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Screening of pesticides and other contaminants in food matrices using a novel high resolution GC/Q-TOF with low-energy capable EI source

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Introduction

The increasing demand on screening for contaminants in food requires an efficient and sensitive technique [1]. High resolution GC/Q-TOF has emerged as a tool to fit this purpose for GC-amenable compounds. The same full-spectrum accurate mass data enables both confident identification of compounds in the sample and quantitation capability to address the stringent requirements on maximum residue levels (MRLs). The addition of low energy electron impact (EI) ionization enhances the possibility to preserve or confirm molecular ions on EI mass spectra, aiding in the study of unknowns. In this work, a novel high resolution, low-energy EI capable GC/Q-TOF was used to screen pesticides and other contaminants in food matrices.

Experimental

Sample Preparation

Homogenized food commodities were extracted using QuEChERS (EN) kit. The cleanup of Avocado extract used EMR-Lipid dSPE and drying pouches. Broccoli extract was cleaned up by dSPE for pigment matrix, and others by dSPE for fruits/vegetables. A mixture of 140+ pesticides was spiked in the organic matrices to evaluate the method. Screening of contaminants was performed on non-organic food extracts.

Figure 1. 7250 GC/Q-TOF system

Experimental

Instrument Analysis

A retention time locked method was set up to acquire data using an Agilent 7250 GC/Q-TOF system (figure 1) configured with a mid-column backflushing system (figure 2). Table 2 lists the operational parameters.

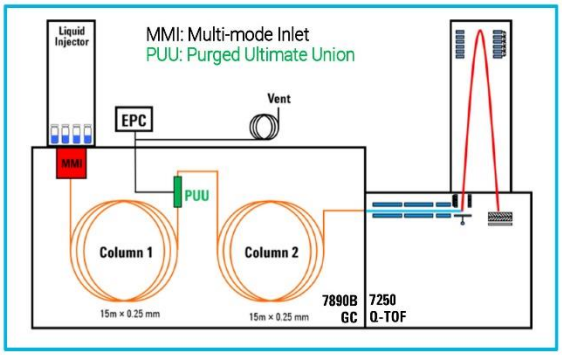

Figure 2. Mid-column back flushing system

Table 1. GC/Q-TOF Operational Conditions.

GC and MS Conditions	Value
Columns (2 ea.)	HP-5 MS UI, 15 m, 0.25 mm ID, 0.25 µm film
Inlet	MMI, 4-mm UI liner single taper w wool
Injection	2 uL, cold splitless
Carrier gas	Helium
Inlet flow (column 1)	~1 mL/min (Chlorpyrifos-methyl locked at 9.143 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) 50 psi (Aux EPC), 2 psi (Inlet)
Transfer line temperature	280 °C
Ion source	EI, 70 eV, 15 eV
Source temperature	280 °C (70eV), 250 °C (15 eV)
Quadrupole temperature	180 °C
Spectral Acquisition	45 to 650 m/z, 5 spectra/sec (70 eV)

Data Analysis

- The data processing used Agilent MassHunter Data Analysis Software B.08.00, including SureMass.
- The targeted screening of pesticides (a combined quantitative and qualitative workflow) was based on a commercial GC/Q-TOF pesticides library [2] which contains accurate mass spectra and retention times for 850+ compounds.
- The untargeted screening of other contaminants relied on the NIST GC/MS library.

Results and Discussion

Food Matrix and Pesticides

The diversity of food matrix complexity in this study is reflected by TICs in figure 3. The pesticides spiked for method evaluation represent OCs, OPs, carbamates, triazoles and pyrethroids, etc.

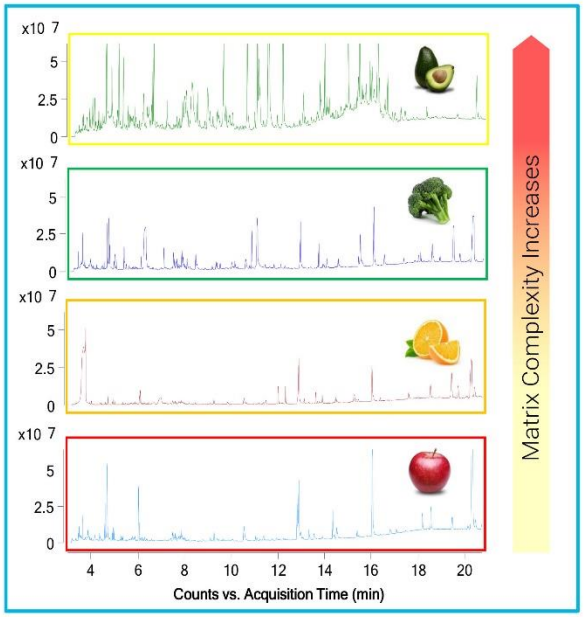

Figure 3. Total ion chromatograms of organic food matrices spiked with 10 ng/mL each pesticide.

Method Repeatability

The repeatability (six replicates) of retention time and response are shown in figure 4 and 5 for all of the identified compounds spiked at 10 ng/mL.

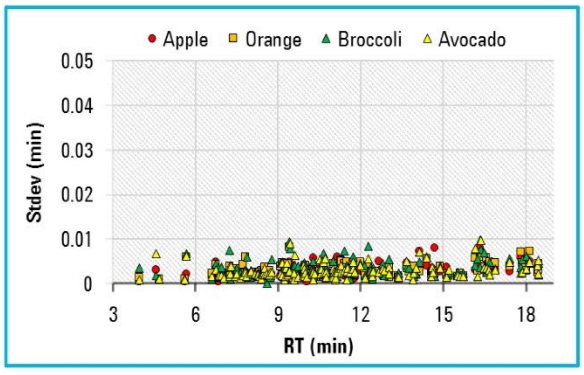

Figure 4. Retention time repeatability (SD ≤ 0.01 min).

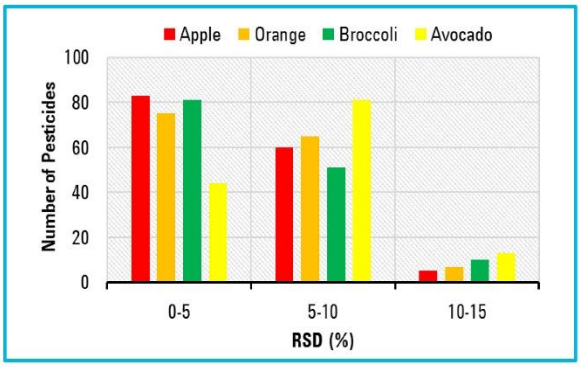

Figure 5. Total ion chromatograms of food matrices.

Matrix Matched Calibration

With SureMass used for quantitation, the multiple-level matrix matched calibration in avocado (triplicates at each level) yielded over 85% of the target pesticides achieving a linear calibration curve with $R^2 \geq 0.99$ in the range of 5-500 ng/mL. The majority of remaining pesticides yielded $R^2 \geq 0.985$ for the same concentration range. Figure 6 displays the examples from various pesticide groups.

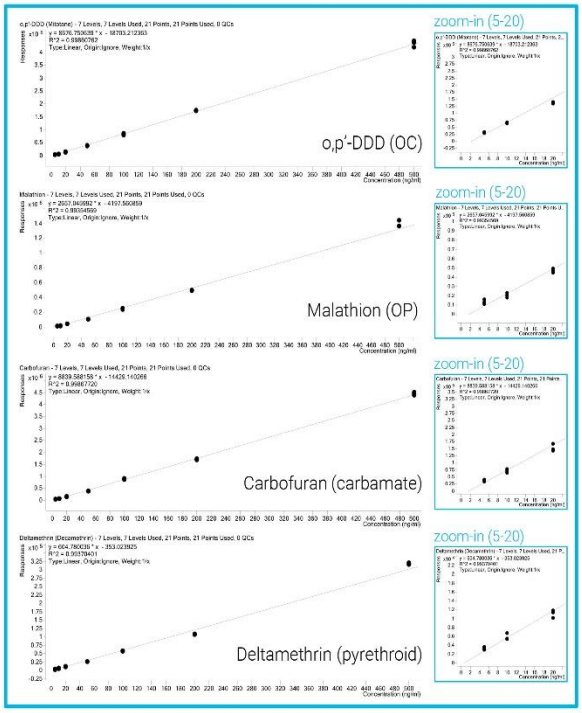

Figure 6. Calibration curves from 5 to 500 ng/mL.

Results and Discussion

Mass Accuracy

Figure 7 shows the mass accuracy of example pesticides over a wide concentration range. At spiking level of 10 ng/mL, all the detected pesticides in each food matrix have been measured with mass accuracy < 5 ppm.

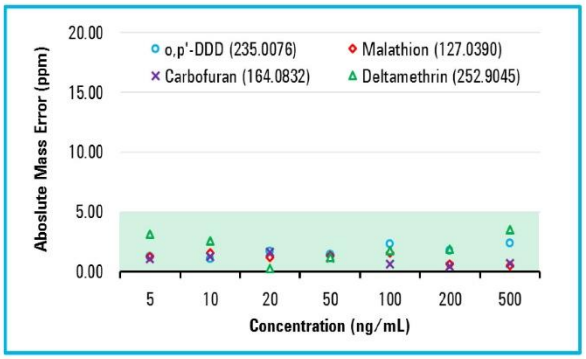

Figure 7. Mass accuracy of example pesticides from 5 to 500 ng/mL in avocado matrix.

Targeted Screening (Quant and Qual Combined)

Targeted screening of pesticides in non-organic food used the accurate mass pesticides library (Table 2).

Table 2. Targeted Screening Results of non-organic food

Matrix	Pesticide Identified *	Amount (ppb)
	Boscalid (Nicobifen)	qual only
	Fludioxonil	qual only
	Pyraclostrobin	qual only
	Pyrimethanil	qual only
	TBZ / Thiabendazole	qual only
	Carbaryl	6.5
	Propiconazole (I & II)	qual only
	Pyrimethanil	qual only
	TBZ / Thiabendazole	qual only
	(1R)-cis-Permethrin	30.7
	(1R)-trans-Permethrin	30.6
	Azoxystrobin	878 (>500)
	Boscalid (Nicobifen)	qual only
	Dimethomorph (E)	535 (>500)
	Fludioxonil	qual only
	Pentachlorobenzonitrile	qual only
	Pyraclostrobin	qual only
	TBP / Tributylphosphate	qual only
	λ-Cyhalothrin	43.0

* Identification criteria: mass error < 5 ppm (≥ two ions), RT ≤ 0.1 min, S/N ≥ 3
qual only = qualitative screening only, standard not available for calibration

Untargeted Screening

Untargeted screening of other contaminants was performed by matching NIST library after SureMass peak detection. Low energy EI spectrum helped to confirm molecular ion (figure 8).

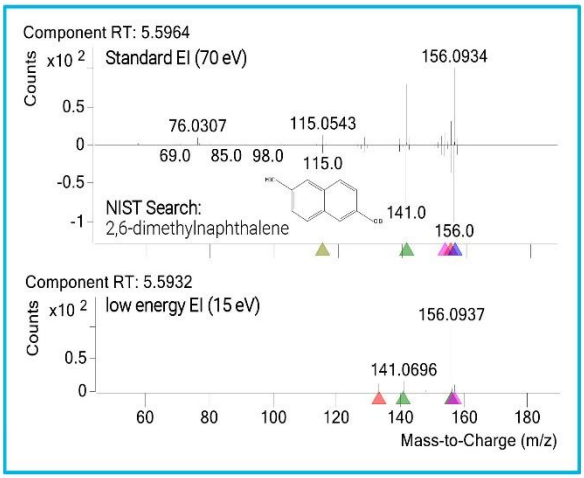

Figure 8. Example result of untargeted screening from non-organic broccoli extract.

Conclusions

- A new GC/Q-TOF has been used to successfully screen pesticides in various food matrices.
- The confidence in results is enhanced by stable RT, repeatable response and good mass accuracy.
- A wide linear response range has been achieved for matrix matched calibration.
- Low energy EI facilitates untargeted screening.

References

[1] Belmonte-Valles, N., et al; Analysis of pesticides residues in fruits and vegetables using gas chromatography-high resolution time of flight mass spectrometry. *Anal. Methods* 7, 2162-2171 (2015).

[2] Chen, K., Nieto, S., Stevens, J.; GC/Q-TOF Surveillance of Pesticides in Food, *Agilent Technologies Application Note*, 5991-7691EN (2016).