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Screening of Contaminants in Food and Natural Products by GC/Q-TOF with an Accurate Mass Pesticides and Environmental Pollutants Library

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Introduction

Screening a broad scope of contaminants by high resolution mass spectrometers has been gaining acceptance in food surveillance labs because the profiling capability from full spectrum data acquisition opens opportunities to study potential contaminants beyond conventional targeted analytical techniques. Recent advances in high resolution GC/Q-TOF offer sufficient sensitivity and quantitative linear range to meet the analytical needs of modern labs. Thus, there is growing interest in adding GC/Q-TOF to complete the workflow of comprehensive screening, and a strong desire to achieve efficient conversion of mass spectrometric data into knowledge on the presence of contaminants. In this work, we present an accurate mass library with pesticides and environmental pollutants to facilitate the screening of contaminants in food samples.

Experimental

Instrument Setup

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

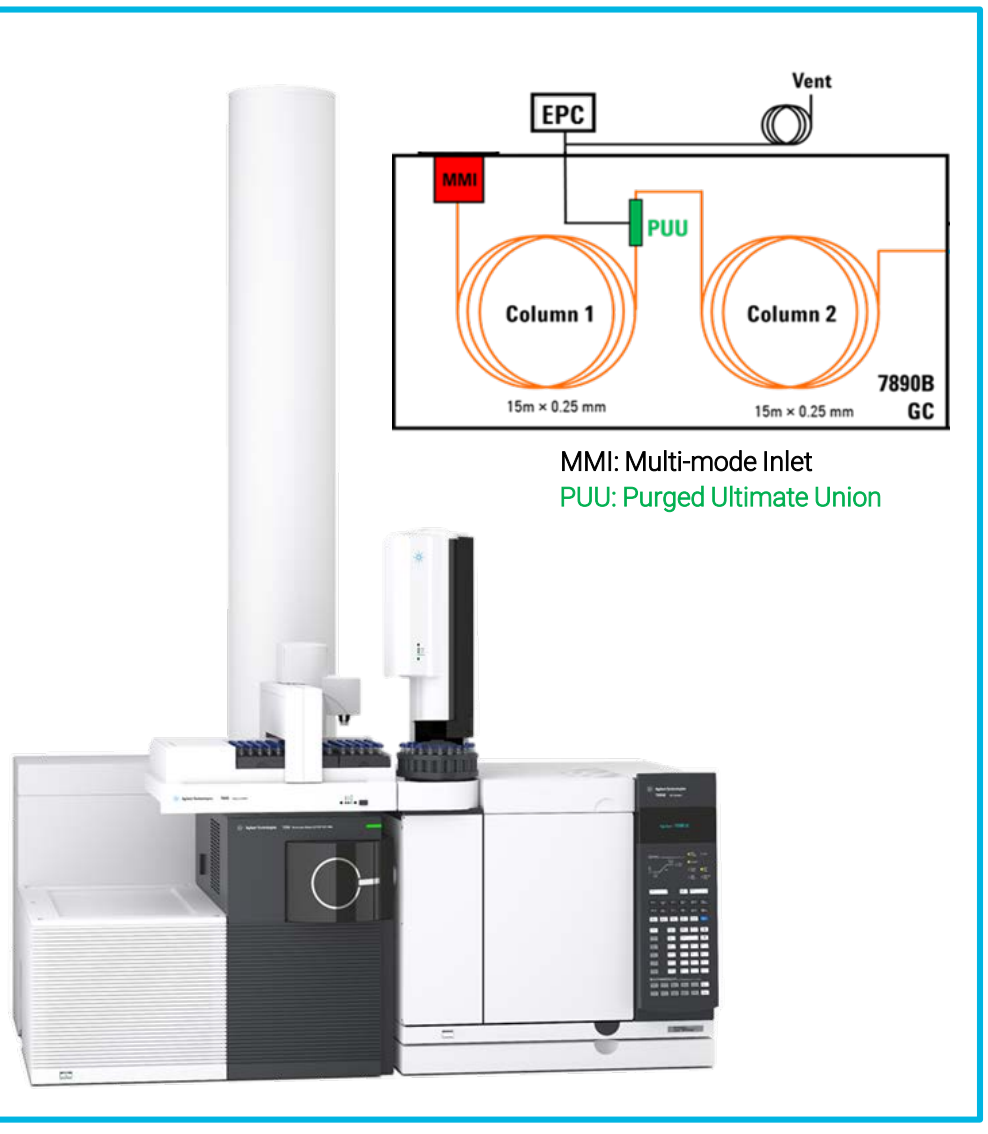

Figure 1. 7250 GC/Q-TOF system

Experimental

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]. Essential oils were diluted 1:50 (v/v) in ethyl acetate for direct injections. 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	2uL, 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

- Targeted screening, a combined quantitative and qualitative workflow [2], was based on the library previously mentioned.
- Untargeted screening relied on MassHunter Unknowns Analyses B.09 (with SureMass enabled) using the NIST 17 GC/MS library.
- The structure elucidation of candidates for the unknown compounds was performed using MassHunter Molecular Structure Correlator B.08.
- The curation of library spectra was performed in Agilent MassHunter Qualitative Analysis B.08 SP1.

Spectrum Curation (Scalable PCDL)

The measured m/z values of any given spectrum are curated to the corresponding theoretical values, and then added into the accurate mass library (Figure 2). The software offers a curation workflow if new compounds of interest need to be added into the library.

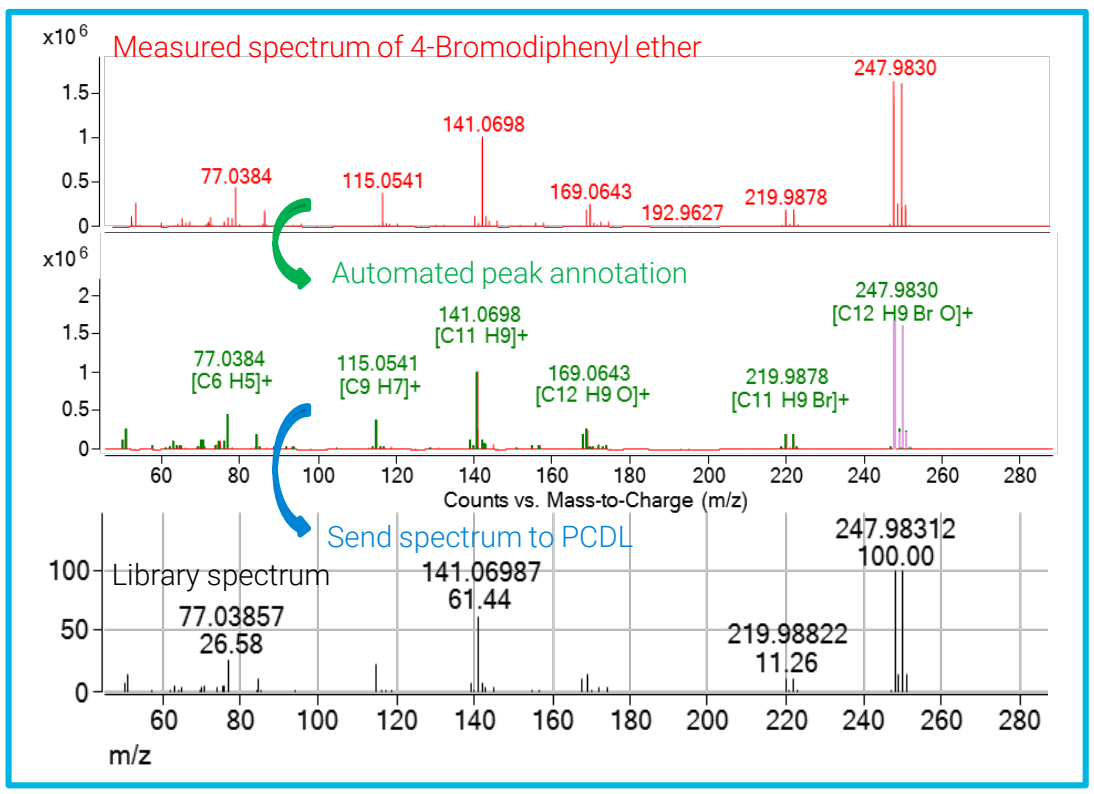

Figure 2. Spectrum curation based on peak annotation

Screening Performance Validation

Several food matrices spiked with 100+ pesticides of known concentrations were previously studied to demonstrate repeatability, mass accuracy and linearity range of the system [1].

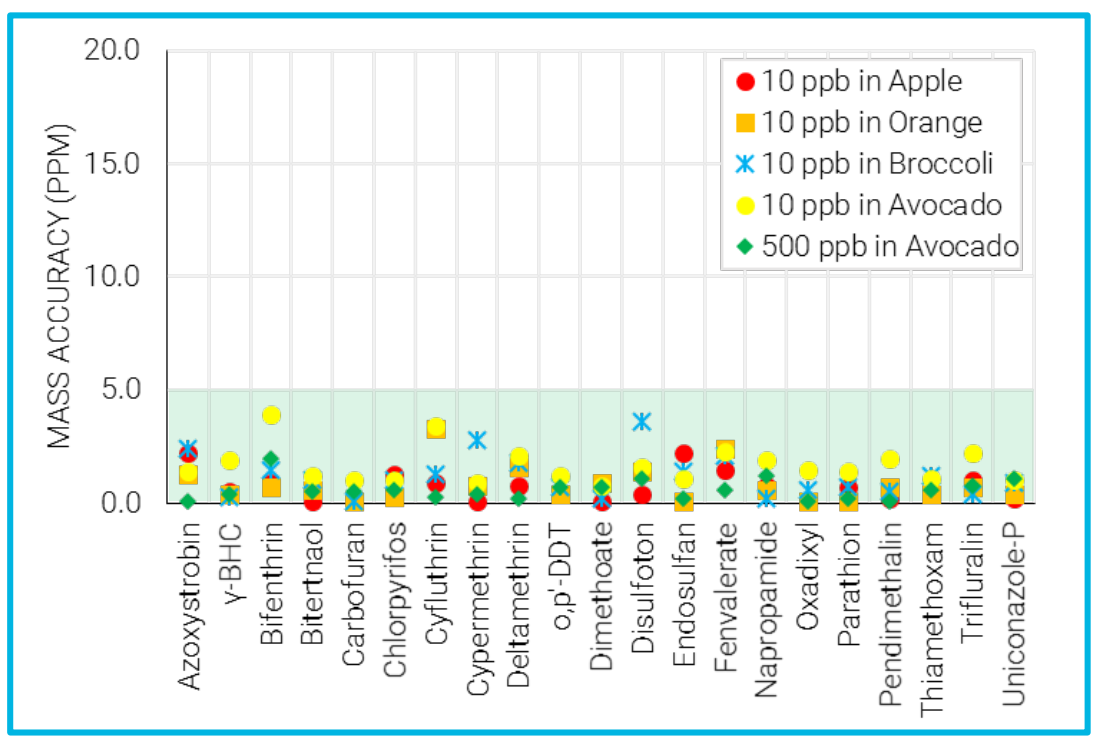

Figure 3. Mass accuracy measured for representative pesticides spiked in organic food matrices. At least two ions were identified for each compound with mass accuracy < 5 ppm and S/N >=3.

Suspect Screening (Fruits & Vegetables)

Non-organic fruits/vegetables were analyzed. Using a targeted screening approach, multiple pesticides and pollutants were detected in apple (15), avocado (1), broccoli (21) and orange (8). Since broccoli is one of the most analytically challenging samples, it is used as an example, with details shown in Figure 4 and Table 2.

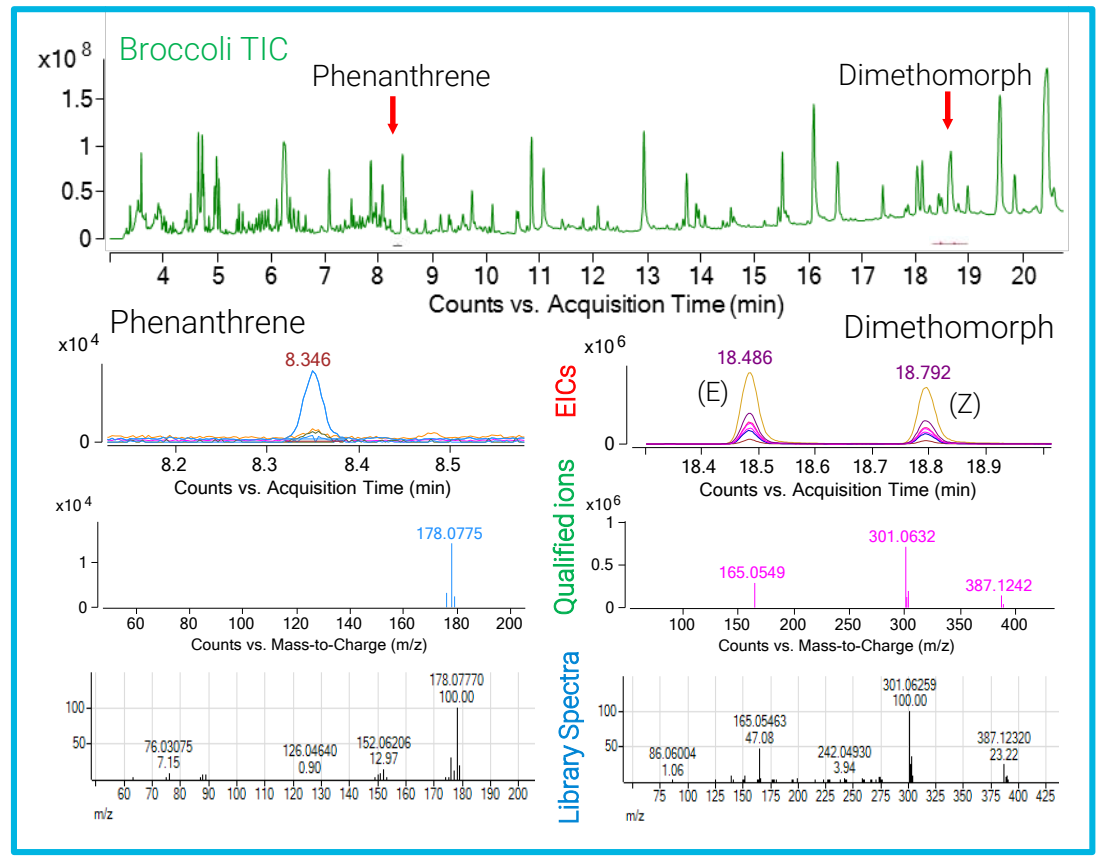

Figure 4. Example chromatograms and spectra of hits identified as pollutants in broccoli.

Table 2. Suspect screening results (broccoli).

Compound name	RT diff	Score		Mass diff
	(min)	Frag ratio	coelution	(ppm)
1,2,3,5-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

Suspect Screening (Natural Products)

Four essential oils were analyzed, with multiple pesticides and pollutants found in neroli oil (10), grapefruit oil (17), orange oil (18) and lemon oil (15). Table 3 lists the results from orange oil as an example.

Table 3. Suspect screening results (orange oil).

Compound name	RT diff	Score		Mass diff
	(min)	Frag ratio	coelution	(ppm)
4,4'-Dichlorobenzophenone	0.009	87.8	94.4	0.74
4-Chloroaniline	0.013	82.2	94.5	2.66
Azoxystrobin	0.019	75.3	70.0	0.32
Benzyl benzoate	0.007	62.8	87.4	1.37
Bifenthrin	0.024	98.5	97.2	2.15
Bis(2-ethylhexyl)adipate	-0.008	84.4	96.0	0.72
Bis(2-ethylhexyl)phthalate	0.032	98.5	99.5	1.26
Chlorpyrifos	0.015	100.0	98.2	0.55
Clomazone	0.009	86.4	94.1	2.60
Diethyl phthalate	0.004	98.7	96.8	0.20
Diisobutyl phthalate	0.016	98.1	97.9	0.46
Dipentyl phthalate	0.024	92.7	97.0	0.90
Imazalil	0.035	84.0	85.7	1.18
Methidathion	0.012	89.6	92.0	1.56
Propargite	0.019	86.2	91.4	4.10
Pyraclostrobin	0.022	86.7	97.9	0.12
Tebuconazole	0.021	94.6	92.6	1.03
Tris(2-butoxyethyl)phosphate	0.047	98.9	96.9	0.68

Explore Unknowns

Study of unknowns discovered in untargeted screening was helped by low energy EI (confirming molecular ion) and accurate mass MS/MS experiments, with an example shown in Figures 5 and 6.

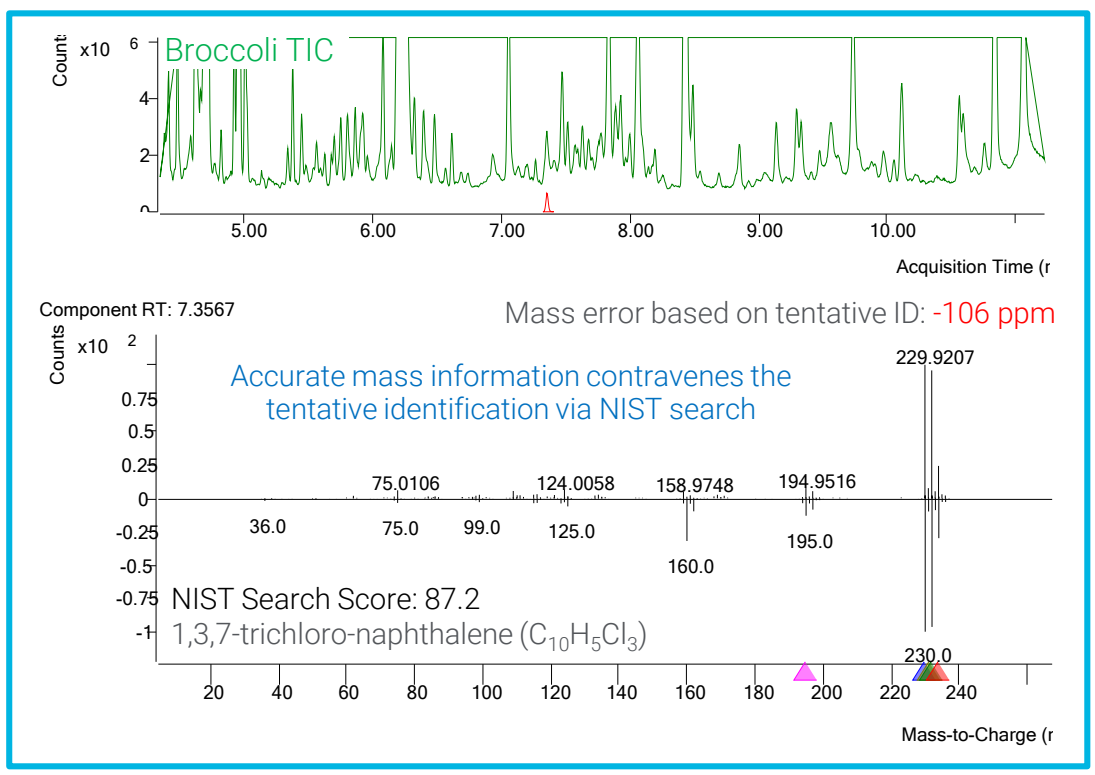

Figure 5. An unknown contaminant found in broccoli.

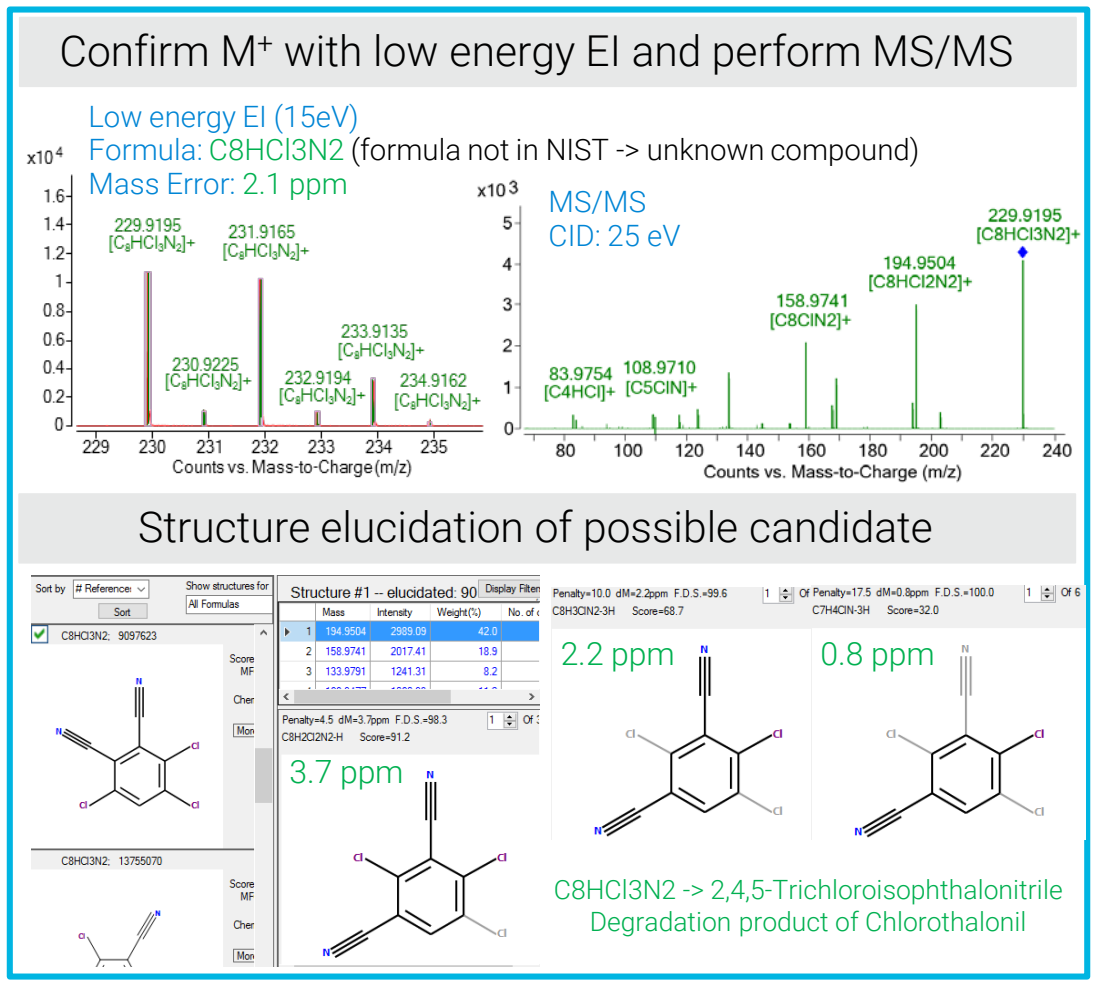

Figure 6. Study of an unknown compound with low energy EI and structure elucidation of a possible candidate.

Acknowledgement

We would like to acknowledge the USEPA for support and assistance in obtaining spectra.

Conclusions

- An updated accurate mass library combined with GC/Q-TOF has been used to successfully screen pesticides and environmental pollutants in various matrices.
- The confidence in results is enhanced by RTL method and excellent mass accuracy.
- Low energy EI and accurate mass MS/MS facilitate untargeted screening and unknowns elucidation.

References

[1] Chen, K., Sanders, J.; Agilent Technologies Application Brief, 5991-8170EN (2017).

[2] Chen, K., Nieto, S., Stevens, J.; *Agilent Technologies Application Note*, 5991-7691EN (2016).

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