

## Introduction

- GC with Triple Quadrupole MS (GC/TQ) detection has become the standard tool for the analysis of volatile contaminants in food.
- GC/TQ methods typically analyze 100 – 300 target compounds.
- There is a need to screen for many more pesticides and environmental contaminants.
- A high resolution accurate mass GC/Q-TOF can be used to screen for an unlimited number of contaminants.
- A newly enlarged Personal Compound Database and Library (PCDL) can be used to screen for 1000+ pesticides and environmental contaminants.

## Experimental

### Instrument Setup

An Agilent 7250 GC/Q-TOF instrument was configured with a mid-column backflushing system (Figure 1) to acquire data using retention time locked methods.

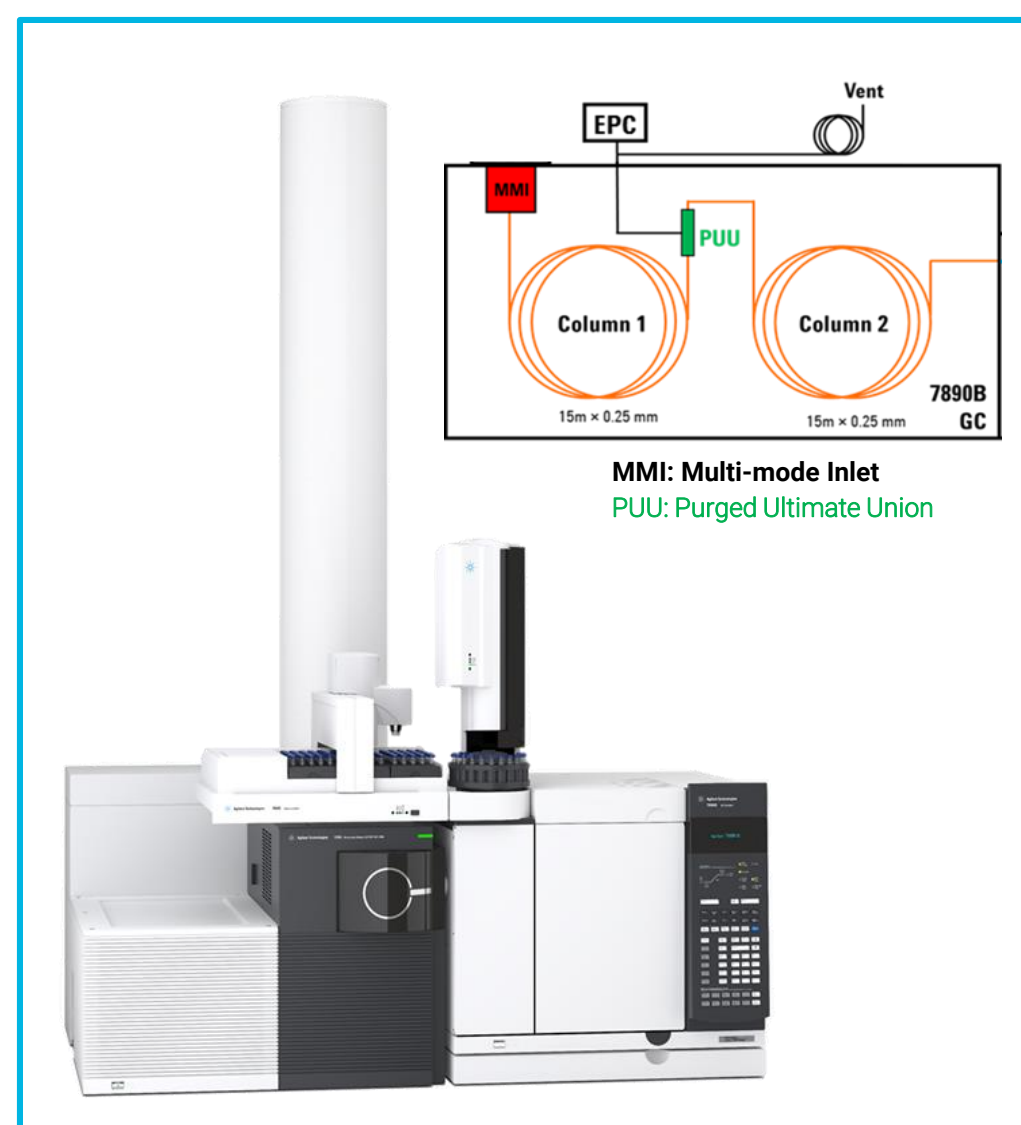


Figure 1. 7250 GC/Q-TOF

### Library Update

An accurate mass pesticides and environmental pollutants library was developed to contain retention times (both 20 and 40 min methods) and mass spectra for 1000+ compounds. Authentic standards were purchased from AccuStandard (New Haven, CT), Restek (Bellefonte, PA) and Ultra Scientific (North Kingstown, RI).

### Sample Preparation & Analysis

Homogenized food commodities were extracted using QuEChERS (EN) kit and followed by clean-up steps with corresponding dSPE [1]. The detailed operational parameters for the GC/Q-TOF are listed in Table 1.

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	2µL, cold splitless
Carrier gas	Helium
Inlet flow (column 1)	~1 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) 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)

## Experimental

### Data Analysis

Three complimentary workflows were followed:

- Quantitative analysis for compounds with standards
- Suspect screening using the PCDL
- Unknowns identification using MassHunter Unknowns Analysis software with SureMass enabled. The structure elucidation of candidates for the unknown compounds was performed using MassHunter Molecular Structure Correlator B.08.

Curation of the library spectra was done using MassHunter Qualitative Analysis B.08 SP1.

## Results and Discussion

### Quantitative Analysis – Pesticides in Avocado

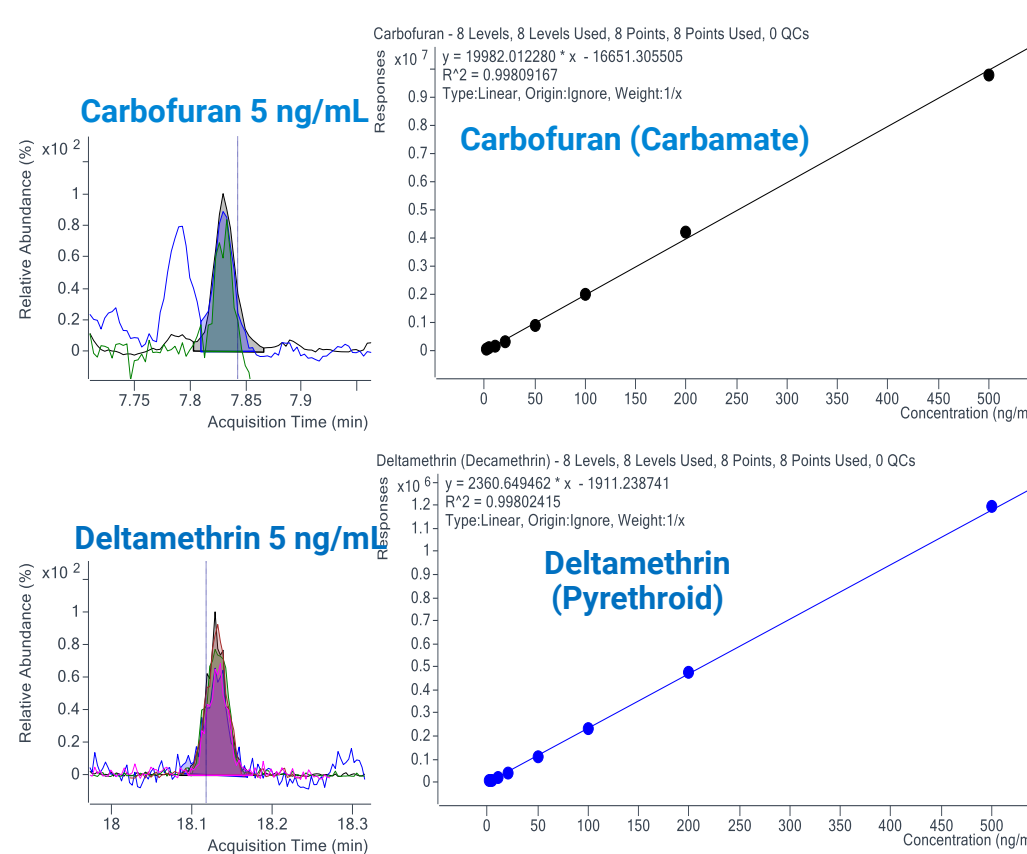


Figure 2. Calibration curves for carbofuran and deltamethrin in an avocado extract.

### Suspect Analysis Using the Agilent PCDL

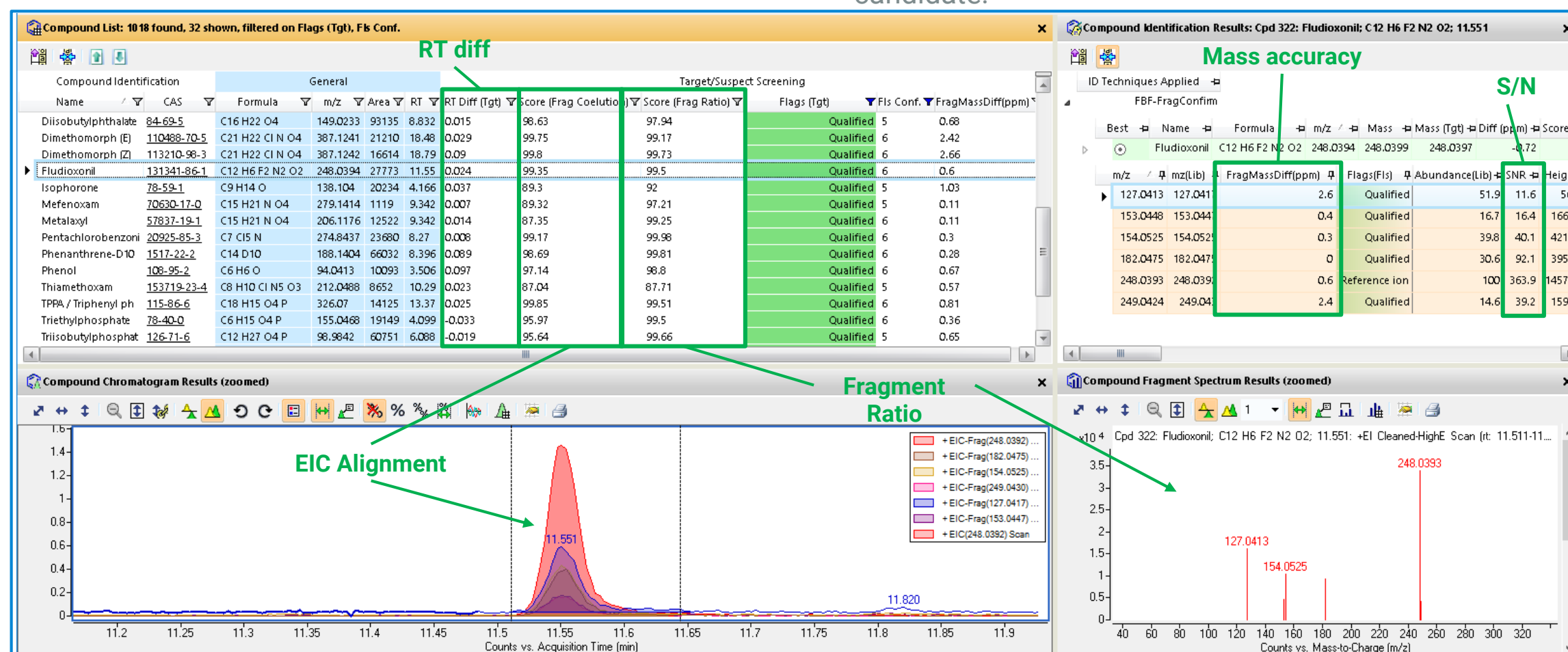


Figure 3. Suspect Screening using Agilent's PCDL for pesticides and environmental contaminants. Mass Hunter "Find by Fragments" software screens for all of the 1000+ compounds in the PCDL. Identification is based on mass accuracy, fragment ion ratios, retention time, and EIC alignment as well as other criteria.

Table 2. Suspect screening results (broccoli).

Compound name	RT diff	Score		Mass diff (ppm)
	(min)	Frag ratio	coelution	
1,2,3,4-tetrachlorobenzene	0.008	85.1	88.8	0.48
1-aminonaphthalene	0.021	72.3	96.6	0.96
Anthraquinone	0.011	84.7	78.2	0.52
Azobenzene	0.049	64.1	86.1	0.51
Azoxystrobin	0.028	99.6	99.5	2.00
Benzyl benzoate	0.009	55.8	74.3	0.07
Boscalid	0.027	99.5	90.7	0.70
Cyfluthrin	0.051	79.9	84.3	0.49
Cyhalothrin	0.025	84.2	96.1	1.68
Chlorthal-dimethyl	0.013	99.9	93.6	0.84
Dimethomorph	0.029	99.2	99.8	2.42
Fludioxonil	0.024	99.5	99.4	0.60
Metalaxyl	0.014	99.3	87.4	0.11
p,p'-DDE	0.015	87.2	90.8	1.70
Pentachlorobenzonitrile	0.008	100.0	99.2	0.30
Permethrin	0.022	98.9	99.5	1.80
Phenathrene	0.003	97.0	91.8	1.08
Pyraclostrobin	0.018	92.8	97.8	0.38
Thiabendazole	0.023	86.7	88.7	0.35
Thiamethoxam	0.023	87.7	87.0	0.57
Triphenylmethane	0.016	85.7	84.4	0.29

## Results and Discussion

### Screening for Unknowns

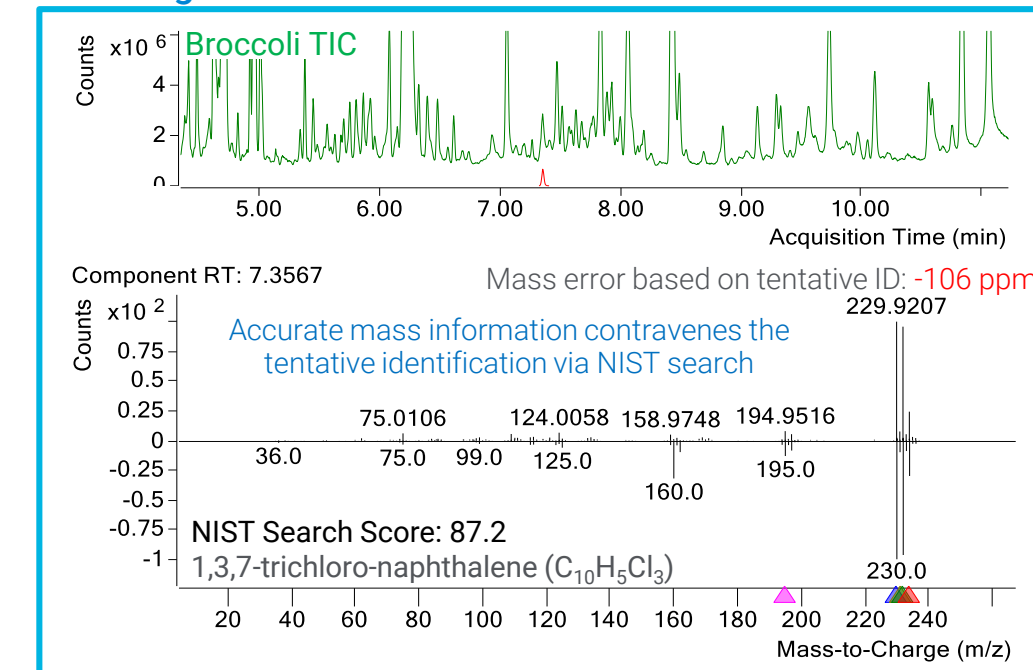


Figure 4. Spectrum from unknown in broccoli

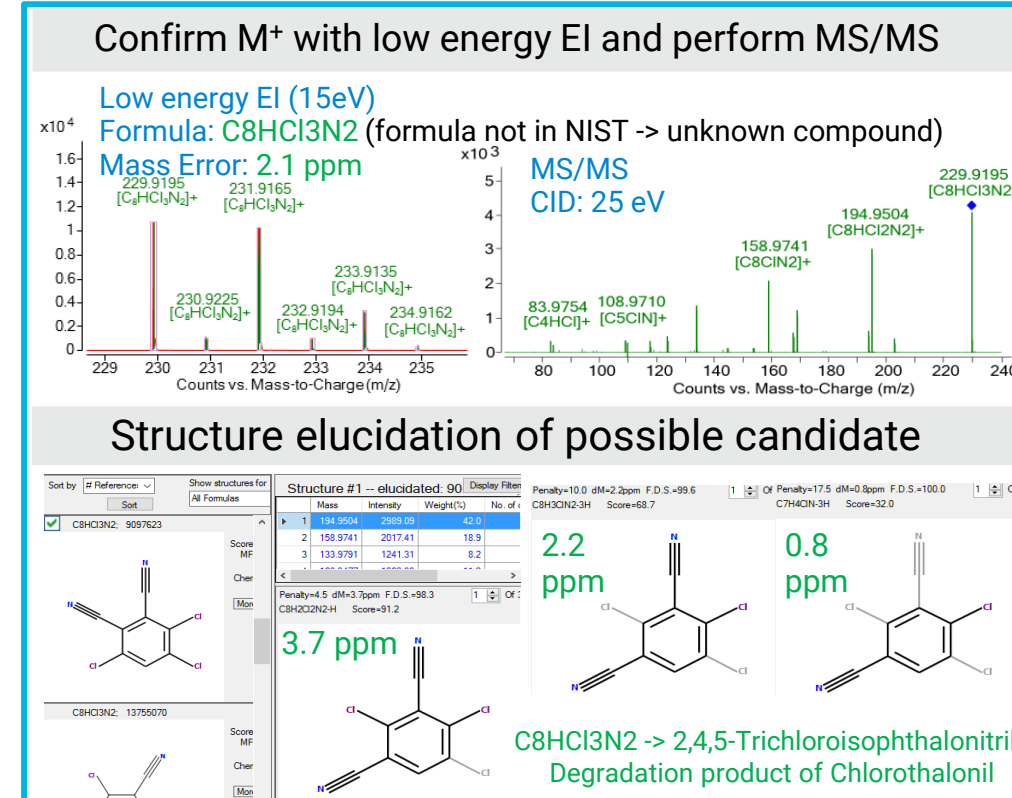


Figure 6. Study of an unknown compound with low energy EI and structure elucidation of a possible candidate.

## Conclusions

- An updated accurate mass library combined with GC/Q-TOF has been used to successfully screen pesticides and environmental pollutants in various matrices.
- Confidence in the results is enhanced by using an RTL method, & by the Q-TOF's excellent mass accuracy & isotopic fidelity.
- Low energy EI and accurate mass MS/MS facilitate untargeted screening and unknowns elucidation.

## References

- Chen, K., Sanders, J.; Agilent Technologies Application Brief, 5991-8170EN (2017).
- Chen, K., Nieto, S., Stevens, J.; Agilent Technologies Application Note, 5991-7691EN (2016).