The Analysis of Red List OP Pesticides in Food by DMI/GC-TOFMS

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Key Words: GC-TOFMS, Pesticides

- **Little if any sample preparation**
- **Fast analysis by GC-TOFMS (Gas Chromatography-Time-of-Flight Mass Spectrometry)**
- **Fast, automated data processing with spectral deconvolution**

1. Introduction

The analysis of target compounds in food substances is usually very difficult, matrices containing fats can be even more tricky. The process of extraction and clean-up of the sample can lose target analytes or high levels of matrix co-extractives can remain, making analysis by GC-MS challenging. Presented here are the chromatograms from the analysis of four red list OP pesticides in three sample matrices using Difficult Matrix Introduction/GC-TOFMS. DMI enables the direct desorption of target compounds from the sample or sample extract without any clean-up. The temperature is controlled to fully transfer the target compounds onto the column while keeping the involatile material within the microvial. Semi-volatile matrix compounds are also transferred, however, the TOFMS enables spectral deconvolution to analytically resolve the target analytes from the coeluting matrix interferents even with little chromatographic resolution. The ability to use a high acquisition rate also reduces sample run times, as fast flow rates and oven temperature ramp rates are possible. Data processing time is greatly reduced using the ChromaTOF® software with Automated Peak Find, spectral deconvolution, and library searching.

2. Experimental Conditions

Instrumentation

- ATASGL Focus Robotic Sample Processor with DTD option
- ATASGL Optic 3 programmable injector
- Agilent 6890N Gas Chromatograph
- LECO Pegasus® III GC-TOFMS with ChromaTOF software

Samples

- Olive oil spiked at 5 ppm with dichlorvos, fenitrothion, malathion, and azinphos-methyl
- Chocolate DCM extract spiked at 5 ppm with dichlorvos, fenitrothion, malathion, and azinphos-methyl
- Chocolate powder spiked at 5 ppm with dichlorvos, fenitrothion, malathion and azinphos-methyl

Principles

- Prepare DTD liners by inserting a long microvial, crimping on a magnetic cap and placing in the autosampler DTD tray
- Place the liquid samples in 2 mL vials and place on a second autosampler tray
- For the solid samples, weigh the sample (1 to 2 mg) into a small microvial, insert into DTD liner and cap
- The Focus takes a portion of liquid sample, removes the old liner from the injector, moves a new liner into the injector and injects the sample into the microvial
- The DTD head is closed and any air flushed out
- The target compounds are desorbed from the sample onto the head of the column, involatile material remains in the microvial
- Fast analysis by TOFMS
- Automated Peak Find, spectral deconvolution, and library searching of the data
- Remove the DTD magnetic caps and dispose of the microvial, the liner can be re-used

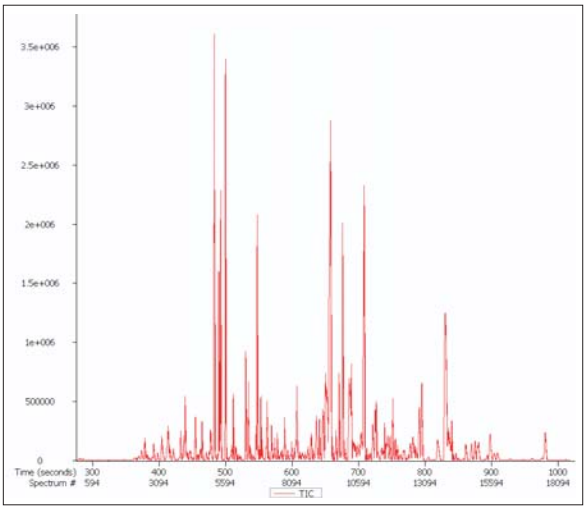

Figure 1. TIC of Olive Oil spiked at 5 ppm.

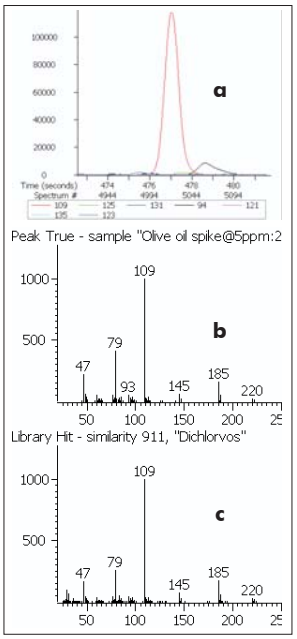

Figure 2. Dichlorvos peak @ 5 ppm
(a) 109 ion in red Rt 477s;
(b) deconvoluted mass spectrum;
(c) library hit of 91.1%.

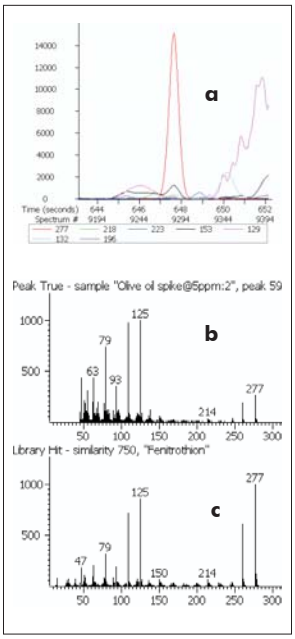

Figure 3. Fenitrothion peak @ 5 ppm
(a) 277 ion in red Rt 647s;
(b) deconvoluted mass spectrum;
(c) library hit of 75%.

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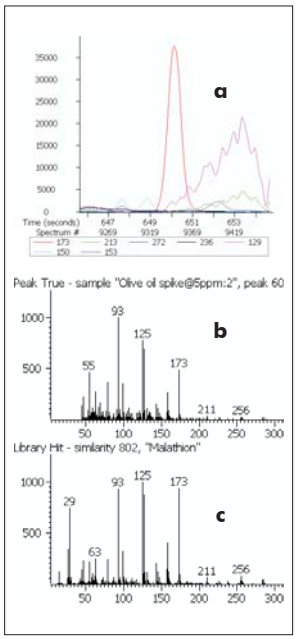

Figure 4. Malathion peak @ 5 ppm
(a) 173 ion in red Rt 650s;
(b) deconvoluted mass spectrum;
(c) library hit of 80.2%.

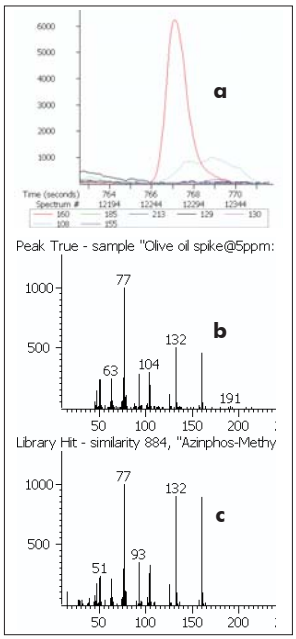

Figure 5. Azinphos-methyl peak @ 5 ppm
(a) 160 ion in red Rt 767s;
(b) deconvoluted mass spectrum;
(c) library hit of 88.4%.

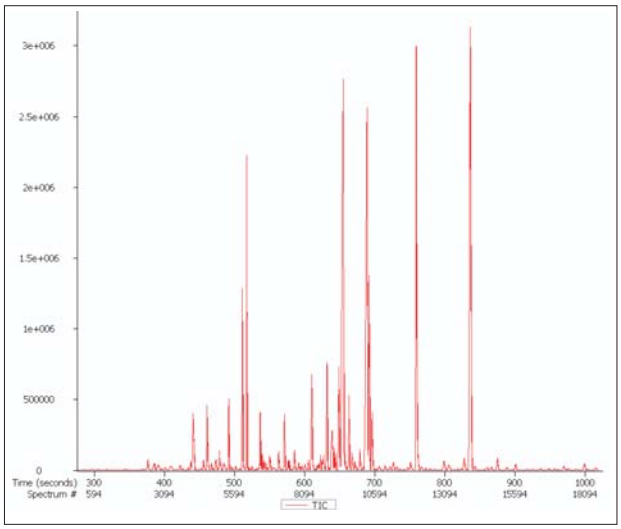

Figure 6. TIC of Chocolate extract spiked at 5 ppm.

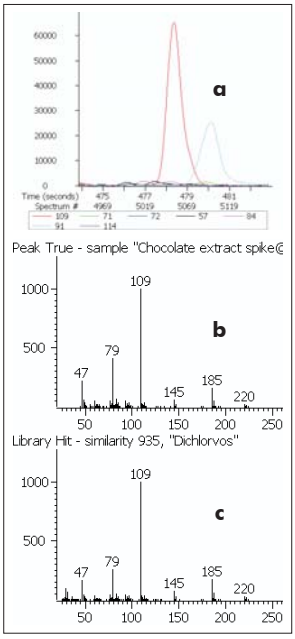

Figure 7. Dichlorvos peak @ 5 ppm
(a) 109 ion in red Rt 478s;
(b) deconvoluted mass spectrum;
(c) library hit of 93.5%.

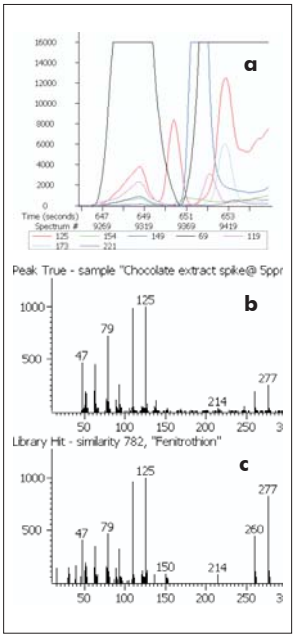

Figure 8. Fenitrothion peak @ 5 ppm
(a) 125 ion in red Rt 650.5s;
(b) deconvoluted mass spectrum;
(c) library hit of 78.2%.

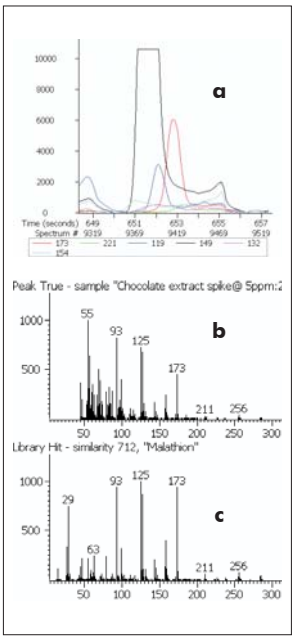

Figure 9. Malathion peak @ 5 ppm
(a) 173 ion in red Rt 653s;
(b) deconvoluted mass spectrum;
(c) library hit of 71.2%.

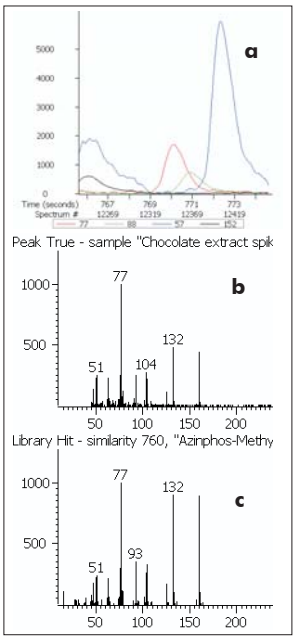

Figure 10. Azinphos-methyl peak @ 5 ppm
(a) 77 ion in red Rt 770s;
(b) deconvoluted mass spectrum;
(c) library hit of 76%.

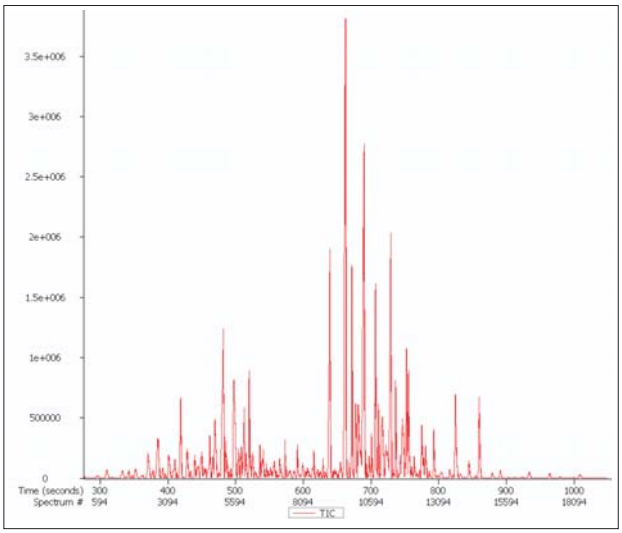

Figure 11. TIC of Chocolate powder spiked at 5 ppm.

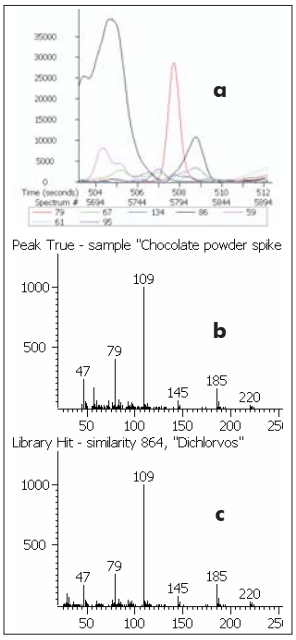

Figure 12. Dichlorvos peak @ 5 ppm
(a) 79 ion in red Rt 508s;
(b) deconvoluted mass spectrum;
(c) library hit of 86.4%.

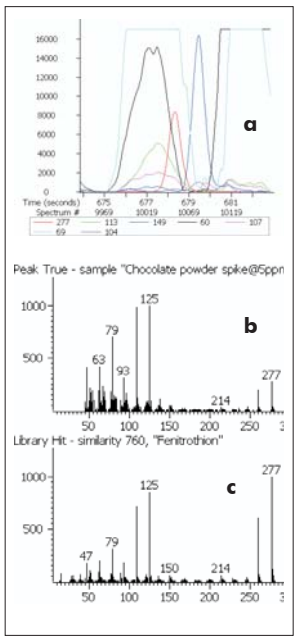

Figure 13. Fenitrothion peak @ 5 ppm
(a) 277 ion in red Rt 678s; (b) deconvoluted mass spectrum;
(c) library hit of 76%.

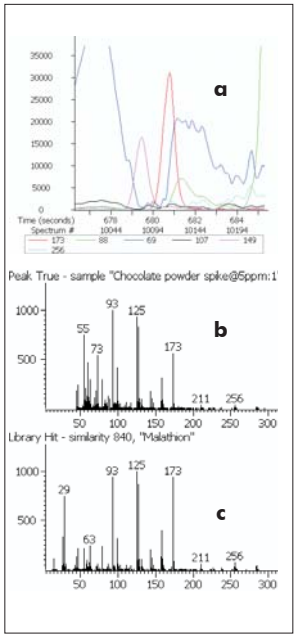

Figure 14. Malathion peak @ 5 ppm
(a) 173 ion in red Rt 681s; (b) deconvoluted mass spectrum;
(c) library hit of 84%.

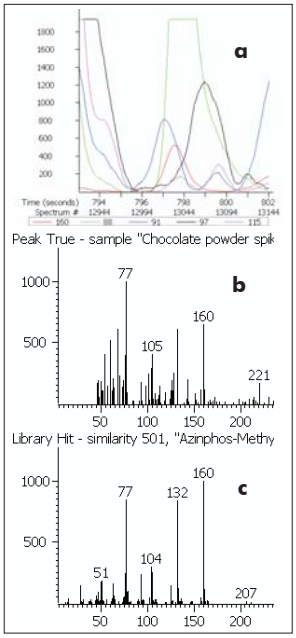

Figure 15. Azinphos-methyl peak @ 5 ppm
(a) 160 ion in red Rt 797.5s;
(b) deconvoluted mass spectrum;
(c) library hit of 50.1%.

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3. Conclusions

DMI/GC-TOFMS is a powerful tool for the analysis of difficult and complex samples. Reducing time for sample preparation, analysis, and data processing, target compounds can be found under the high matrix background using Automated Peak Find and deconvolution, avoiding the difficult and tedious task of background subtraction. This is a promising technique for this analysis.

4. Appendix: Conditions

Optic

Liquid samples

Method:	DMI 1 µL
Mode:	Expert
Equilibration Time:	5 seconds
End Time:	17 minutes
Initial Temperature:	35°C
Delay:	20 seconds
Ramp Rate:	5°C/second
Final Temperature:	280°C
Column Flow:	1 mL/minute constant
Sweep Split Flow:	100 mL/minute
Splitless Time:	3.5 minutes
Split Flow:	50 mL/minute

Powder samples

Method:	DMI powder
Mode:	Expert
Equilibration Time:	5 seconds
End Time:	17.5 minutes
Initial Temperature:	35°C
Delay:	20 seconds
Ramp Rate:	16°C/second
Final Temperature:	250°C
Desorption Column Flow:	0.3 mL/minute
Desorption Time:	2.5 minutes
Transfer Column Flow:	2 mL/minute
Transfer Time:	2 minutes
Column Flow:	1 mL/minute constant
Sweep Split Flow:	100 mL/minute
Desorption Split Flow:	10 mL/minute
Split Flow:	50 mL/minute

GC Oven

Column:	DB5-MS 20 m x 0.18 mm ID x 0.18 µm
Initial Temperature:	40°C
Initial Time:	4 minutes (4.5 minutes powder)
Ramp Rate:	20°C/minute
Final Temperature:	280°C
Final Time:	1 minute

TOFMS

Low Mass:	45
High Mass:	400
Acquisition Rate:	20 spectra/second
Transfer Line:	260°C
Ion Source:	230°C
Solvent Delay:	4.6 minutes

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