Targeted and Untargeted Analysis of Pesticides and Other Contaminants in Fruits and Vegetables Using Multi-Platform GC-MS/MS and GC/Q-TOF

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The increasing demand for analysis of contaminants in food requires an efficient workflow and sensitive detection. Triple quadrupole GCMS (GC-MS/MS) provides excellent sensitivity and selectivity in analyzing complex matrices and is recognized as the gold standard for the targeted analysis of GC-amenable contaminants. In this case, targeted analytes are decided beforehand and are present in the multiple reaction monitoring (MRM) method. In contrast, high resolution GC/Q-TOF analysis results in full-spectrum accurate mass data including profiling information of contaminants for a broad screening scope. This study explores both targeted and untargeted analysis of pesticides and other contaminants in fruits and vegetables using GC-MS/MS and GC/Q-TOF. It not only provides flexible and comprehensive analysis methods, but also offers a well-organized workflow using different platforms.

Sample Preparation

Fruit and vegetable samples were prepared using a multi-functional filter based on the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method. This convenient preparation allowed fast cleanup for analysis of hundreds of pesticides and other contaminants at low concentrations with a single extraction for both GC-MS/MS and GC/Q-TOF analysis.
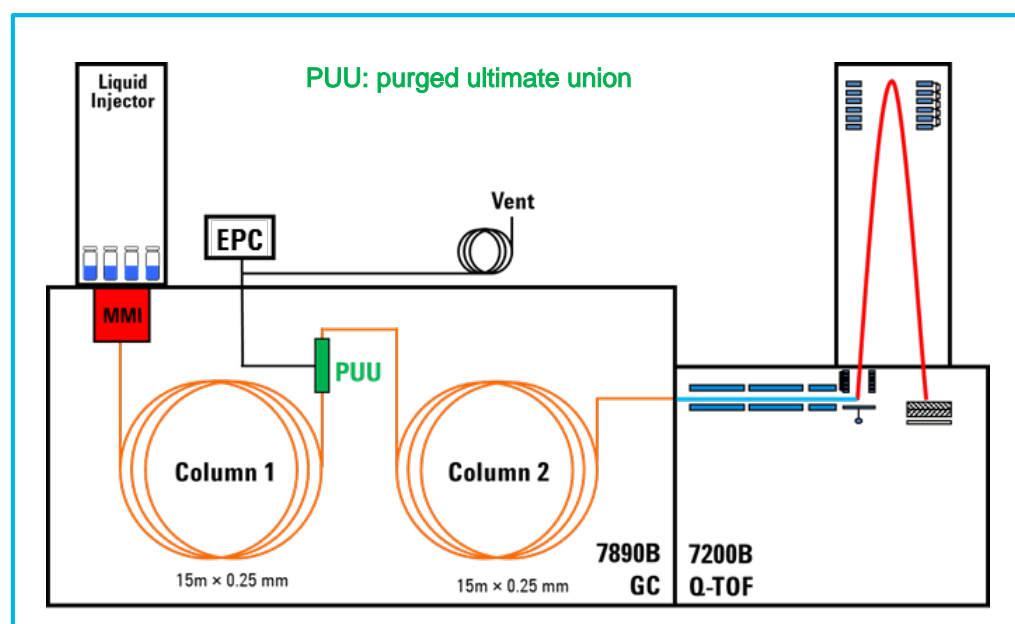

Figure 1. Mid-column back flushing system

Instrument Analysis

The samples were analyzed in EI mode by:

• Agilent 7890 GC and 7200 high resolution accurate mass GC/Q-TOF

• Agilent 7890 GC and 7010 GC-MS/MS

The GC-Q/TOF system was configured with a mid-column backflush setup (Figure 1). A 20-min constant flow retention time locked method (chlorpyrifos-methyl locked at 9.143 min) were identical on both platforms for chromatographic separation, which was listed in Table 1. The key GC-MS/MS parameters are as follows: The injection was 1 µL with cold splitless mode and temperature was 280 °C; the interface and source temperatures were 280 °C and 300 °C, respectively.

Table 1. Operational Conditions.

GC and MS Conditions	Value
Column (2 ea.)	HP-5MS UI, 15 m, 0.25 mm ID,0.25 µm film
Inlet	MMI,4-mm UI liner with wool
Injection	1µL,cold splitless
Injection temperature	280 °C
Inlet flow (column 1)	~ 1.0 mL/min
PUU flow (column 2)	column 1 flow + 0.2 mL/min
Oven program	60 °C for 1 min 40°C/min to 170°C,0 min 10°C/min to 310°C,3 min
Backflushing conditions	5 min (Post-run),310 °C(Oven) 50psi (Aux EPC),2 psi (Inlet)
Transfer line temperature	280°C
Ion source	EI, 70 eV
Ion source temperature	300°C
Quadrupole temperature	180 °C
Q-TOF Spectral Acquisition	45-550 m/z, 5 spectra/sec

Data Analysis

• The data processing used Agilent MassHunter Data Analysis software, including SureMass.

• The target screening of pesticides was based on a commercially available GC/Q-TOF accurate mass Personal Compound Database and Library (PCDL)[1].

• The untargeted screening of other contaminants relied on the NIST library through MassHunter Unknowns Analysis.

Workflow of Compound Screening and Quantification

Analysis by GC/Q-TOF provided comprehensive screening of pesticides and other contaminants. An accurate mass pesticides library was employed to perform targeted screening using a tool to search by principle ions of each compound with the identified hits verified via mass accuracy, RT match and coelution score. The NIST GC/MS library was used to expand the scope for untargeted screening of other contaminants. Positive hits were then confirmed and quantitated by GC-MS/MS (MRM). This workflow provided a detailed, comprehensive multi-platform and targeted and untargeted screening approach (Figure 2).
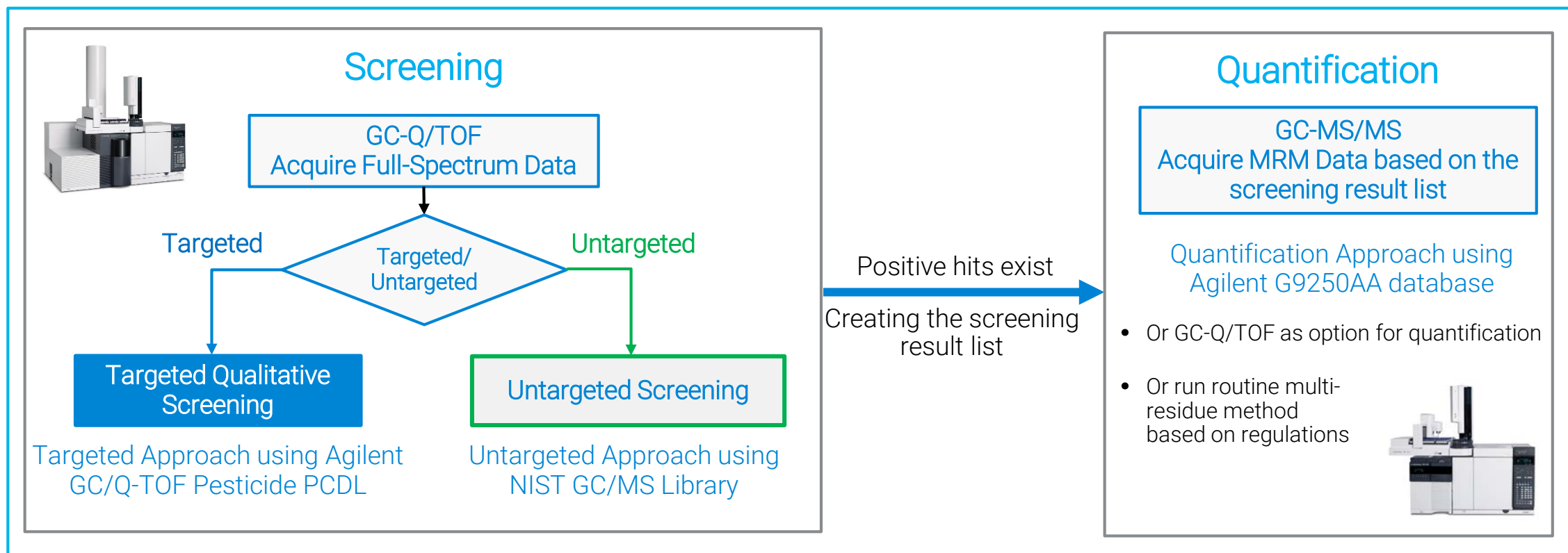

Figure 2. Workflow of Compound Screening and Quantification using GC-Q/TOF and GC-MS/MS.

Targeted Screening

Targeted screening was set up to automatically extract six ions per pesticide from the PCDL, and to require at least two of these to produce EICs with a coelution score ≥70 and an S/N ≥ 3. If a compound passing these requirements had an RT within ±0.15 minutes, it was considered identified. 63 commonly detected pesticides were spiked in fruit and vegetable samples to evaluate the effectiveness of this approach. It was found that over 60 spiked pesticides at 10 ng/mL were identified in all investigated food matrices and at least two ions of each compound had a mass error below 5ppm. The mid-column backflush method resulted in good instrument precision, with a retention time standard deviation of less than 0.01 min for most identified pesticides. Screening results of 18 representative pesticides (10 ng/mL) spiked in grape matrices are shown in Table 2. Included is a column for a custom field utilized for localized (Chinese) compound names.

Untargeted Screening

Untargeted screening of other contaminants was performed by NIST library search after SureMass peak detection (Figure 3). The screening analyzed 128 real fruit and vegetable samples and identified several pesticides and other contaminants (e.g., PAHs and phthalates).
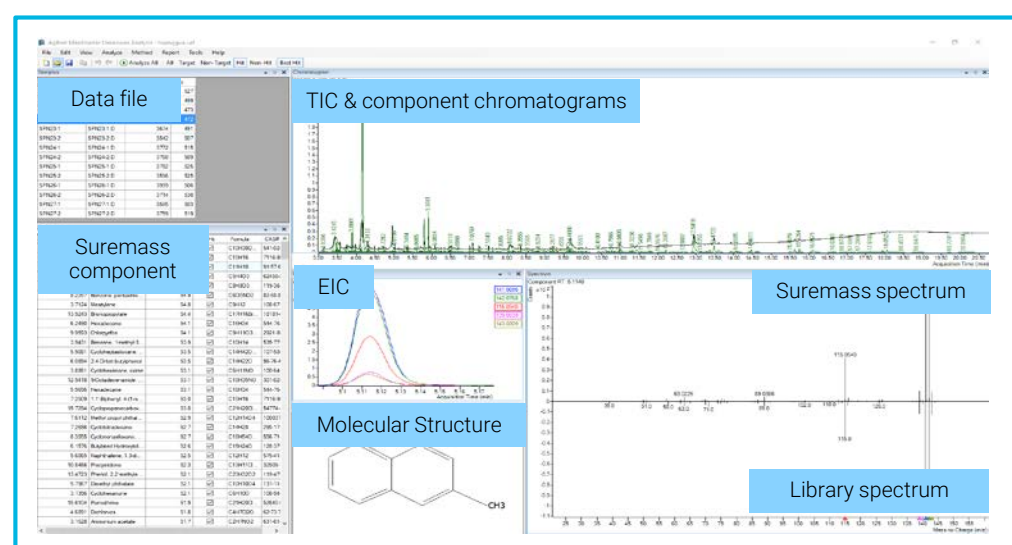

Figure 3. SureMass peak detection using the Unknowns Analysis software.

Table 2. Screening Results of 18 representative pesticides (10 ng/mL) spiked in grape matrices.

Name	Chinese Name	CAS	Formula	Identified?	RT (min)	RT Diff(min)	FIs Conf.	Reference ion		Qualified Ion		Coelution Score
								m/z	diff (ppm)	m/z	diff (ppm)	
Dichlorvos	敌敌畏	62-73-7	C4H7Cl2O4P	Yes	4.679	0.010	5	184.9765	1.3	186.9738	0.6	97.18
Trifluralin	氟乐灵	1582-09-8	C13H16F3N3O4	Yes	7.247	-0.004	6	264.0227	3.0	306.0696	2.0	99.08
Phorate	甲拌磷	298-02-2	C7H17O2PS3	Yes	7.504	-0.002	6	230.9732	0.6	96.9508	4.0	96.62
Dimethoate	乐果	60-51-5	C5H12NO3PS2	Yes	7.791	0.016	4	124.9821	4.6	78.9943	1.8	79.27
Atrazine	莠去津	1912-24-9	C8H14ClN5	Yes	7.887	0.006	6	215.0932	2.4	200.0697	2.1	94.70
Quintozene	五氯硝基苯	82-68-8	C6Cl5NO2	Yes	8.235	-0.007	6	292.8366	2.2	236.8408	2.9	95.90
Diazinon	二嗪磷	333-41-5	C12H21N2O3PS	Yes	8.285	0.000	6	304.1005	4.3	179.1179	0.6	90.45
Parathion-methyl	甲基对硫磷	298-00-0	C8H10NO5PS	Yes	9.139	0.005	4	263.0012	3.2	124.9821	1.2	90.81
Chlorpyrifos-methyl	甲基毒死蜱	5598-13-0	C7H7Cl3NO3PS	Yes	9.143	0.001	6	285.9256	3.0	287.9293	1.5	99.53
Metalaxyl	甲霜灵	57837-19-1	C15H21NO4	Yes	9.328	0.008	6	206.1176	0.6	160.1121	0.5	97.09
Chlorpyrifos	毒死蜱	2921-88-2	C9H11Cl3NO3PS	Yes	9.954	0.005	6	313.9569	2.5	198.9167	3.3	98.34
Parathion	对硫磷	56-38-2	C10H14NO5PS	Yes	9.967	0.006	4	291.0325	3.3	155.0036	3.5	80.34
Isocarbophos	水胺硫磷	24353-61-5	C11H16NO4PS	Yes	10.070	0.015	6	135.9977	2.8	112.9998	1.5	98.06
Isofenphos-methyl	甲基异柳磷	99675-03-3	C14H22NO4PS	Yes	10.402	0.008	6	199.0155	2.5	121.0284	1.7	99.15
Chlorfenapyr	虫螨腈	122453-73-0	C15H11BrClF3N2O	Yes	12.036	0.016	4	363.9407	0.9	247.0481	1.3	88.47
Bromopropylate	溴螨酯	18181-80-1	C17H16Br2O3	Yes	13.910	0.016	6	340.8995	1.0	184.9420	0.1	98.95
Bifenthrin	联苯菊酯	82657-04-3	C23H22ClF3O2	Yes	13.913	0.006	5	181.1012	0.5	165.0699	2.1	99.24
Cis-Permethrin	氯菊酯	54774-46-8	C21H20Cl2O3	Yes	15.602	0.006	5	183.0804	2.5	165.0699	2.2	98.01

Quantification Result

Positive hits from 128 real fruit and vegetable samples were confirmed and quantitated by GC-MS/MS. Example pesticides were selected to quantify by GC-Q/TOF. Four example pesticide quantification result in different matrices on GC-Q/TOF and GC-MS/MS are shown in Figure 4. The results showed the good agreement.
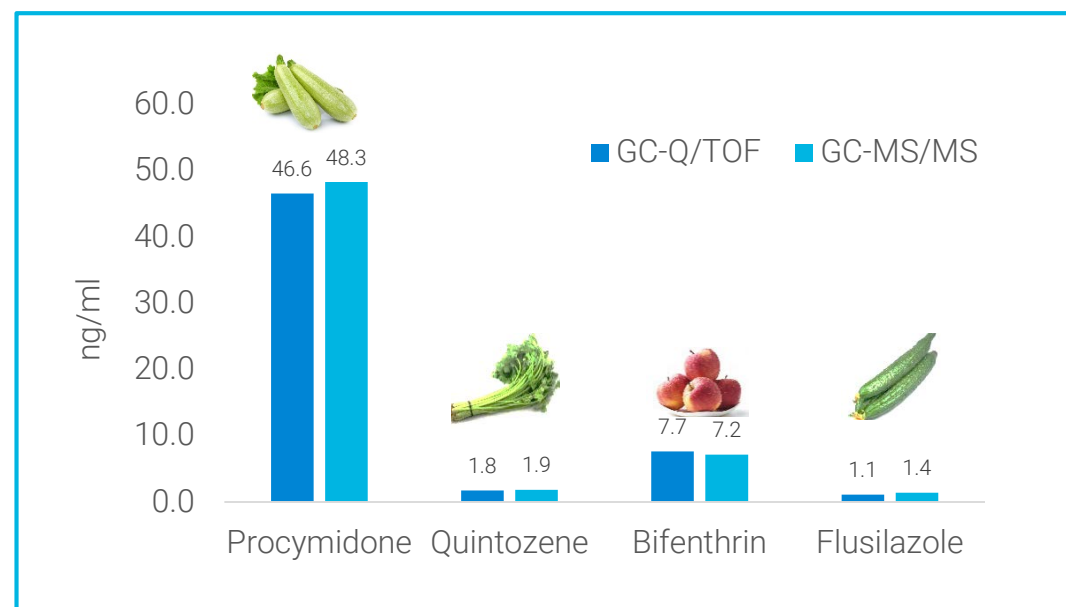

Figure 4. Quantification results of four pesticides in different matrices on GC-Q/TOF and GC-MS/MS.

- This work demonstrated a comprehensive multi-platform workflow for targeted and untargeted analysis of pesticides and other contaminants in fruits and vegetables.

- The confidence in identification of pesticides and other contaminants was enhanced by stable RT and excellent mass accuracy as a result of using an RTL backflush method and high resolution accurate mass measurement.

[1] Chen, K., Stevens, J., Nieto, S.; GC/Q-TOF Screening of pesticides in Food, *Agilent Technologies Application Note*, 5991-6884EN (2016).

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