.9997            | 0.5 to 100               | 92                              | 1.2     | 81           | 2.6     |
| Carbendazim         | 0.9995            | 0.5 to 100               | 102                             | 3.3     | 74           | 3.8     |
| Carbofuran          | 0.9999            | 0.5 to 100               | 93                              | 1.1     | 82           | 2.6     |
| Chlorantraniliprole | 0.9995            | 0.5 to 100               | 95                              | 4.7     | 77           | 2.3     |
| Chlordimeform       | 0.9994            | 0.5 to 100               | 86                              | 4.4     | 66           | 4.1     |
| Chlorpyrifos        | 0.9994            | 0.5 to 100               | 87                              | 4.3     | 85           | 2.0     |
| Coumaphos           | 0.9997            | 0.5 to 100               | 105                             | 2.7     | 78           | 3.2     |
| Cymoxanil           | 0.9996            | 0.5 to 100               | 94                              | 5.1     | 82           | 2.9     |
| Diazinon            | 0.9996            | 0.5 to 100               | 97                              | 2.0     | 93           | 1.8     |

| Targets            | CF R <sup>2</sup> | Calibration Range (ng/g) | QC with 15 mL Carbon S dSPE Kit |         |              |         |
|--------------------|-------------------|--------------------------|---------------------------------|---------|--------------|---------|
|                    |                   |                          | 4 ng/g                          |         | 50 ng/g      |         |
|                    |                   |                          | Accuracy (%)                    | RSD (%) | Accuracy (%) | RSD (%) |
| Dichlorvos         | 0.9995            | 2 to 100                 | 86                              | 3.7     | 82           | 4.7     |
| Diflubenzuron      | 0.9995            | 0.5 to 100               | 76                              | 1.7     | 78           | 3.1     |
| Dimethoate         | 0.9996            | 0.5 to 100               | 93                              | 5.9     | 80           | 3.3     |
| Ethoprophos        | 0.9999            | 1 to 100                 | 96                              | 2.0     | 81           | 2.7     |
| Fenazaquin         | 0.9970            | 0.5 to 100               | 74                              | 6.9     | 81           | 3.0     |
| Fonofos            | 0.9986            | 4 to 100                 | 91                              | 2.2     | 81           | 1.7     |
| Forchlorfenuron    | 0.9999            | 0.5 to 100               | 73                              | 2.4     | 63           | 3.3     |
| Isazofos isotope   | 1.0000            | 0.5 to 100               | 99                              | 2.9     | 82           | 3.6     |
| Metalaxyl          | 0.9999            | 0.5 to 100               | 91                              | 2.4     | 83           | 1.9     |
| Methamidophos      | 0.9998            | 0.5 to 100               | 103                             | 1.3     | 73           | 3.5     |
| Methomyl           | 0.9998            | 0.5 to 100               | 85                              | 0.6     | 80           | 3.4     |
| Omethoate          | 0.9996            | 0.5 to 100               | 94                              | 1.7     | 78           | 3.8     |
| Paclobutrazol      | 0.9999            | 0.5 to 100               | 94                              | 2.0     | 82           | 1.8     |
| Phorate            | 0.9995            | 1 to 100                 | 91                              | 2.4     | 86           | 4.0     |
| Phorate sulfone    | 0.9998            | 0.5 to 100               | 97                              | 2.2     | 82           | 1.7     |
| Phorate sulfoxide  | 0.9999            | 0.5 to 100               | 94                              | 1.3     | 81           | 2.1     |
| Phosalone          | 0.9995            | 0.5 to 100               | 86                              | 1.5     | 81           | 4.4     |
| Phoxim             | 0.9995            | 0.5 to 100               | 99                              | 4.7     | 87           | 3.7     |
| Prochloraz         | 0.9994            | 0.5 to 100               | 94                              | 4.4     | 81           | 2.5     |
| Profenofos         | 0.9994            | 0.5 to 100               | 96                              | 2.5     | 81           | 2.5     |
| Pyridaben          | 0.9969            | 0.5 to 100               | 95                              | 3.4     | 101          | 4.5     |
| Tebufenozide       | 0.9997            | 0.5 to 100               | 96                              | 2.5     | 82           | 4.9     |
| Terbufos-sulfone   | 0.9998            | 0.5 to 100               | 90                              | 9.6     | 82           | 4.1     |
| Terbufos-sulfoxide | 0.9999            | 0.5 to 100               | 97                              | 3.0     | 81           | 2.2     |
| Thiabendazole      | 0.9997            | 0.5 to 100               | 79                              | 1.2     | 67           | 3.7     |
| Thidiazuron        | 0.9997            | 0.5 to 100               | 69                              | 1.4     | 61           | 3.9     |
| Triadimefon        | 0.9999            | 0.5 to 100               | 96                              | 4.8     | 85           | 3.5     |
| Triazophos         | 0.9998            | 0.5 to 100               | 94                              | 1.5     | 83           | 3.8     |

Additionally, it was noticed that a few pesticides in celery showed higher responses with improved signal-to-noise (S/N) ratio when dSPE cleanup with the U-dSPE with Carbon S was used. Fenazaquin and chlorpyrifos are two good examples, as shown in Figure 6. At a postspiking level of 4 ng/g, the U-dSPE with Carbon S demonstrated much higher responses than the U-dSPE with GCB. Nevertheless, there is no obvious difference between these two kits on the recoveries of samples prespiked at 4 ng/g in celery with matrix matched calibration, which are both above 80% for chlorpyrifos, and above 70% for fenazaquin. This illustrates the advantage of Carbon S on matrix removal for less ion suppression.



**Figure 6.** Chromatogram of fenazaquin and chlorpyrifos at 4 ng/g postspiking in celery using the Agilent Bond Elut QuEChERS Universal dSPE kits with either GCB or Carbon S.

## Conclusion

A novel Agilent Bond Elut QuEChERS U-dSPE with Carbon S kit demonstrated exceptional performance for both planar and nonplanar pesticides analysis compared to the traditional Agilent Bond Elut QuEChERS U-dSPE with GCB kit. Both 2 and 15 mL U-dSPE with Carbon S kits delivered improved recoveries and reproducibility for planar pesticides, and thus more consistent and reliable quantitative results.

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