GC-TOFMS and GCxGC-TOFMS of Organophosphate Pesticides in Ash Leaves

LECO Corporation; Saint Joseph, Michigan USA

Key Words: GCxGC-TOFMS, Pesticides

1. Introduction

Organophosphate pesticides such as Chlorpyrifos, Diazinon, and Malathion are sometimes used on ornamental plants to control nuisance insects. Monitoring these plants for the insecticides can be a challenge because the residual levels are often small and the matrix (the plant material) is chemically complex. This note describes the analysis of an ash leaves extract for Chlorpyrifos, Diazinon, and Malathion by Gas Chromatography—Time-of-Flight Mass Spectrometry (GC-TOFMS) and comprehensive two-dimensional GC-TOFMS (GCxGC-TOFMS). Advantages offered by automated peak find and spectral deconvolution routines are discussed, and the benefit of enhanced peak capacity for complex samples is shown.

2. Experimental Conditions

Sample Extraction

An ash leaves extract was prepared by the United States Department of Agriculture in Gulfport, Mississippi.

GC-TOFMS

GC:
Agilent 6890 Gas Chromatograph
Column:
20 m x 0.25 mm x 0.71 µm Rtx-TNT (Restek)
Carrier:
Helium at 2 mL/minute, constant flow
Injection:
1 µL splitless at 250°C, valve time 60 seconds
Oven Program:
80°C (1 minute), 20°/minute to 340°

MS:	LECO Pegasus® TOFMS
Ionization:	Electron ionization at 70 eV
Source Temperature:	225°C
Stored Mass Range:	45 to 550 u
Acquisition Rate:	20 spectra/second

GCxGC-TOFMS

GCxGC:
Agilent 6890 Gas Chromatograph equipped with a LECO GCxGC Thermal Modulator and Secondary Oven
Column 1:
10 m x 0.18 mm x 0.20 µm Rtx-5 (Restek)
Column 2:
2 m x 0.10 mm x 0.10 µm Rtx-PCB (Restek)
Carrier:
Helium at 0.7 mL/minute, constant flow
Injection:
1 µL splitless at 275°C, valve time 60 seconds
Oven 1 Program:
80°C (1 min), 10°/minute to 300°
Oven 2 Program:
35°C offset from oven 1
Modulation Time:
3 seconds

MS:	LECO Pegasus TOFMS
Ionization:	Electron ionization at 70 eV
Source Temperature:	225°C
Stored Mass Range:	45 to 550 u
Acquisition Rate:	100 spectra/sec.

Data Processing

LECO ChromaTOF® software with automated peak find and spectral deconvolution.

3. Results and Discussion

Figure 1 simultaneously illustrates the complexity of the ash leaves extract and the power of automated peak find and spectral deconvolution afforded by the fast acquisition capability and spectral reproducibility of TOFMS. The matrix peaks, especially the off-scale m/z 124, hide the orange peak representing Diazinon (approximately 50 pg), and a caliper spectrum at the Diazinon peak apex is representative of the background from the ash leaves. Note that the deconvoluted mass spectrum matches nicely with a reference spectrum for Diazinon.

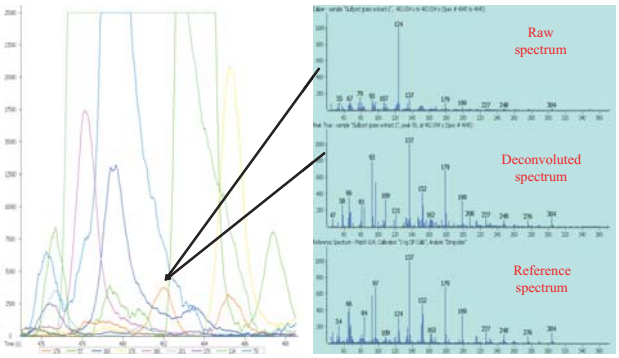

Figure 1. Chromatogram of 50 pg Diazinon (orange peak) in an ash leaves extract plotted with ions representing the matrix. The raw spectrum taken at the peak apex for Diazinon is representative of the matrix interferences. The deconvoluted TOF mass spectrum matches well with the reference spectrum.

A similar chromatographic situation exists for Malathion in the complex ash leaves extract as shown in Figure 2. Again, the raw spectrum taken at the peak apex for Malathion (approximately 125 pg) is mainly showing ions for the matrix interferences, particularly 167, the turquoise off-scale peak in Figure 2. The deconvoluted spectrum, while not perfect (it still contains some 167 ion), shows a similarity of 806 (out of 999) against the first-hit library spectrum for Malathion.

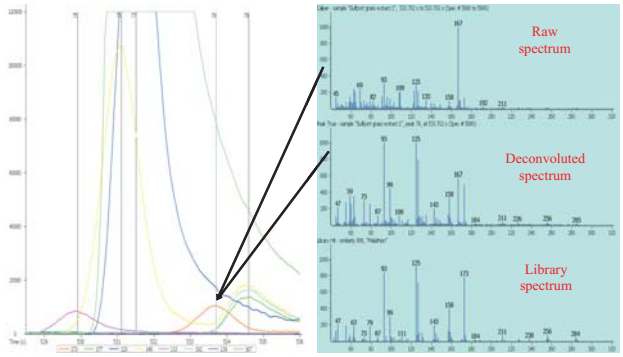

Figure 2. Chromatogram of 125 pg Malathion (orange peak) in an ash leaves extract plotted with ions representing the matrix. The raw spectrum taken at the peak apex for Malathion hardly hints that Malathion may be present. The deconvoluted TOF mass spectrum, even though it contains some residual 167 ion from the huge matrix interference, matches well with a library spectrum.

Another way to tackle complex samples is to increase the chromatographic separating power by applying GCxGC. The benefit of this approach is easily visualized when viewing the contour plot, or GCxGC chromatogram, of Figure 3. Notice how separations are now occurring in two dimensions, one along the X-axis (Rtx-5) and the other along the Y-axis (Rtx-PCB). The potential to move pesticides away from matrix interferences is substantially increased. In fact, in this example, both Malathion and Chlorpyrifos would have coeluted with high-concentration matrix interferences in a one-dimensional analysis with Rtx-5. But the Rtx-PCB has located the pesticides away from these interferences in the second dimension (Figure 4), resulting in the high quality, library-searchable spectra seen in Figure 5. The similarities for both pesticides are greater than 900 (out of 999).

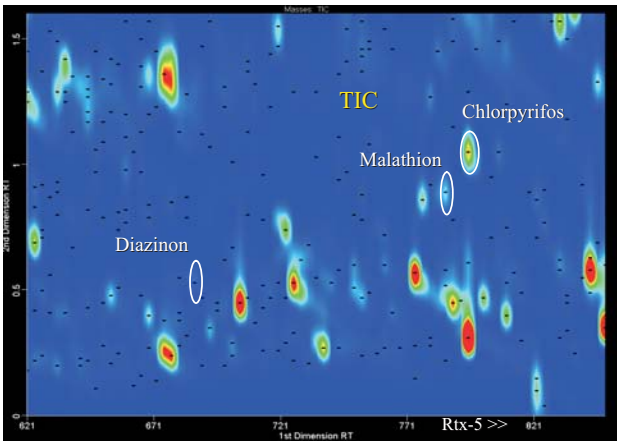

Figure 3. Contour plot of organophosphate pesticides in an ash leaves extract. Note how separations are occurring in two dimensions, and where Malathion and Chlorpyrifos have been separated in the second dimension from substantial matrix interferences (at a first dimension retention time of approximately 800 seconds).

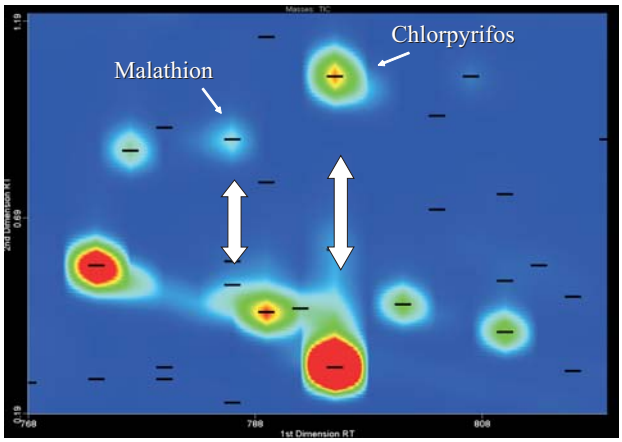

Figure 4. Zoom of contour plot from Figure 3. Malathion and Chlorpyrifos are separated in the second dimension from substantial matrix interferences as noted by the white arrows.

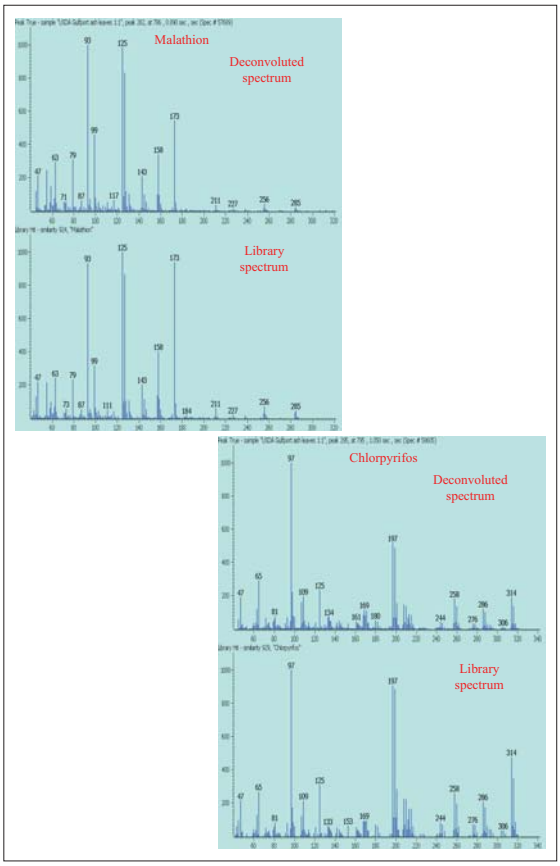

Figure 5. TOF mass spectra from the GCxGC analysis of Malathion and Chlorpyrifos in an ash leaves extract. The similarities versus library spectra are greater than 900 (out of 999).

One observation for the spectrum of Malathion produced with GCxGC of ash leaves was the absence of the 167 ion (from matrix) that was present in the deconvoluted spectrum for the one-dimensional analysis. Figure 6 helps illuminate the reason behind this, which simply put, is the increased separating power available with GCxGC. Close inspection of the GCxGC portion of this figure (or of the contour plots in Figures 3 and 4) will reveal that the GCxGC peaks, due to thermal focusing close to the detector, are only about 100-200 ms wide at their base. Because the peaks are so narrow, TOFMS, which can acquire data at up to 500 spectra/second, is the only mass spectrometer appropriate for GCxGC.

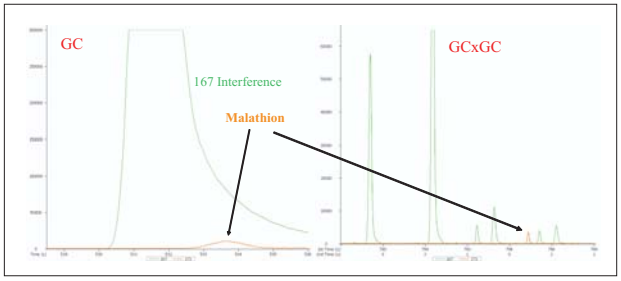

Figure 6. Linear chromatograms for one-dimensional (GC) and two-dimensional (GCxGC) analyses of Malathion in ash leaves. Malathion coelutes with a large matrix peak in GC, but is easily separated from this same compound using GCxGC.

The separation of Diazinon from its interference in the one-dimensional analysis was also better when employing GCxGC (Figure 7).

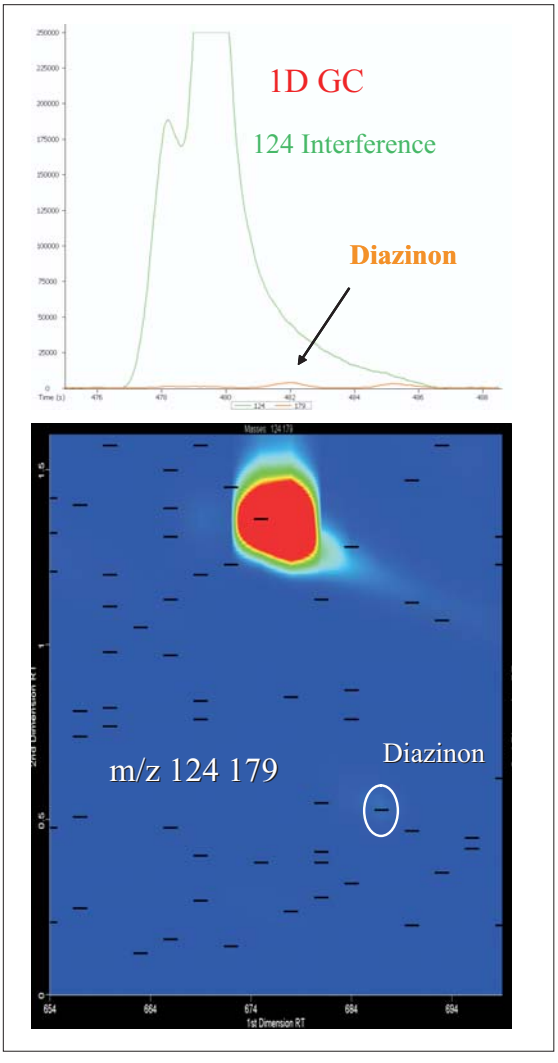

Figure 7. One-dimensional GC (1D GC) and GCxGC (contour plot on right) analyses for Diazinon in ash leaves. The matrix interference that contains substantial 124 ion and is coeluting with Diazinon in 1D GC is easily resolved from Diazinon using GCxGC. The peak containing the 124 ion is the large red spot in the contour plot.

4. Conclusions

GC-TOFMS and GCxGC-TOFMS are both powerful techniques for determining pesticides in matrix due to automated peak find and spectral deconvolution, and because of the peak capacity increase afforded with GCxGC. GCxGC-TOFMS has the potential to produce better spectra for organophosphate pesticides in the most complex matrices. TOFMS is the only mass spectrometer that has the acquisition speed to support GCxGC, and a full mass spectrum is always obtained.

5. Acknowledgment

John Gallagher at the United States Department of Agriculture in Gulfport, Mississippi provided the ash leaves extract. The GC columns were from Frank Dorman at Restek Corporation.

Life Science and Chemical Analysis Solutions

LECO Corporation • 3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977
info@leco.com • www.leco.com • ISO-9001:2000 • No. FM 24045 • *LECO is a registered trademark of LECO Corporation.*

