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Combination of GC/MS/MS and LC/MS/MS to Analyze Multiclass Pesticides in Orange Using One QuEChERS Sample Preparation Method

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Introduction

Hundreds of pesticides are commercially available and are widely used on fruit plants during cultivation process. These pesticides may accumulate and pass onto the final products, causing safety issues. To regulate the use of pesticides, Chinese National Health and Family Planning Commission, Ministry of Agriculture, China Food and Drug Administration released a national food safety standard-GB 2763. It regulates maximum residue limits (MRLs) of 433 pesticides and related metabolites in different food matrices.

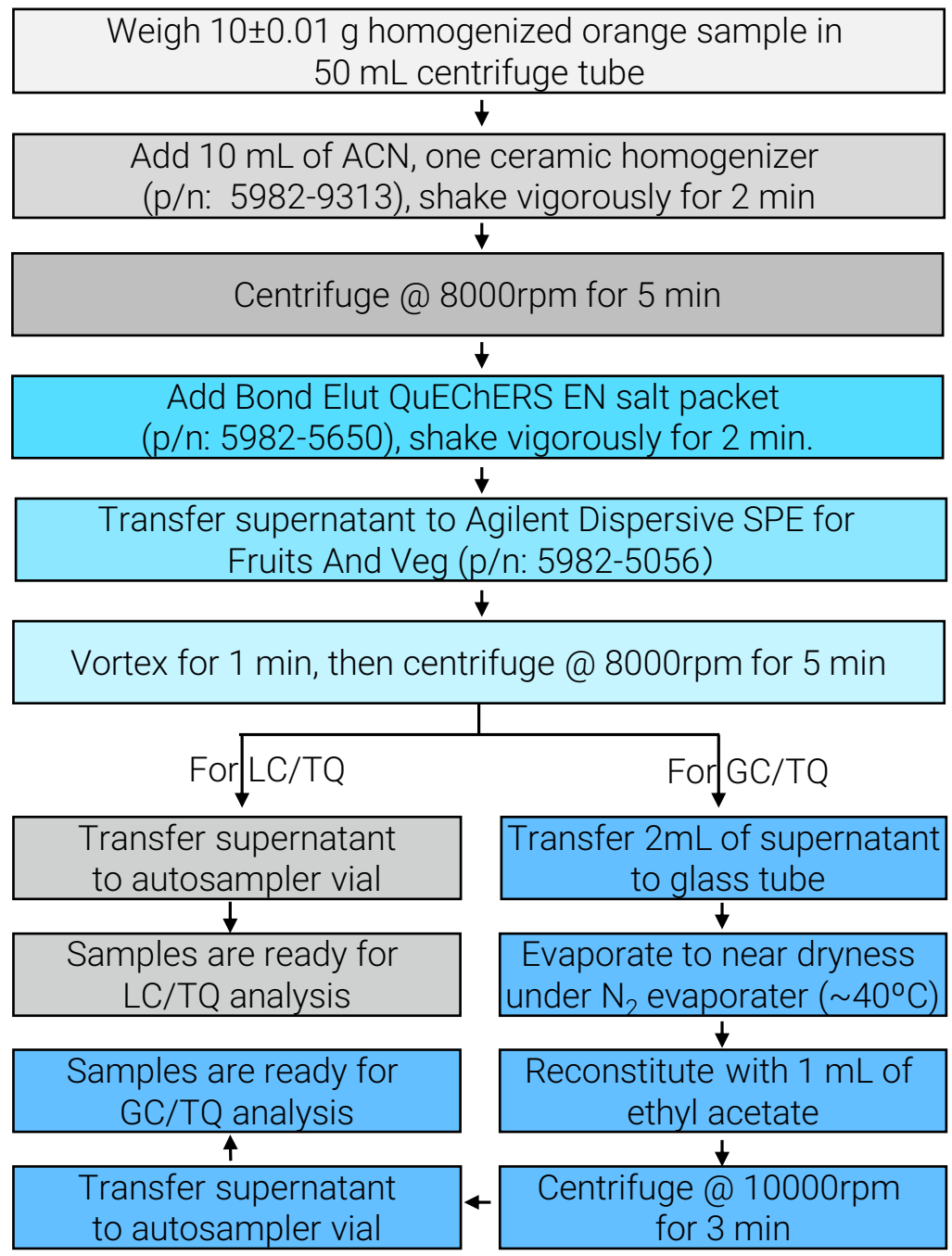
For safety and compliance requirements, these regulated pesticides need to be analyzed by many labs (government labs, commercial labs, corporate labs, etc.) as routine work. However, there isn't a specific method developed to analyze > 300 pesticides listed in GB 2763. To analyze all these pesticides, at least 100 standard methods need to be run, which is very time and cost consuming, so a simple and efficient solution is highly desired.

With the combination of 7000D GC/MS/MS and Ultivo LC/MS/MS platforms, a total solution was developed for analyzing 455 pesticides (including isomers, metabolites) in orange. 293 pesticides were analyzed by GC/TQ, while 326 pesticides were analyzed by LC/TQ. There were 164 pesticides been analyzed on both of GC/TQ and LC/TQ, which brought extract values for positive confirmation.

Figure 1. 1260Prime LC + Ultivo; 7890GC + 7000D

Experimental

Sample Prep.



Analysis Parameters

Table 1. LC Conditions

Column	Eclipse Plus C18 3.0 x 150 mm, 1.8µm (p/n: 959759-302)				
Column temp	45 °C				
Injection volume	2 µL				
Mobile phase	A: Water + 4.5mM ammonium formate, 0.5mM NH4F, 0.1% Formic Acid B: Methanol + 4.5mM ammonium formate, 0.5mM NH4F, 0.1% Formic Acid				
Flow rate	0.5 mL/min				
Gradient	Time (min.)	B%	Time (min.)	B%	
	0	2	16	0	
	0.5	2	18	0	
	1	50	18.1	98	
	4	35	20	98	
Stop Time	20 min (Post Time 1.5 min)				

Table 2. GC Conditions

Column	Two HP-5ms 15 m x 0.25 mm ID x 0.25 µm (p/n: 19091S-431UI)		
Injection liner	4 mm IDliner, UI, splitless, single taper, glass wool (p/n: 5190-2293)		
Injection volume	1 µL		
Injection mode	splitless		
Inlet temp.	280 °C		
Carrier gas	He		
Gas flow	Column 1 = ~ 1 mL/min Column 2 = Column 1 flow + 0.2 mL/min		
Oven program		60 °C	1 min
	40 °C/min	120 °C	0 min
	5 °C/min	310 °C	0 min
Mass transfer line	280 °C		
Stop Time	20 min (Post Time 1.5 min)		

Table 3. Ultivo settings

Gas temp.	250 °C
Gas flow	11 L/min
Nebulizer	40 psi
Sheath gas temp.	350 °C
Capillary voltage	3500(+) / 3500(-)
Nozzle voltage	300(+) / 1000(-)

Table 4. 7000D settings

Electron energy	70 EV
EM gain	Gain fator = 10
Collision cell	1.5 mL/min N_2 2.25 mL/min He
Source temp.	280 °C
Quad temp.	150 °C

Analytes Separation and Responses

Excellent chromatogram separations were achieved with the analysis methods on both of LC/TQ and GC/TQ. Figure 2-3 show the chromatograms of 10 ng/g analytes spiked in orange.

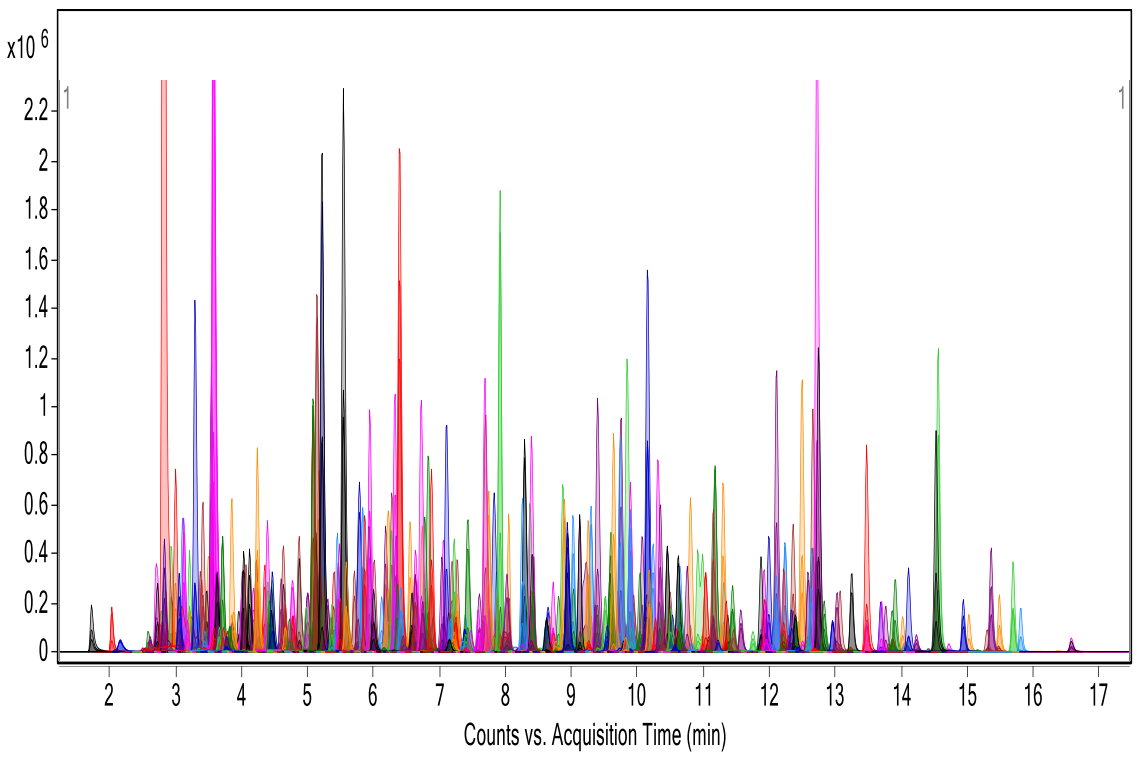


Figure 2. Chromatogram of an orange sample fortified with 326 pesticides at 10 ng/g (Ultivo LC/TQ)

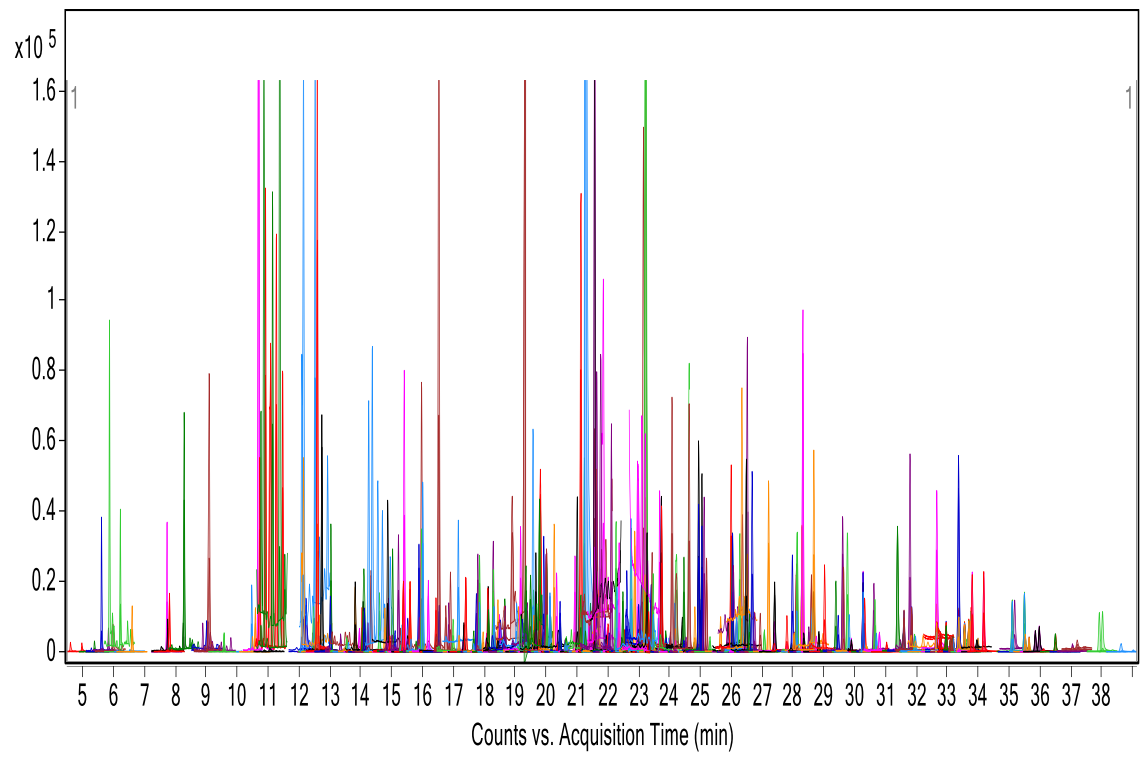


Figure 3. Chromatogram of an orange sample fortified with 293 pesticides at 10 ng/g (7000D GC/TQ)

Results and Discussion

Accuracy

Accuracy was expressed by the recovery. Blank orange samples were spiked with pesticides at different concentration levels (10 µg/kg, 20 µg/kg, 50 µg/kg) with 5 replicates for each level. These spiked samples went through the sample preparation. The recovery was calculated using matrix matched method. Very good accuracy results were achieved. For example, 90% of the analytes had recoveries between 70-120% at 20 ng/g spiked level on both of GC/TQ and LC/TQ method.

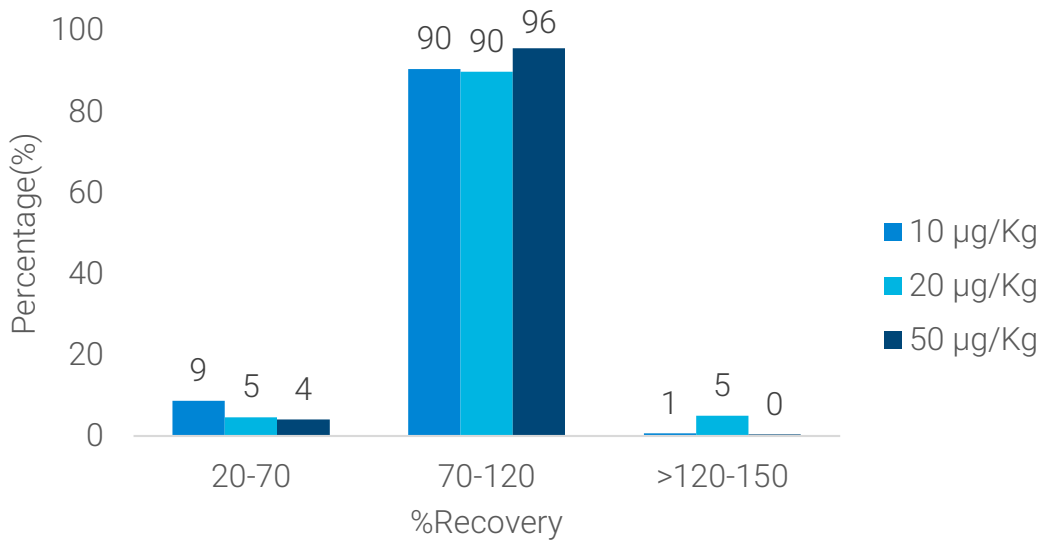


Figure 4. Distribution of % recoveries at different fortified levels (Ultivo LC/TQ)

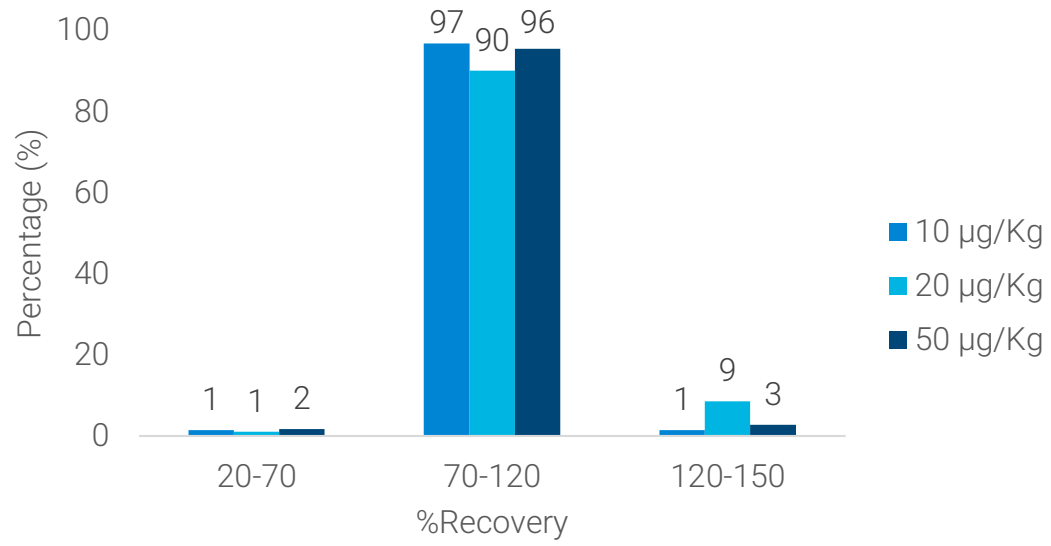


Figure 5. Distribution of % recoveries at different fortified levels (7000D LC/TQ)

Precision

The precision of the method was estimated by calculating %RSD of 5 replicates from accuracy. Excellent precision results were achieved: 90% of the analytes had RSD ≤ 10% at 20 ng/g spiked level(n=5) on GC/MS/MS, while 92% of the analytes had RSD ≤ 10% on LC/MS/MS at the same spiked level.

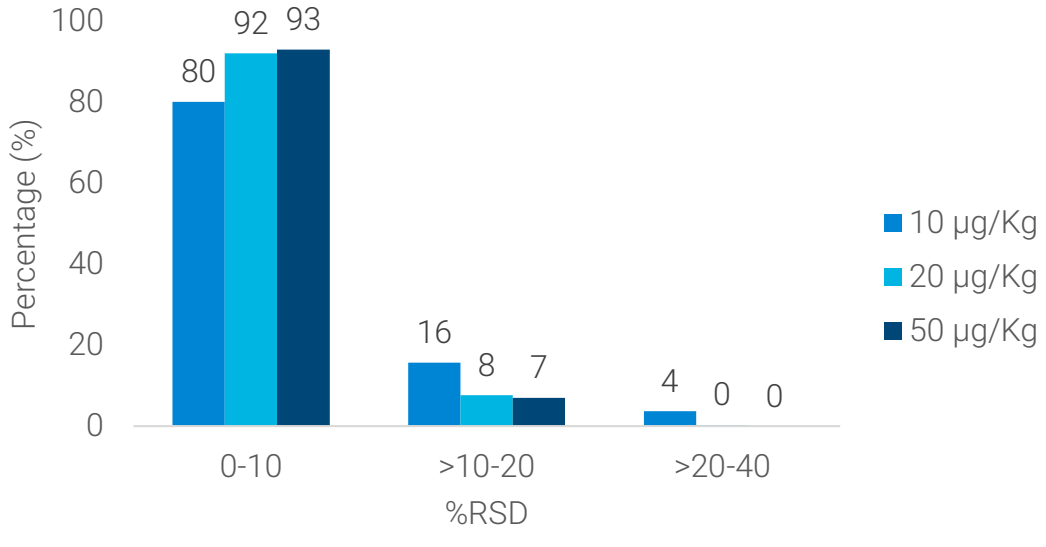


Figure 4. Distribution of % RSDs at different fortified levels (Ultivo LC/TQ)

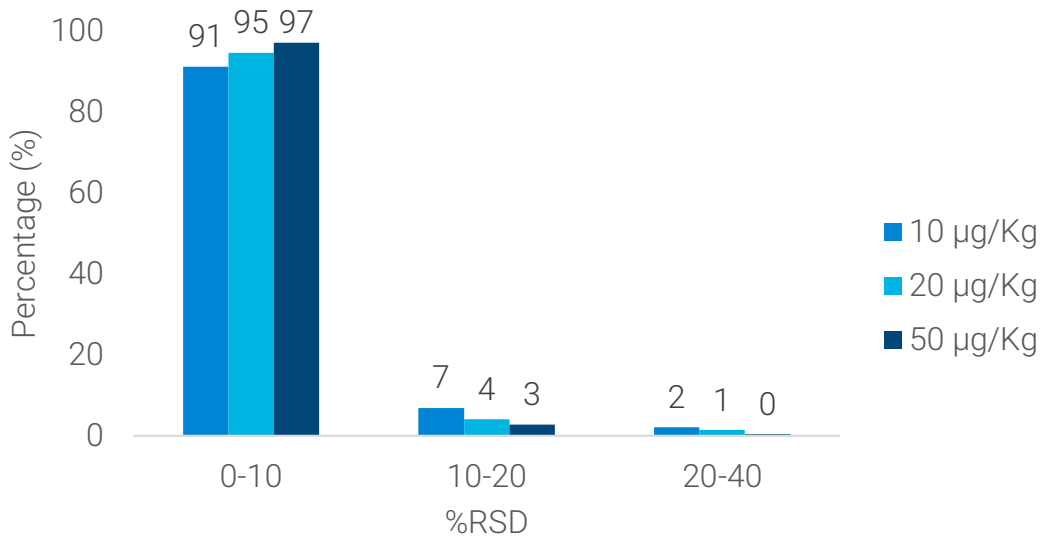


Figure 4. Distribution of % RSDs at different fortified levels (Ultivo LC/TQ)

Conclusions

High throughput, Time efficient, Low cost

This is an innovative combination of both GC/TQ and LC/TQ platforms, by which >450 GB2763 regulated pesticides were analyzed using a single QuEChERS sample prep.

Primary data shows that this solution can surely provide accurate and reliable answers to the labs doing routine analysis of GB2763 regulated pesticides.

References

[1]GB2763-2016: National food safety standard- Maximum residue limits for pesticides in food.

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