



Screening of Pesticides and Other Contaminants in Food Matrices Using a Novel High-resolution GC/Q-TOF with a Low-energy-capable EI Source

Application Brief

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Introduction

The increasing demand of 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 enable both the confident identification of compounds in the sample and quantitation capabilities to address stringent maximum residue level (MRL) requirements. The addition of low-energy electron impact (EI) ionization enhances the possibility to preserve or confirm molecular ions in EI mass spectra, aiding in the study of unknowns. This work describes the use of a novel high-resolution, low-energy EI-capable GC/Q-TOF to screen pesticides and other contaminants in food matrices.



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Experimental

Sample preparation

Homogenized food commodities were extracted using a 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. To evaluate the method, a mixture of 140+ pesticides was spiked into the organic matrices. Screening of contaminants was performed on nonorganic food extracts.

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 1 lists the operational parameters.



Figure 1. Agilent 7250 GC/Q-TOF system.

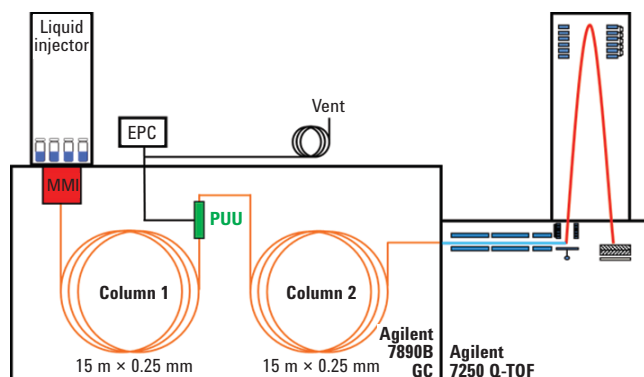


Figure 2. Mid-column backflushing system.

Table 1. Agilent 7250 GC/Q-TOF Operational Conditions

Parameter	Value
Columns (2 each)	Agilent HP-5 MS UI, 15 m × 0.25 mm, 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 minutes)
PUU Flow (column 2)	Column 1 flow + 0.2 mL/min
Oven program	60 °C for 1 minute 40 °C/min to 170 °C, 0 minutes 10 °C/min to 310 °C, 3 minutes
Backflushing conditions	5 minutes (post run) 310 °C (oven) 50 psi (Aux EPC) 2 psi (inlet)
Transfer line temperature	280 °C
Ion source	El, 70 eV, 15 eV
Source temperature	280 °C (70 eV) 250 °C (15 eV)
Quadrupole temperature	180 °C
Spectral acquisition	45 to 650 m/z 5 spectra/sec (70 eV)

Data analysis

For data processing, Agilent MassHunter Data Analysis Software B.08.00, including SureMass, was used.

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

Figure 3 shows the diversity of food matrix complexity reflected by TICs in this study. The pesticides spiked for method evaluation represent organochlorines, organophosphorus, carbamates, triazoles, pyrethroids, and others.

Method repeatability

Figures 4 and 5 show the repeatability (six replicates) of retention time and response for all identified compounds spiked at 10 ng/mL.

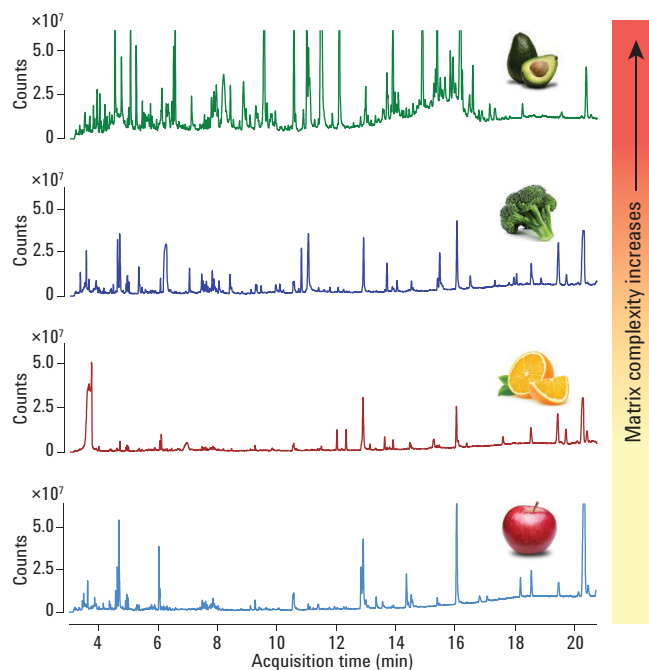


Figure 3. Total ion chromatograms of organic food matrices spiked with 10 ng/mL of each pesticide.

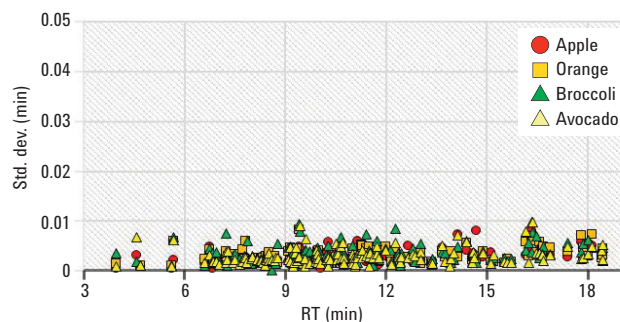


Figure 4. Retention time repeatability ($SD \leq 0.01$ minutes).

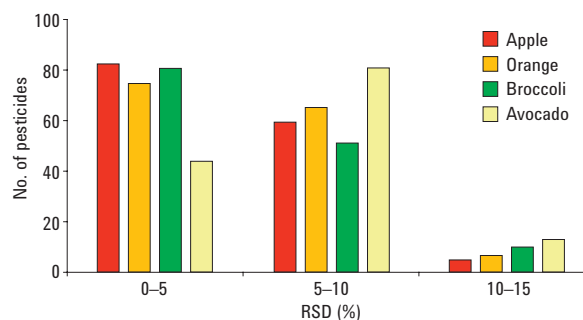


Figure 5. RSD% of responses of pesticides in food matrices.

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 groups. Figure 6 displays examples from various pesticide groups.

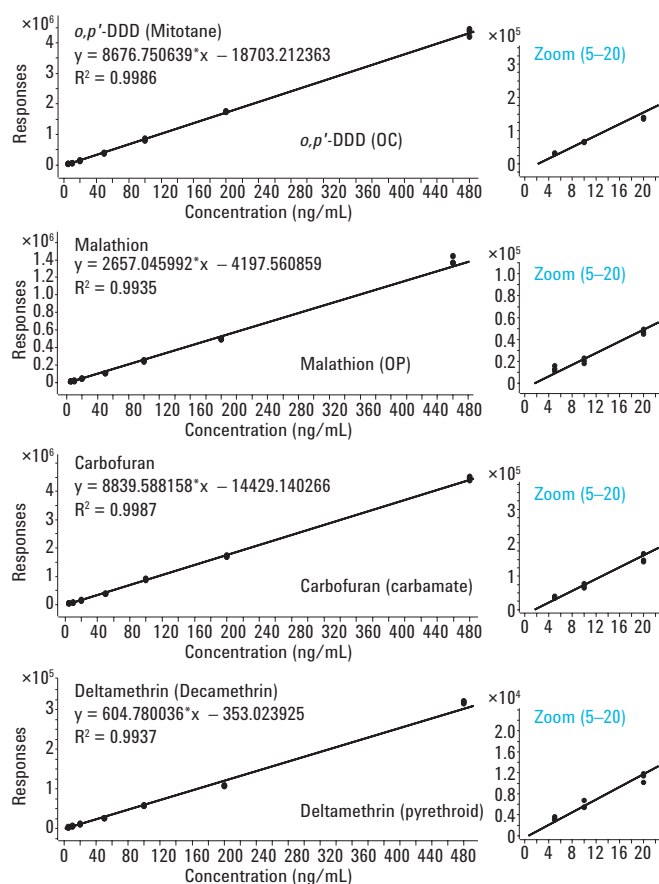


Figure 6. Calibration curves from 5 to 500 ng/mL.

Mass accuracy

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

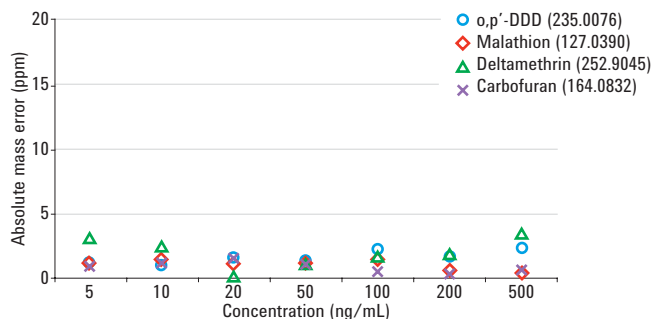


Figure 7. Mass accuracy of example pesticides from 5 to 500 ng/mL in avocado matrix.

Targeted screening (Quant and Qual combined)

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

Table 2. Targeted Screening Results of Nonorganic Food

Matrix	Identified pesticide*	Amount (ppb)
Apple	Boscalid (Nicobifen)	Qual only
	Fludioxonil	Qual only
	Pyraclostrobin	Qual only
	Pyrimethanil	Qual only
	TBZ/Thiabendazole	Qual only
Orange	Carbaryl	6.5
	Propiconazole(I and II)	Qual only
	Pyrimethanil	Qual only
	TBZ/Thiabendazole	Qual only
Broccoli	(1R)- <i>cis</i> -Permethrin	30.7
	(1R)- <i>trans</i> -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 (Find by Fragments): mass error <5 ppm (\geq two ions), RT \leq 0.1 minutes, S/N \geq 3.

Qual only = qualitative screening only; standard not available for calibration.

Untargeted screening

Untargeted screening of other contaminants was performed by matching the NIST library after SureMass peak detection. Low-energy EI spectra helped to confirm molecular ions (Figure 8).

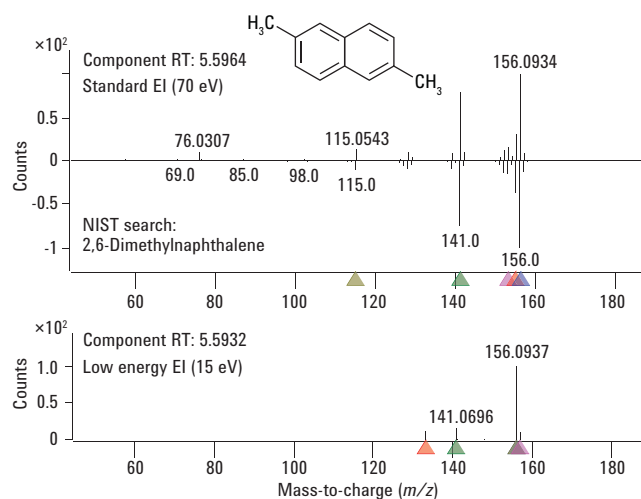


Figure 8. Example result of untargeted screening from nonorganic broccoli extract.

Conclusions

- An Agilent 7250 GC/Q-TOF was used successfully to screen pesticides in various food matrices.
- Confidence in results is enhanced by stable RT, repeatable response, and good mass accuracy.
- A wide linear response range was achieved for matrix-matched calibration.
- Low-energy EI facilitates untargeted screening.

References

1. N. Belmonte-Valles, *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. K. Chen, S. Nieto, J. Stevens, GC/Q-TOF Surveillance of Pesticides in Food, *Agilent Technologies Application Note*, 5991-7691EN (2016).

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