Reverse Searching of a Large Peak Table for Phosmet in Michigan Blueberries after Analysis by Gas Chromatography—Time-of-Flight Mass Spectrometry

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Key Words: GC-TOFMS, Flavor and Fragrance

1. Introduction

Time-of-flight mass spectrometry (TOFMS)—specifically its spectral reproducibility and acquisition speed (up to hundreds of spectra/second)—allows construction of Automated Peak Find and Spectral Deconvolution algorithms. For LECO's Pegasus GC-TOFMS, these algorithms are an inherent part of the data processing package, ChromaTOF®. Results from peak find and deconvolution are displayed in a Peak Table with headers such as Retention Time, Name, Library Match, Peak Area, etc.

In a complex sample such as a fruit or vegetable extract, a Peak Table with hundreds or even thousands of components can be generated, depending on the S/N parameter used to define the Peak Find. Trying to find pesticides in a large Peak Table (or complex chromatogram) can be handled in several ways. The obvious way is to have the actual pesticide standard on hand, analyze it, and have the retention time and mass spectrum available. Unfortunately, especially when there are thousands of pesticides on the market, it is not always possible to have a standard. A second option is to scroll through the whole Peak Table looking for the pesticide of interest. Sometimes, this presumes the analyst knows the IUPAC name for the pesticide as the NIST library may give that as a first hit. The third way to locate pesticides in matrix is to plot extracted ion chromatograms for the pesticide of interest, assuming that a mass spectrum is available for the pesticide being searched. In a complex chromatogram though, this can result in a tedious "hunt-and-peck" approach to locating the pesticide. The only way this system can work is if the spectral data has been acquired over a significant mass range, and will not work if selected ion recording has been used.

A better way is to let ChromaTOF do the work via its Reverse Search of the Peak Table. This feature allows quick location of pesticides in qualitative Peak Tables by selecting a pesticide mass spectrum from the NIST Library or other files that contain mass spectra. This application note illustrates Reverse Search for Phosmet, an organophosphate insecticide, in Michigan blueberries.

2. Experimental Conditions

Gas Chromatography: LECO Pegasus III GC-TOFMS
Column:
10 m x 0.18 mm x 0.18 µm DB-5 (J&W Scientific)
Carrier:
Helium at 0.4 ml/minute, constant flow
Injection:
1 µl splitless at 250°C, 60 second valve
Oven Program:
80°C (1 minute), 20°/minute to 320°
Total Run Time: 13 minutes

Mass Spectrometry

Ionization:	Electron ionization at 70eV
Source Temperature:	225°C
Stored Mass Range:	45 to 550 u
Acquisition rate:	20 spectra/second

Data Processing:
LECO ChromaTOF software with Automated Peak Find and Deconvolution

Extraction of Michigan Blueberries

The Florida-modified California Department of Food and Agriculture method was used to prepare an extract from fresh Michigan blueberries picked at the height of the season.

3. Results

Analysis of Blueberry Extract

The blueberry extract was analyzed by GC-TOFMS. A Data Processing Method (Figure 1) was used to automatically find peaks, deconvolute mass spectra, and library search the resulting spectra to produce a Peak Table containing over 450 compounds (Figure 2).

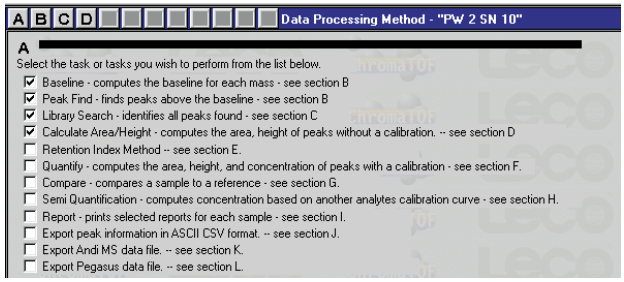

Figure 1. Data Processing Method showing Peak Find and Library Search.

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Peak Table - "Michigan Blueberries Screen:1"

Peak #	R.T. (seconds)	Name
1*	181.775	Aspartame
2	183.175	Dodecanoic acid, 2-(acetyloxy)-1-[(acetyloxy)methyl]ethyl ester
3	183.575	1-Dodecanamine
4	183.775	4-[4-Diethylamino-1-methylbutylamino]-1,2-dimethoxy-6-bromonaphtl
5	184.025	Unknown 1
6	184.325	Cathinone
7	184.475	D-Streptamine, O-6-amino-6-deoxy-à-D-glucopyranosyl-(1-4)-O-(3-
8	184.625	Unknown 2
9	185.025	Acetic acid, 4-acetoxy-5-acetoxymethyl-2-oxo-tetrahydro-furan-3-y
10	185.875	Valeraldehyde, 2,2-dimethyl-, oxime
11	186.425	Acetamide, N-(2-acetyl-3-oxo-4-isoxazolidinyl)-
12	186.625	Unknown 3
13	186.775	Unknown 4
14	186.925	9-Oxymo-2,7-bisethoxyfluorene
15	187.075	9-Oxymo-2,7-bisethoxyfluorene
16	187.275	2-Amino-4-hydroxypteridine-6-carboxylic acid
17	187.725	Unknown 5
18	188.575	Octacosanoic acid, methyl ester
19	188.775	Unknown 6
20	189.025	1-Nitro-2-acetamido-1,2-dideoxy-d-glucitol
438	764.125	Unknown 65
439	764.425	Unknown 66
440	765.825	Propanoic acid, 3,3'-thiobis-, didodecyl ester
441	766.525	Morphinan-4,5-epoxy-3,6-di-ol, 6-[7-nitrobenzofurazan-4-yl]amino-
442	767.425	2-Nonadecanone 2,4-dinitrophenylhydrazine
443	767.775	Unknown 67
444	768.225	1',1'-Dicarboethoxy-1á,2á-dihydro-17á-propionoxy(3'H)cyhcloprop['
445	769.025	Unknown 68
446	769.675	4'-Apo-á,psi.-carotenoic acid, methyl ester
447	769.875	9-Desoxo-9-x-acetoxy-3-desoxy-7.8.12-tri-O-acetylingol-3-one
448	770.375	1',1'-Dicarboethoxy-1á,2á-dihydro-17á-propionoxy(3'H)cyhcloprop['
449	770.525	9,12,15-Octadecatrienoic acid, 2,3-bis[(trimethylsilyl)oxy]propyl este
450	772.025	9,12,15-Octadecatrienoic acid, 2,3-bis[(trimethylsilyl)oxy]propyl este
451	773.575	Demecolcine
452	774.575	(22S)-21-Acetoxy-6á,11á-dihydroxy-16à,17à-propylmethylenedioxy
453	775.075	Unknown 69
454	775.375	Demecolcine
455	776.325	5-(5-{5-[Cyano-(9,9-dimethyl-1,4-dioxa-7-aza-spiro[4.4]non-7-en-8-
456	776.475	Unknown 70
457	777.875	Demecolcine
458	778.075	Lycopene

Figure 2. Qualitative Peak Table for blueberry extract that contains over 450 compounds. Peak Table is split to show the first few compounds and the last few compounds.

Phosmet has a mass spectrum in the NIST library (Figure 3), so one option for locating it in the Peak Table is to plot an extracted ion chromatogram for 160 and review each chromatographic peak to determine whether it is Phosmet. However, there are numerous peaks in the extracted ion chromatogram (Figure 4) and this would be a tedious task.

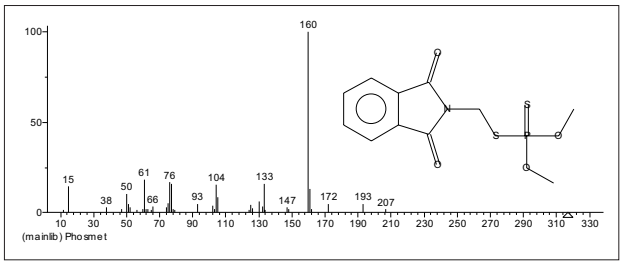

Figure 3. NIST Library mass spectrum for the insecticide Phosmet.

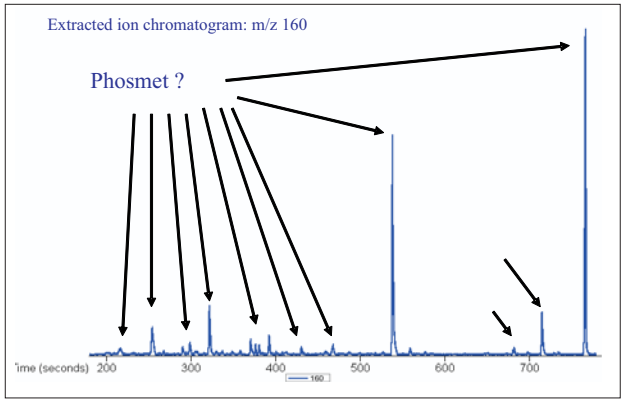

Figure 4. Looking for Phosmet in a blueberry extract by plotting a 160 m/z chromatogram.

Reverse Search of Peak Table for Phosmet

Reverse Search is a ChromaTOF feature that is enabled by choosing a mass spectrum from either a calibration, acquired sample, or a library (NIST or other library, including user-generated libraries). Other limiting criteria, such as minimum match value, can be attached to Reverse Search (Figure 5). Once the spectrum has been chosen, mouse-clicking "OK" starts the search of the Peak Table for Phosmet. The results for the Reverse Search of Phosmet in Michigan blueberries are displayed in Figure 6. Reverse Search of the whole Peak Table took only a few seconds. Subsequent purchase and analysis of a Phosmet standard confirmed the Reverse Search identification, with the Phosmet peak located at a retention time of 538.1 seconds (Figure 7).

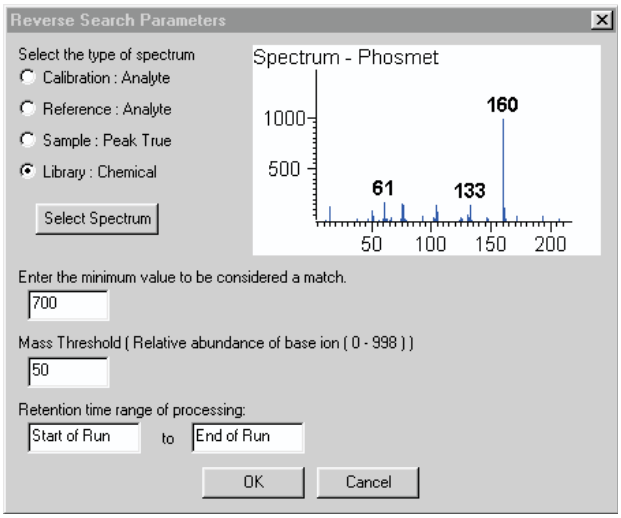

Figure 5. Reverse Search screen from ChromaTOF. The Phosmet mass spectrum has been chosen from the NIST library.

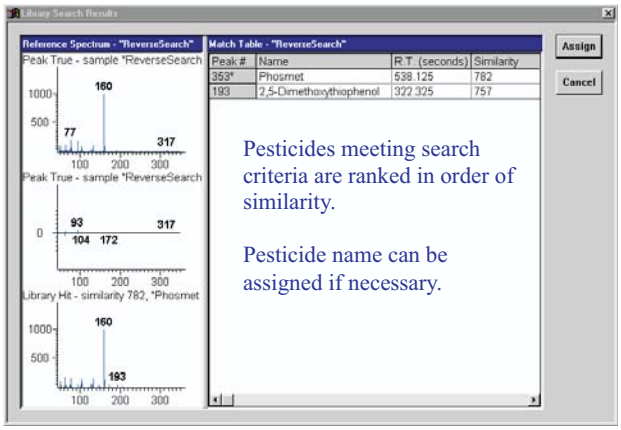

Figure 6. Results from Reverse Search for Phosmet in Michigan blueberries.

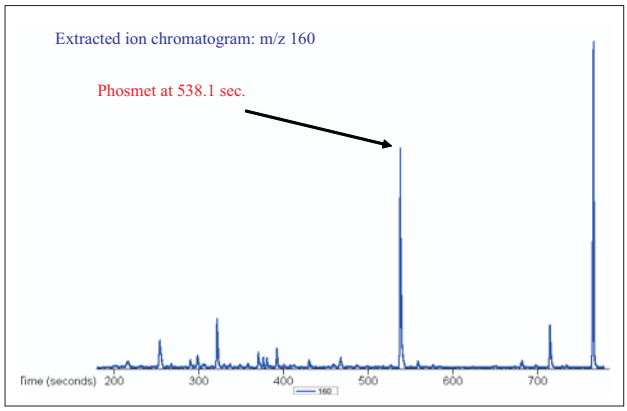

Figure 7. The Phosmet peak in Michigan blueberries as identified by Reverse Search with subsequent confirmation by standard analysis.

4. Conclusions

The power of Reverse Search when doing qualitative pesticide work is two-fold. First, the manual task of searching a large Peak Table for a suspected pesticide is eliminated. Second, and perhaps more importantly, it is possible to quickly review archived data for "new" pesticides, those pesticides that have likely not made it to target analyses yet because their registration is so recent. Of course this benefit can only be realized if a full mass spectrum is available, and with TOFMS, that is always the case.

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