Determination of Pesticides in Food Matrix by GC-TOFMS

LECO Corporation; Saint Joseph, Michigan USA

Key Words: GC-TOFMS, Quantification, Environmental, Pesticides, Deconvolution

1. Introduction

The determination of pesticide residues in foods and food products is of great importance to food processors as well as consumers. There is great concern that pesticides persist in the food products even after washing and preparation. The determination of pesticides in foods is very challenging since they may be present at low concentrations under a large amount of matrix. For this reason the samples must be prepared before analysis. These procedures can be cumbersome and take significant amounts of time. In addition, long chromatographic runs are needed to guarantee minimal coelutions of the analytes within the matrix.

The LECO Pegasus® GC-TOFMS offers several advantages over other types of GC-MS systems—one of which are its fast data acquisition rates of up to 500 spectra/second. This allows accurate definition of the narrowest GC peaks. In addition, the ion ratios for a spectrum in a TOF system do not change across the peak; this means that the spectrum across the peak gives an accurate representation of the ion ratios for that particular analyte. The spectra obtained are non-skewed. This is known as "spectral continuity".

Fast data acquisition rates as well as spectral continuity across peaks allowed the development of algorithms that can be used to deconvolute complex chromatographic coelutions and extract the spectrum of each analyte (which can then be used for library identification). Thus, it is possible to analyze complex samples with minimal sample preparation using a Time-of-Flight (TOF) system.

The purpose of this analysis is to demonstrate the capability of the Pegasus platform to analyze a complex food matrix that contains trace levels of pesticides. By taking advantage of Pegasus' hardware/software combination to generate non-skewed spectra, it is possible to detect and quantify analytes even when they are well below the level of the TIC.

2. Experimental Conditions

GC-Parameters: Agilent 6890

Column:
RTX-5®; 30 m x 0.25 mm x 0.25 µm film

Injector Temperature:
250°C

Split Mode:
Splitless for 30 seconds, 20 ml purge flow

Oven Program:
70°C for 1 minute to 325°C at 40°C/minute, hold 2.75 minutes

Flow Rate: 1.8 ml/minute

Injection Size: 2.0 µl fast

MS-Parameters: Pegasus II GC-TOFMS (EI Mode)

Mass Range:	45 to 400 amu
Acquisition Rate:	20 spectra/second
Ion Source Temperature:	170°C
Total Acquisition Time:	10 minutes

3. Results and Discussion

The calibration samples were prepared by first taking 50 g of applesauce and extracting it with 50 ml of Hexane to obtain the sample matrix. The extract was then spiked with a number of pesticides at a concentration of 200 ppb. This spiked sample was then sequentially diluted with unspiked extract down to 10 ppb. Each of these samples was then concentrated ten-fold so that the pesticide concentration in the samples ranged from 100 ppb to 2 ppm. This is a typical procedure used to prepare food extracts.

Figure 1 shows a typical chromatogram of an applesauce that was spiked with various pesticides at a concentration level of 100 ppb (10 ppb before concentration). A number of pesticides eluted in the region between 340 and 450 seconds of Figure 1, where a large number of matrix components also elute. Most of the pesticides present in the sample are below the baseline and do not show on the TIC, but the Peak Find algorithm is able to detect them and extract the correct spectrum so that a library search can be performed. Figure 2 shows a section of the chromatogram where four pesticides are located.

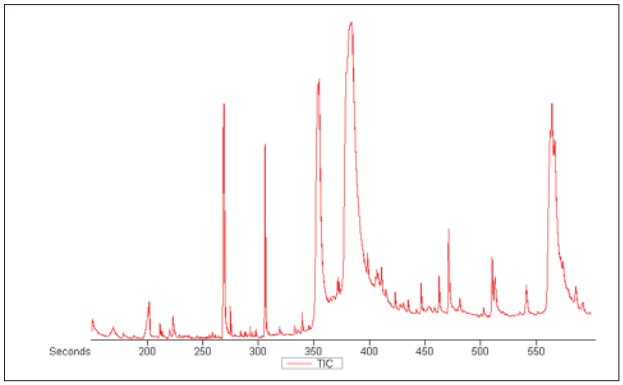

Figure 1. Total Ion Chromatogram of applesauce extract spiked at 100 ppb with pesticides.

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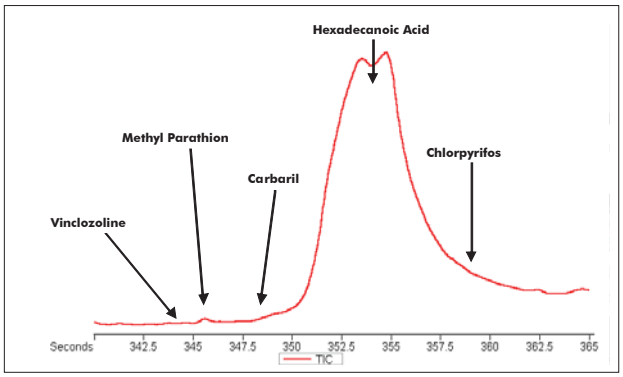

Figure 2. Chromatogram section where pesticides elute.

By plotting the unique mass for chlorpyrifos (m/z 197), one can see that there is a peak under the large Hexadecanoic Acid matrix peak. Figure 3 shows the Selected Ion Chromatogram using m/z 197. The TIC was scaled down so that the small peak could be seen. The insert shows the deconvoluted spectrum for Chlorpyrifos.

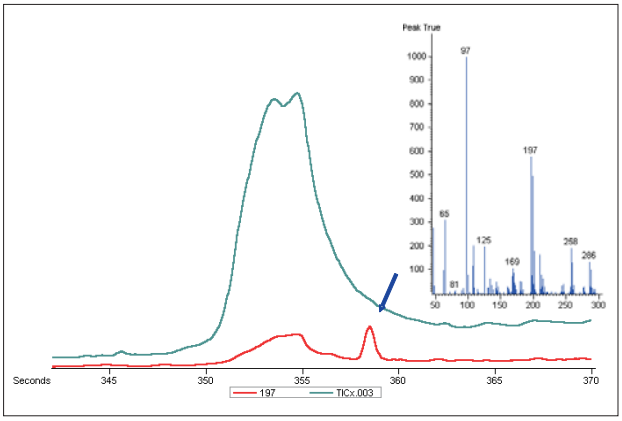

Figure 3. TIC, Selected Ion Chromatogram, and deconvoluted spectrum for Chlorpyrifos (100 ppb).

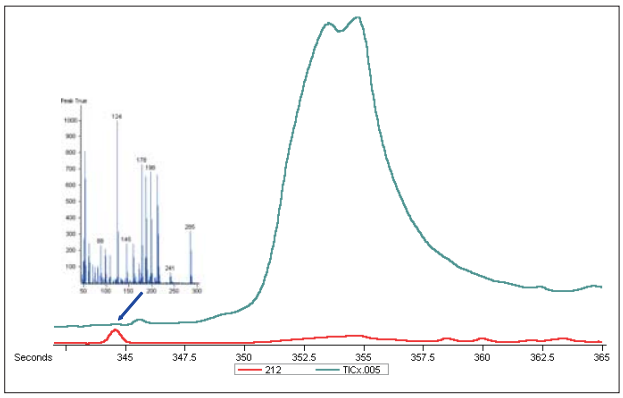

Figure 4. TIC, Selected Ion Chromatogram, and deconvoluted spectrum for Vinclozoline (100 ppb).

Figure 4 shows the Selected Ion Chromatogram for Vinclozoline. This peak is also below the TIC and would normally be missed if not targeted. The Peak Find and Deconvolution algorithms can extract the peak to obtain a clean spectrum that can be library searched for identification. The insert shows the extracted spectrum for Vinclozoline.

Calibration curves were done for the eight pesticides listed in Table 1. The curves were linear over the concentration range analyzed with good correlation coefficients. Three parameters must be defined for the calibration. First, a retention deviation must be specified for each analyte. Second, a "matching" factor must be specified to make sure that the spectrum of the analyte matches the reference. Third, an area and signal-to-noise (S/N) threshold must be met in order to have a positive analyte ID. Figures 5 and 6 show the calibration curves for Chlorpyrifos and Vinclozoline.

Table 1. Calibration Table for pesticides in applesauce matrix.

ANALYTE	NAME	ABSOLUTE R.T.	RF	MASSES	EQUATION	CORRELATION COEFFICIENTS
1	DICHLORAN	320.37	370.59	206	Y= +448.968X - 18718.2	0.9951
2	VINCLOZOLINE	344.37	657.65	124	Y= +794.652X - 32716.9	0.9985
3	METHYL PARATHION	346.17	456.42	263	Y= +603.25X - 35064.6	0.9874
4	CARBARIL	348.67	978.33	115	Y= +1164.26X - 44399.9	1.0000
5	CHLORPYRIFOS	358.27	755.7	197	Y= +809.982X - 12963.7	0.9986
6	PROPICONAZOLE	413.07	77.545	259	Y= +104.047X - 6328.99	0.9993
7	PROPARGITE	415.22	502.49	173	Y= +750.534X - 59235.4	0.9985
8	AZINPHOS-METHYL	439.87	590.2	160	Y= +804.725X - 51229.6	0.9984

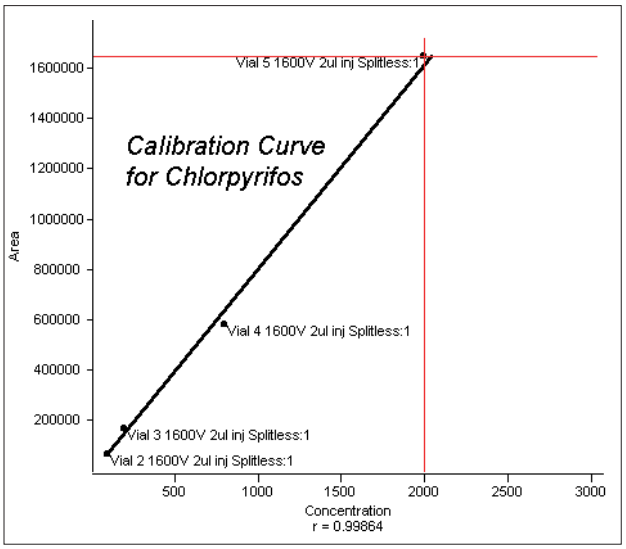

Figure 5. Calibration Curve for Chlorpyrifos.

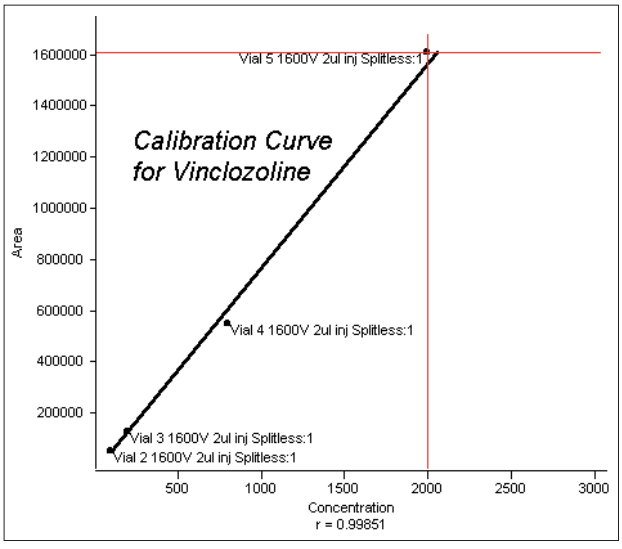

Figure 6. Calibration Curve for Vinclozoline.

By taking advantage of the deconvolution, it is possible to analyze for the target analytes while seeing other components of interest (such as unknowns) at the same time. An example of this is shown in Figure 7, where a phthalate was found in the sample matrix allowing the analyst to "see" the whole picture.

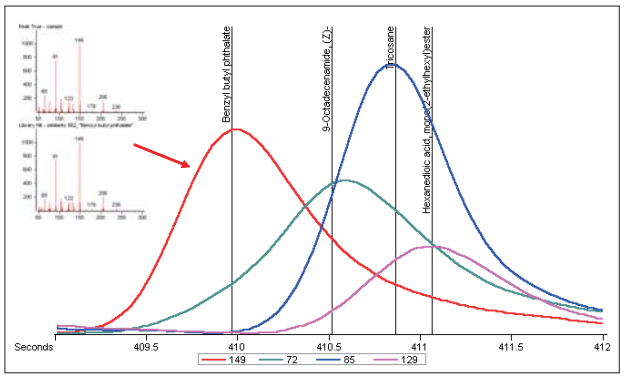

Figure 7. Other components of interest present in the matrix.

4. Conclusions

Using the Pegasus GC-TOFMS it is possible to analyze complex samples as well as detect unknown analytes of interest even when they elute with the sample matrix or are below the TIC level. By taking advantage of the Peak Find and Deconvolution algorithms it is possible to minimize the amount of time and effort spent cleaning and preparing the samples for analysis. The strength of the Pegasus GC-TOFMS for the analysis of these complex mixtures lies in its automated data handling capabilities. Peak finding, spectral determination, and library searching can be accomplished very rapidly, improving analytical results and productivity.

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LECO Corporation • 3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977
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