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Analysis of Pesticides
and Environmental
Pollutants in Essential
Oils Using Multi-
Platform GC/MSD,
GC/TQ and GC/Q-
TOF

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Introduction

Essential oils are concentrated liquids containing volatile aroma compounds from various plants and are widely used in flavors and fragrances. Traces of pesticides are sometimes present in these oils, resulting in the need to screen them. This analysis is challenging due to the intense matrix background interference presented by oils, therefore traditional GC/MS is limited in capacity to perform the task. This work demonstrates the use of enhanced techniques for pesticide screening in essential oils.

The enhanced techniques are:

- **GC/MSD:** Use of a retention time locked (RTL) spectral library of 950+ compounds and screening based on match scores of deconvoluted spectra.
- **GC/TQ:** Initial screening of samples using scan mode (as above) with subsequent MRM analysis for trace level identity confirmation and quantitation.
- **GC/Q-TOF:** Use of a RTL library containing accurate mass spectra for 850+ compounds and screen using six principle accurate mass ions, fragment ratios and RT matching.

This multi-platform GC/MSD, GC/TQ and GC/Q-TOF approach also offers a streamlined workflow utilizing different platforms offering enhanced qualitative and quantitative capabilities.

Experimental

Sample Preparation

Eight essential oils were diluted 10:1, 50:1 and 100:1 by volume in ethyl acetate for direct injection on GC/MSD, GC/Q-TOF and GC/TQ, respectively. A mixture of 150+ pesticides standards was spiked in Lavender oil (100:1 dilution) at 0.02–200 ng/mL (two calibration sets, low & high concentrations) for matrix matched calibration on GC/TQ.

Instrumental Analysis

The samples were analyzed in EI mode by:

- Agilent 7890B GC and 7250 high resolution accurate mass GC/Q-TOF
- Agilent 7890B GC and 5977B GC/MSD
- Agilent 7890B GC and Agilent 7010 GC/TQ

All three systems were configured with a mid-column backflush setup (Figure 1). A 20 minute constant flow RTL method (chlorpyrifos-methyl locked at 9.143 min) has been used for chromatographic separation, with parameters listed in Table 1.

Experimental

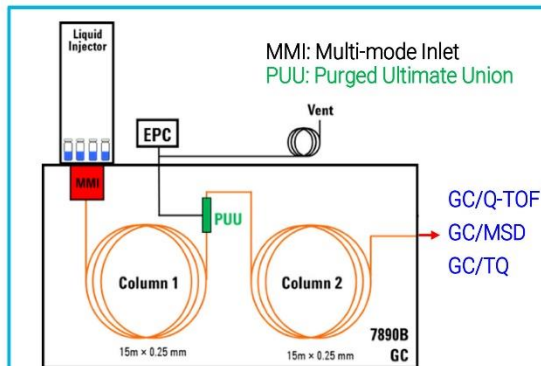


Figure 1. Mid-column backflush system

Table 1. GC and MS operational conditions

GC and MS Conditions	Value
Columns (2 ea.)	Agilent J&W HP-5ms UI 15 m x 0.25 mm x 0.25 μ m (P/N: 19091S-431 UI)
Inlet	MMI, 4-mm UI liner with wool
Injection	1 or 2 μ L 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 for 0 min 10°C/min to 310°C for 3 min (Total Run Time 20.75 min)
Backflush Conditions	5 min (Post-run). 310 °C (Oven). 50 psi (Aux EPC pressure). 2 psi (Inlet pressure)
Transfer line temperature	280 °C
Ion source temperature	280 °C
Quadrupole temperature	150 °C

Data Analysis

The Agilent Pesticides and Endocrine Disruptors mass spectral library/database [1] was modified with the retention times for the constant flow 20 minute method utilized in the MSD, TQ and Q-TOF systems. This unit mass library with 950+ compounds was then used on GC/MSD, GC/TQ and GC/Q-TOF for compound identification through MassHunter Unknowns Analysis B.08.00. In addition, an accurate mass pesticides library (PCDL) with 850+ compounds was employed for compound identification on GC/Q-TOF via Find by Fragments in MassHunter Qualitative Analysis [2]. The GC/TQ used MRMs from the database supplied with the Pesticides & Environmental Pollutants Analyzer (M7412AA) [3].

Results and Discussion

Compound Identification on MSD, Q-TOF and TQ

Eight essential oils were analyzed. Nothing of interest was detected in eucalyptus oil, rosemary oil or lavender oil. Multiple pesticides were detected in grapefruit oil, lemon oil, neroli oil, orange oil (Brazil origin) and orange oil (California origin). Grapefruit oil (Figure 2) is one of the most challenging of the 8 matrices and is used as an example in this work.

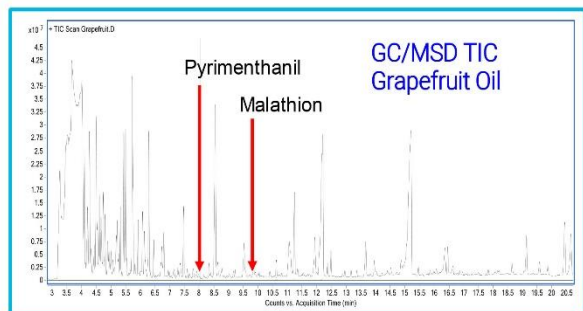


Figure 2. TIC Chromatograms of Grapefruit Oil

Pyrimethanil was identified on all three platforms. The raw MSD spectrum where pyrimethanil elutes is shown in Figure 3. With the help of deconvolution, a clean spectrum of pyrimethanil on MSD was obtained with a library spectrum match score of 90 (Figure 4).

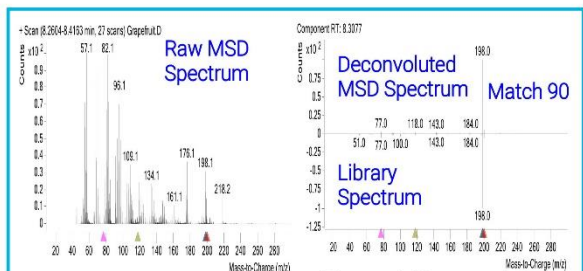


Figure 3. Raw MSD Spectrum

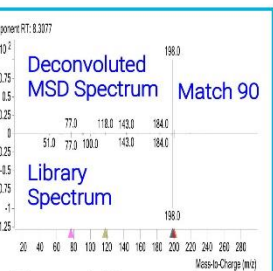


Figure 4. Deconvoluted and Library MSD Spectra

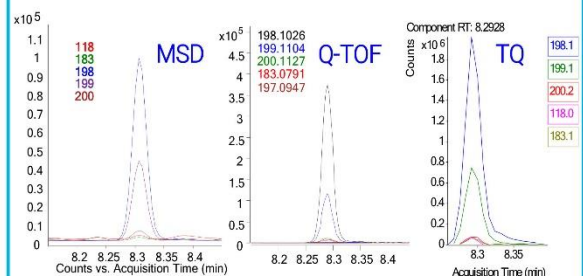


Figure 5. EICs of Pyrimethanil on Three Platforms

On TQ, the library match score is 87.8 for MS1 full scan and 88 for MS2 full scan. On Q-TOF, the Frag Ratio Score is 98.05 and the mass error (ppm) is 3.68. The EICs of pyrimethanil from all platforms are shown in Figure 5.

Screening Power of Q-TOF

All three platforms perform well in the identification of pyrimethanil, whose quantitation result by GC/TQ is 29.4 ng/mL (100:1 dilution). However, malathion was initially not found in the MSD and TQ deconvolution scan mode screens. The red arrow in Figure 6 shows where malathion should have been detected.

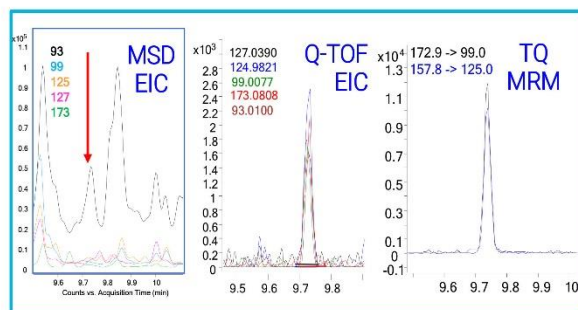


Figure 6. Chromatograms of Malathion on 3 Platforms

The Q-TOF screen, however, had a high confidence identification of malathion with small RT difference, good fragment ratio score and mass accuracy (Table 2). The TQ MRM mode then confirmed the presence of malathion, with an amount of only 1.26 ng/mL quantified. At this trace level, malathion cannot be identified by using scan mode on the MSD and TQ in heavy matrix. This illustrates that for low level screening in complex matrices, the Q-TOF screen is highly desirable due to its high selectivity over matrix interferences.

Workflow

GC/Q-TOF, GC/MSD and GC/TQ can all provide screening capability which relies on deconvolution to process full spectrum acquisition data (GC/Q-TOF) or full scan data (GC/MSD or GC/TQ). The initial identification was achieved by searching deconvoluted compound spectra against a unit mass library. The accurate mass data from GC/Q-TOF can also be used for suspect screening. This process consists of selecting principle ions of each compound from an accurate mass PCDL for screening, with the identified hits verified via mass accuracy, fragment ratio and RT match. Positive hits are then sent to TQ (MRM) for further confirmation and quantification. This provides a detailed comprehensive multi-platform screening and quantification workflow (Figure 7).

Results and Discussion

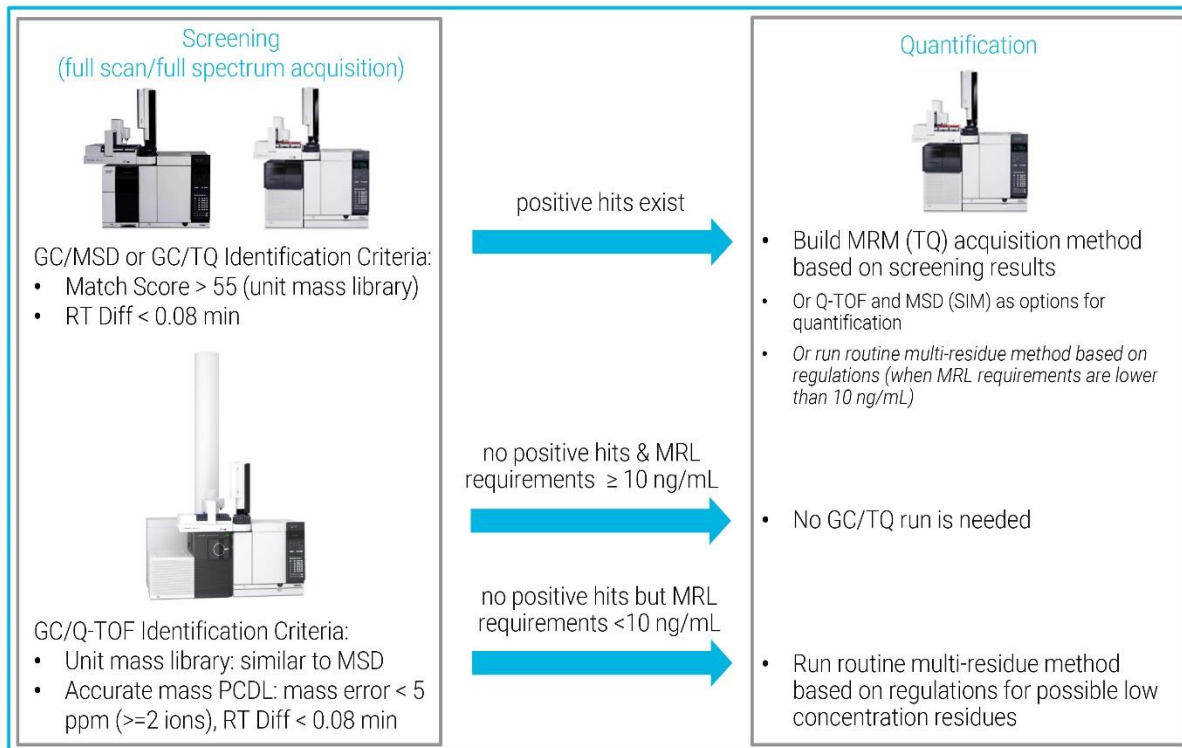


Figure 7. Workflow of Compound Screening and Quantification using GC/MSD, GC/TQ and GC/Q-TOF

The example results of this comprehensive workflow is shown in Table 2.

Table 2. Identification and Quantification Results from Grapefruit Oil by Multiple Platforms

Compound Name	GC/MSD		GC/Q-TOF			GC/TQ (MRM)	
	Match Score	RT Diff (min)	Frag ratio Score	RT Diff (min)	mass diff (ppm)	RT Diff (min)	Conc. (ng/mL)
Aniline	68	0.068	rejected after review			<i>n.d.</i>	<i>n.d.</i>
Pyrimethanil	96	0.023	98.05	0.015	3.68	0.012	29.41
Chlorpyrifos Methyl	79	0.000	99.92	0.005	1	0.006	3.33
Chlorpyrifos	93	-0.002	95.33	0.006	0.42	0.009	30.69
Imazalil	57	0.047	95.99	0.048	0.88	0.019	25.20
Pyriproxyfen	81	0.020	85.83	0.019	1.55	0.016	10.86
Malathion	<i>n.d.</i>	<i>n.d.</i>	82.15	0.014	0.17	0.011	1.26
Primiphos-methyl *	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.011	0.22
Oxadixyl *	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.021	0.36
Methidathion *	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.004	0.54

* quantified by the routine multi-residue method on TQ
n.d. = not detected or identified

Conclusions

- This work demonstrates a comprehensive multi-platform untargeted and targeted analysis workflow with examples in complex matrix.
- For untargeted screening, Q-TOF > MSD > TQ.
- TQ can quantify analytes at low concentration which may not be identified by MSD or Q-TOF screening.

Reference

- Wylie, P.L.; Screening for 926 Pesticides and Endocrine Disruptors by GC/MS with Deconvolution Reporting Software and a New Pesticide Library. *Agilent Technologies Application Note*, 5989-5076EN (2006).
- Chen, K., Stevens, J., Nieto, S.; GC/Q-TOF Screening of Pesticides in Food. *Agilent Technologies Application Note*, 5991-6884EN (2016).
- Westland, J., Stevens, J.; An Optimal Method for the Analysis of Pesticides in a Variety of Matrices. *Agilent Technologies Application Note*, 5991-7303EN (2017).

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