



Peak Area Reproducibility Using GC-TOFMS and GCxGC-TOFMS

Purpose of Analysis

Confident quantitative analysis by Gas Chromatography—Mass Spectrometry (GC-MS) requires knowledge of the reproducibility of the results obtained. In an ideal world, repetitive injections of the same material should produce the same peak areas. However, variations in injection volume, chromatographic performance, detector response etc., conspire to induce variations in the measured peak areas for repetitive injections. This note addresses these issues for GC—Time-of-Flight Mass Spectrometry (TOFMS) and comprehensive two-dimensional GC-TOFMS (GCxGC-TOFMS).

Background

While the determination of peak area for one-dimensional GC-MS is a relatively simple measurement, determination of peak area using GCxGC-TOFMS is a much more complex procedure. This is because with GCxGC, the peak arising from a single compound may be split across several modulations. To obtain accurate peak areas in GCxGC requires recognizing the different "slices" of a single peak, accurately measuring their individual areas, and recombining these to obtain an overall area. In the LECO Pegasus® 4D GCxGC-TOFMS instrument, the ChromaTOF® software handles this process automatically. Second dimension retention time and mass spectral matching determines recombination of peak modulations. This note describes the reproducibility of this process in measuring peak area, and compares it to that which can be obtained with a one-dimensional GC-TOFMS system.

Sample Used in the Analysis

Ms. B-J De Vos from the National Metrology Laboratory, CSIR, Pretoria, South Africa, who also participated in the experiments described, supplied the sample used for analysis in this study. The sample consisted of a mixture of the pesticides Lindane, p,p'-DDE, and p,p'-DDT. Approximate concentrations of these materials in an iso-octane solution were 310.8, 284.8, and 582.6 ppb, respectively. To this solution were added ¹³C₆-Lindane, ¹³C₁₂-p,p'-DDE, and ¹³C₁₂-p,p'-DDT (all at 238.5 ppb) as internal standards.

Materials & Methods

GC Columns

Column 1: 30 m x 0.25 mm x 0.25 μm Rtx-CLPesticides (Restek)
Column 2: 2 m x 0.10 mm x 0.10 μm Rtx-1701 (Restek)

GC Parameters

Agilent 6890N

Injection: 1 μL splitless at 200°C
Carrier: Helium at 1.0 mL/min, constant flow

GC-TOFMS Analysis

Oven 1 Program: 120°C (1 min), 12°/min to 275° (2 min)
Oven 2 Program: 5°C offset from oven 1
Modulator Offset: 5°C
Modulation Time: 0 seconds

GCxGC-TOFMS Analysis

Oven 1 Program: 120°C (1 min), 12°/min to 275° (2 min)
Oven 2 Program: 130°C (1 min), 12°/min to 280° (2 min)
Modulator Offset: 10°C
Modulation Time: 6 seconds

MS Parameters

Pegasus® III GC-TOFMS

Ionization: Electron ionization at 70 eV
Source Temperature: 225°C
Stored Mass Range: 100-350 u
Acquisition Rate: 10 spectra/second
Transfer Line Temp: 250°C

Pegasus® 4D GCxGC-TOFMS

Ionization: Electron ionization at 70 eV
Source Temperature: 225°C
Stored Mass Range: 100-350 u
Acquisition Rate: 125 spectra/second
Transfer Line Temp: 250°C

GC-TOFMS Results

The sample was run 6 times consecutively using the GC-TOFMS conditions described above. A sample chromatogram is shown in Figure 1.

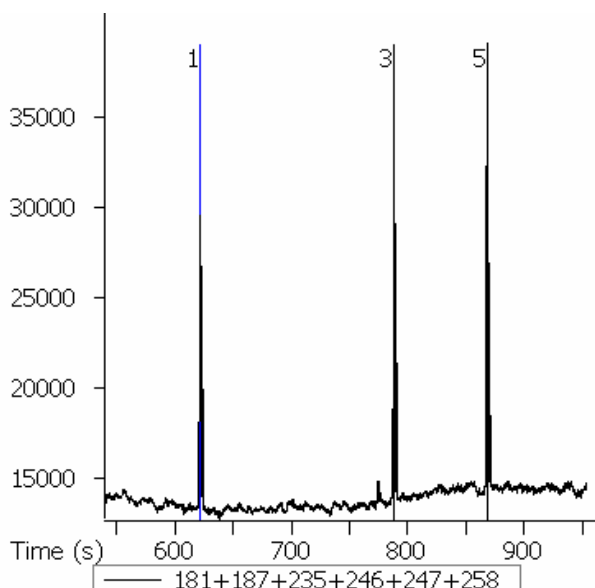


Figure 1. Summed ion chromatogram for the pesticide sample.

Under the chromatographic conditions used, there is little separation of a pesticide from its isotopically labeled congener. An example of a typical separation is shown below for Lindane, where the 181 ion represents Lindane and the 187 ion the $^{13}\text{C}_6$ -labeled Lindane.

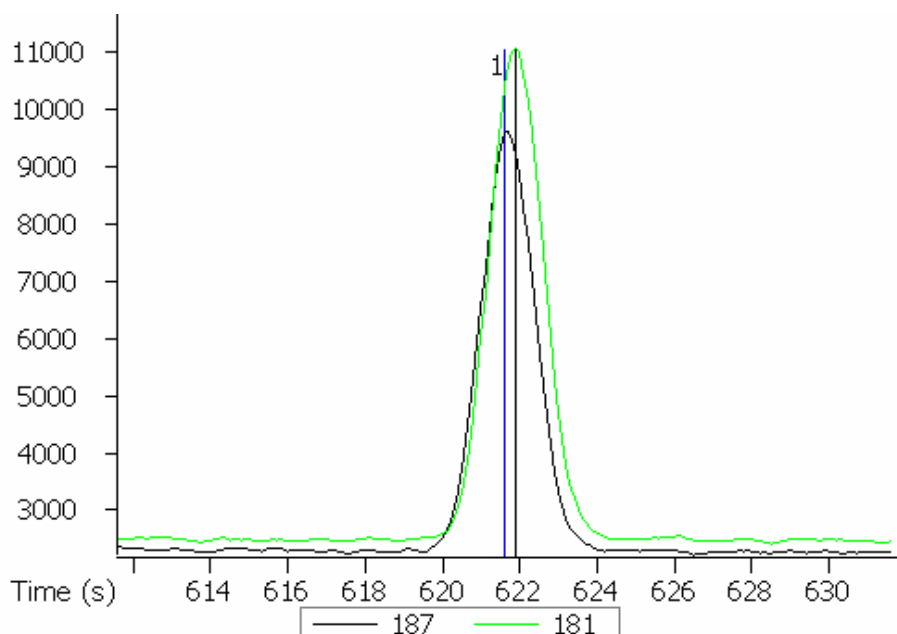


Figure 2. Chromatographic separation of $^{13}\text{C}_6$ -Lindane (187) and Lindane (181).

Despite the close proximity of the peak apexes for the two compounds shown above, the Deconvolution algorithm of the ChromaTOF software is still able to produce clean spectra for both of the compounds, as shown in Figures 3 and 4 below. Each figure contains the deconvoluted (or Peak True) spectrum at the top, with the library match in the middle, and the caliper spectrum at the bottom. The caliper spectrum is the raw spectrum taken at the point where the peak apex occurs, and indicates the degree of spectral overlap between components.

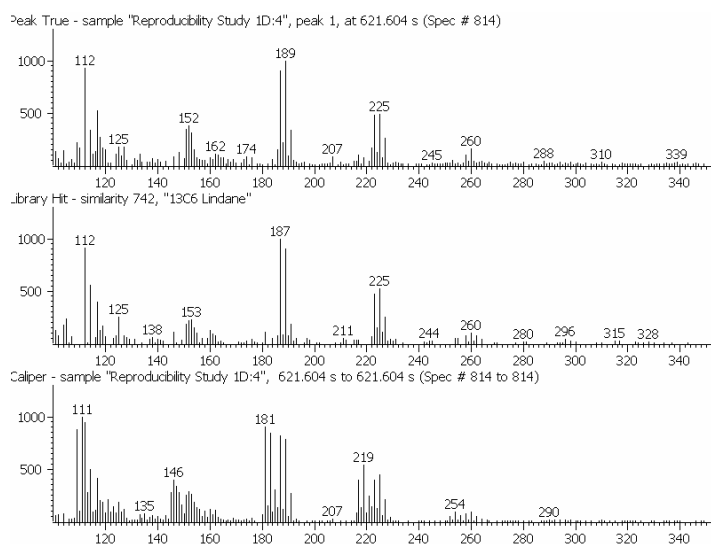


Figure 3. Deconvoluted (top), library (middle), and caliper (bottom) mass spectra for $^{13}\text{C}_6$ -Lindane.

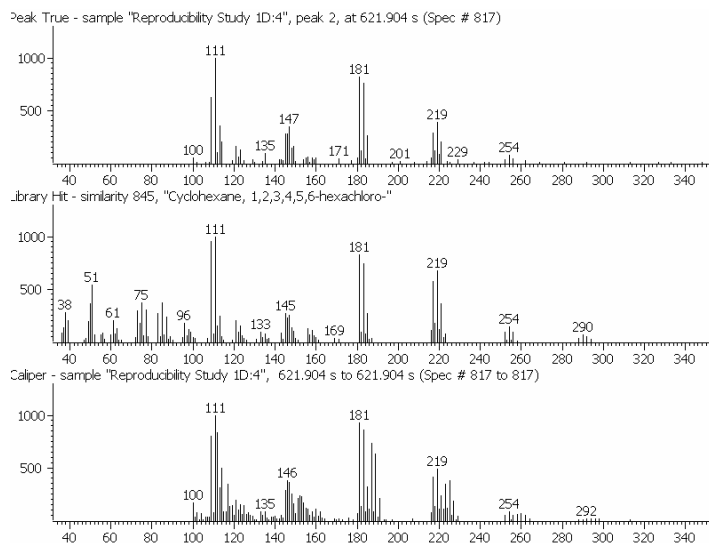


Figure 4. Deconvoluted (top), library (middle), and caliper (bottom) mass spectra for Lindane.

The peak area values obtained for the six consecutive runs are shown in Table 1, along with the Relative Standard Deviation percent (RSD %) values for the uncorrected pesticide peak areas, and for those when the labeled pesticide was used as an internal standard for the native pesticide. Although the software allows the analyst to correct area calculations by manually adjusting the beginning and end of each peak, this was not performed, and the values displayed are those obtained from the software integration. The following ions were used to obtain peak areas: Lindane 181; ¹³C₆-Lindane 187; p,p'-DDE 246; ¹³C₁₂-p,p'-DDE 258; p,p'-DDT 235; ¹³C₁₂-p,p'-DDT 247.

Table 1. Pesticide peak areas and repeatability for GC-TOFMS.

Quant Mass >>	181	187	246	258	235	247
Sample 1	117,839	99,989	105,684	84,208	184,629	85,340
Sample 2	119,414	103,205	105,300	85,961	184,590	86,561
Sample 3	134,050	117,487	106,833	88,573	166,132	76,035
Sample 4	126,769	114,894	107,763	90,218	157,859	72,553
Sample 5	125,782	110,448	106,659	88,682	155,291	71,416
Sample 6	119,709	105,089	105,769	87,308	158,360	74,308

No Internal Standard	Std Dev.	RSD %
Lindane	6,152	5.0
p,p'-DDE	917	0.9
p,p'-DDT	13,508	8.0

Internal Standard	Std Dev.	RSD %
Lindane	2,477	2.2
p,p'-DDE	1,830	1.8
p,p'-DDT	1,976	1.1

GCXGC-TOFMS Results

The pesticide sample was run 12 times consecutively using the GCxGC-TOFMS conditions described above. A sample GCxGC chromatogram, also known as a contour plot, is shown in Figure 5. The peak area values obtained for the twelve consecutive runs are shown in Table 2 (again with RSD % values for the uncorrected pesticide peak areas, and for those when the labeled pesticide was used as an internal standard for the native pesticide). The values displayed are those obtained from the software integration. Calculations were performed using the same ions as listed in the GC-TOFMS results.

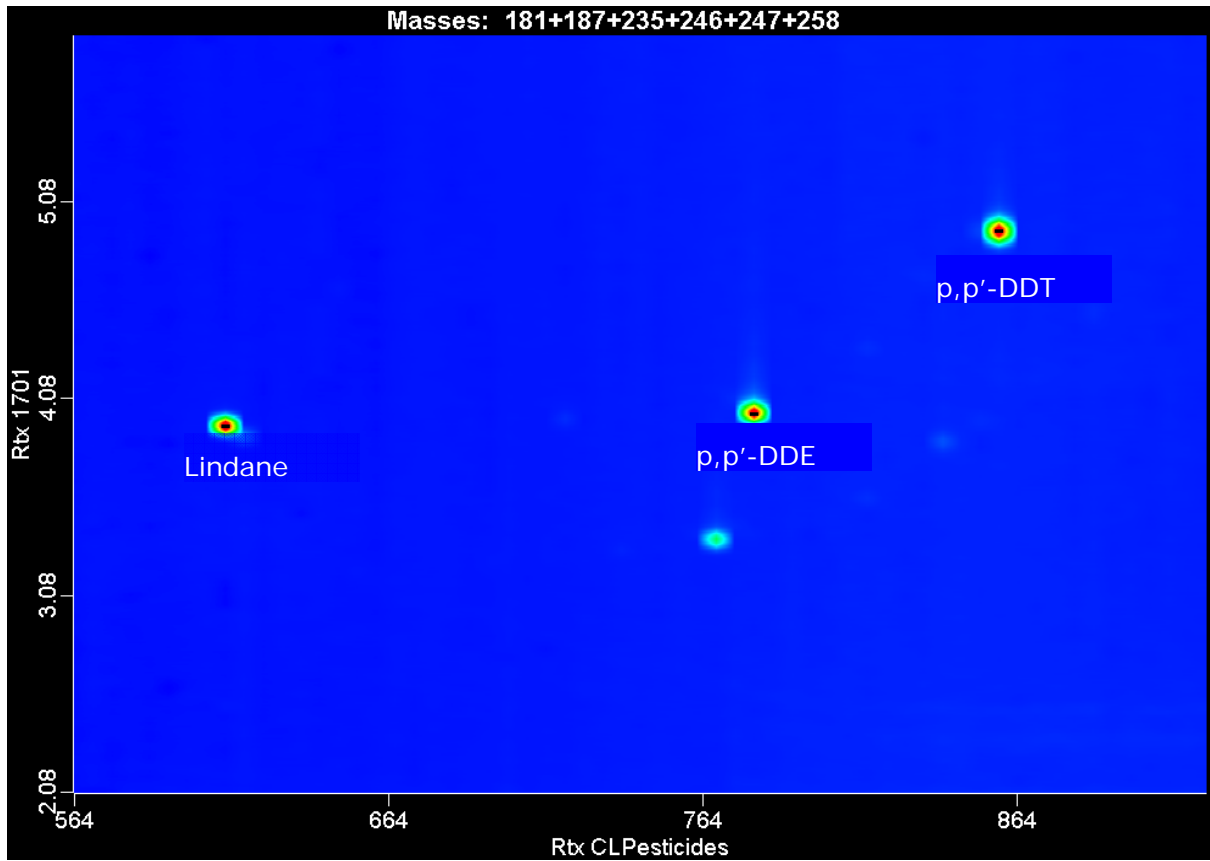


Figure 5. GCxGC chromatogram, or contour plot, of pesticides. The X-axis represents the separation occurring for Rtx-CLPesticides, and the Y-axis shows the Rtx-1701 separation.

Table 2. Pesticide peak areas and repeatability for GCxGC-TOFMS.

Quant Mass >>	181	187	246	258	235	247
Sample 1	87,202	76,379	73,736	62,529	119,841	54,475
Sample 2	92,117	81,668	77,698	64,880	123,807	55,860
Sample 3	95,591	85,999	81,435	67,734	129,627	59,345
Sample 4	84,206	73,300	70,498	59,206	111,405	49,832
Sample 5	95,505	82,194	77,235	62,371	117,633	53,210
Sample 6	94,486	82,572	76,196	62,700	116,826	52,386
Sample 7	90,703	80,610	73,201	59,962	113,385	49,508
Sample 8	87,285	75,349	71,242	58,388	105,065	46,227
Sample 9	85,500	74,234	71,996	59,289	112,911	49,651
Sample 10	89,748	78,729	73,114	59,519	110,910	49,881
Sample 11	83,183	73,170	73,517	59,427	111,029	49,863
Sample 12	89,584	79,131	79,249	63,723	119,562	54,217

No Internal Standard	Std Dev.	RSD%
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Lindane	4,268	4.8
p,p'-DDE	3,399	4.5
p,p'-DDT	6,641	5.7

Internal Standard	Std Dev.	RSD%
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Lindane	1,105	1.3
p,p'-DDE	1,254	1.6
p,p'-DDT	1,772	1.5

Discussion

As is to be expected, RSD % values are better when the internal standards are factored in. There are no significant differences in RSD % values for GC-TOFMS and GCxGC-TOFMS results. This is somewhat unexpected as in the GCxGC-TOFMS case, the area value is obtained from the sum of several "slices". However, in the GCxGC-TOFMS experiment, peak widths are much narrower than for the GC-TOFMS peaks due to the thermal focusing that occurs with GCxGC. This peak narrowing, with corresponding increase in peak height and signal-to-noise ratio may well make it easier for the software to choose the beginning and end of the peaks, thus explaining the comparative RSD % values.

Conclusions

Both GC-TOFMS and GCxGC-TOFMS provide excellent repeatability for the determination of peak area. Internal standards increase the reliability of the results, and are necessary for the lowest RSD % values.



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