# 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


## Authors

Kai Chen and Jennifer Sanderson

Agilent Technologies, Inc.

Santa Clara, CA, USA


## 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.*

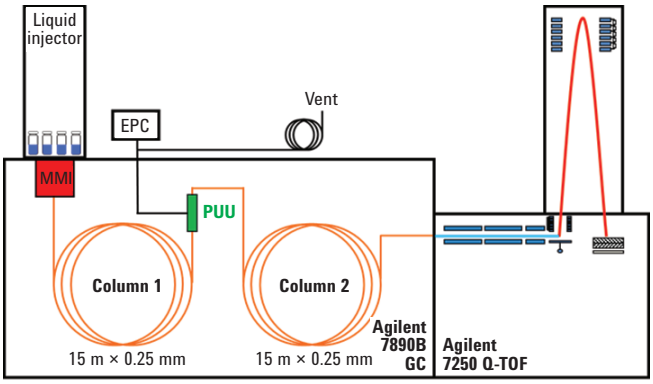


*Figure 2. Mid-column backflushing system.*

*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<br>(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<br>40 °C/min to 170 °C, 0 minutes<br>10 °C/min to 310 °C, 3 minutes |
| Backflushing conditions | 5 minutes (post run)<br>310 °C (oven)<br>50 psi (Aux EPC)<br>2 psi (inlet) |
| Transfer line temperature | 280 °C |
| Ion source | EI, 70 eV, 15 eV |
| Source temperature | 280 °C (70 eV)<br>250 °C (15 eV) |
| Quadrupole temperature | 180 °C |
| Spectral acquisition | 45 to 650 *m/z*<br>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.

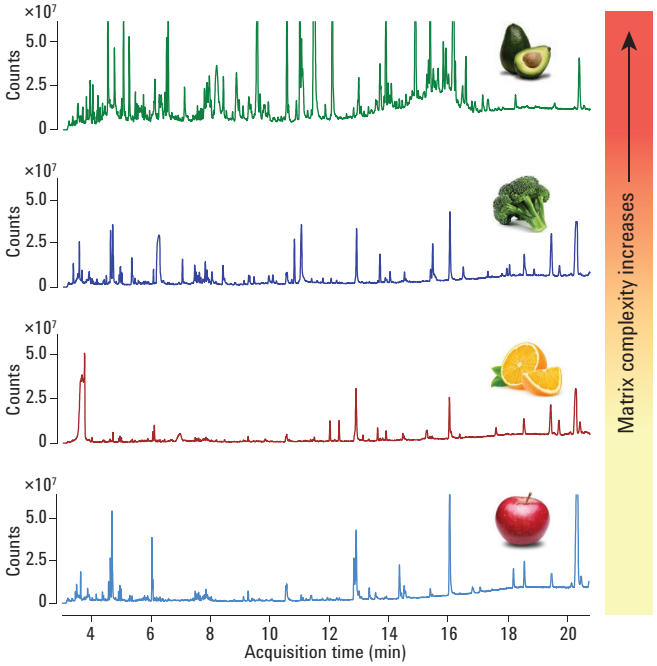


*Figure 3. Total ion chromatograms of organic food matrices spiked with 10 ng/mL of each pesticide.*

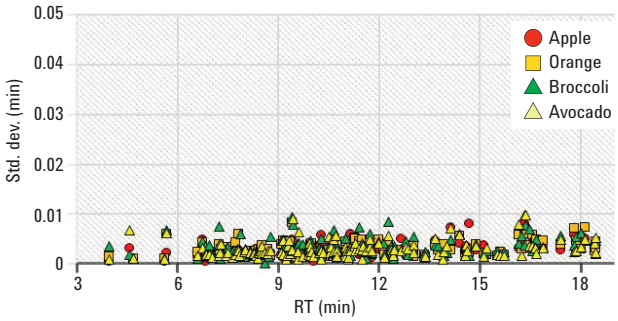


*Figure 4. Retention time repeatability (SD ≤0.01 minutes).*

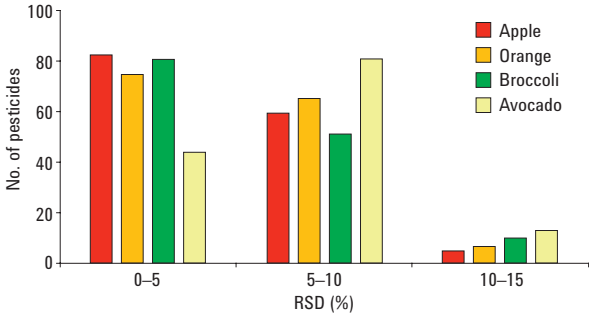


*Figure 5. RSD% of responses of pesticides in food matrices.*

## 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 $R^2$ ≥0.99 in the range of 5–500 ng/mL. The majority of remaining pesticides yielded $R^2$ ≥0.985 for the same concentration range. Figure 6 displays examples from various pesticide groups.

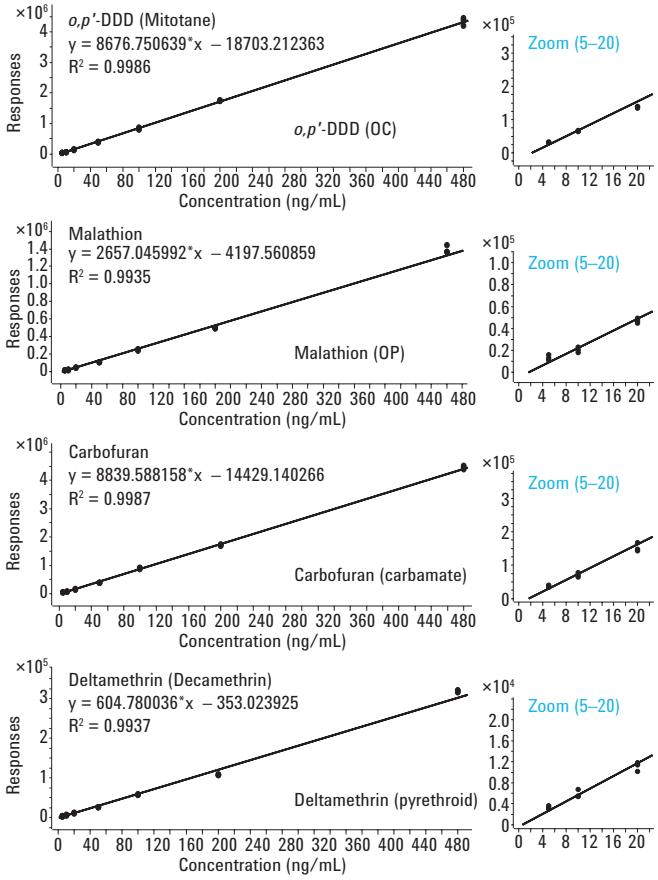


*Figure 6. Calibration curves from 5 to 500 ng/mL.*

## 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.

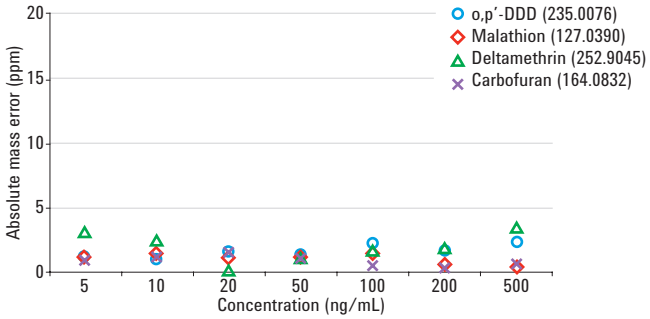


*Figure 7. Mass accuracy of example pesticides from 5 to 500 ng/mL in avocado matrix.*

## 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)-*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 (Find by Fragments): mass error <5 ppm (≥two ions), RT ≤0.1 minutes, S/N ≥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).

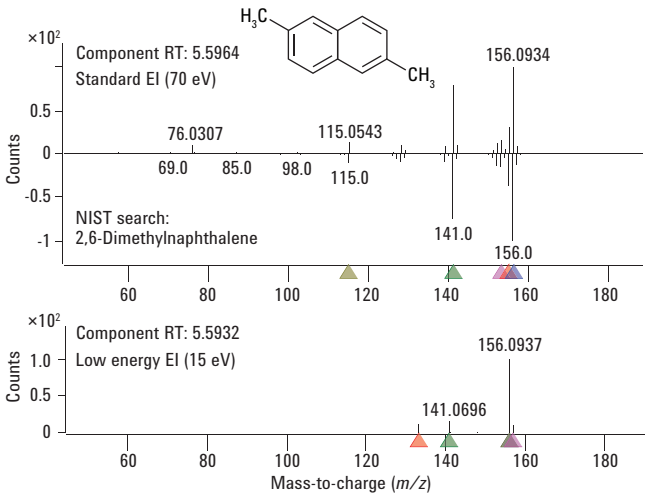


*Figure 8. Example result of untargeted screening from nonorganic broccoli extract.*

## 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**).


## For More Information

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