Improvement to Targeted and Untargeted Pesticide Residue Analysis: Fast and Flexible Analyte Finding For GC-MS and GCxGC-MS

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Introduction

In recent years there has been a dramatic expansion in the number of pesticides utilized in food products, especially in emerging markets and commodities. With this expansion, analytical techniques with the ability to excel in non-targeted workflows have become increasingly important. However, large lists of target compounds can be challenging and time-consuming to maintain, often requiring multiple standard and sample injections in order to develop methods for different matrix interferences and analytical conditions. This presentation will showcase the creation and utilization of a target list of pesticides using software tools designed to make processing comprehensive data faster, easier, and more effective. With enhanced flexibility in data processing parameters, fewer injections are needed to fully develop an easy-to-update, automated data processing method for targeted and emerging analytes.

Pegasus® BT 4D

- StayClean® Ion Source
- Exceptional sensitivity of target and non-target analytes
- Industry leading deconvolution and non-target detection
- ChromaTOF® brand software – A single software for total hardware control and data processing
- Benchtop footprint

A dilution series from 0.2 ng/g to 2000 ng/g of GC Multi-residue Pesticide Mix 2 (Restek) in a bulk QuEChERS extract of spinach was prepared for GC-MS analysis, as well as a raw extract unfortified, to investigate the occurrence of incurred pesticides. The instrument conditions used are shown in the table below.

Method Conditions

Mass Spectrometer	**LECO Pegasus BT 4D**
Ion Source Temperature	250 °C
Mass Range	45-560 m/z
Acquisition Rate	8 spectra/sec (1D) 280 spectra/sec (GCxGC)
Gas Chromatograph	**Agilent 7890A w/LECO 2nd oven and dual stage, quad jet thermal modulator**
Injection	1µL Splitless, Inlet Temp 225 °C
Carrier Gas	He at 1.4 mL/min, Constant Flow
Columns	Primary 30 m x 0.25 mm x 0.25 µm df Rxi-5MS (Restek, Bellefonte PA) Secondary 1 m x 0.25 mm x 0.25 µm df Rtx-200 (Restek, Bellefonte PA)
Oven Program	Primary Oven 75 °C (1 min), 10.2 °C /min to 320 °C hold (8 min) Secondary Oven +5 °C Offset
Modulation Period (GCxGC)	2 seconds
Transfer Line	320 °C

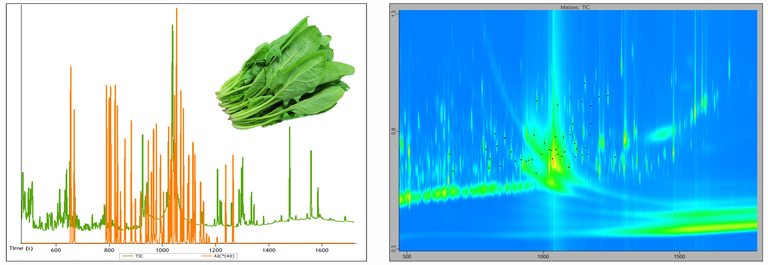

Figure 1. Overlay of the spinach extract spiked with pesticide mix at 100 ng/g. The 1D chromatogram (left) compares the TIC (green), comprised mostly of spinach extract overlaid with the targeted pesticides' signals (orange), multiplied by 40. The Contour Plot (right) is displaying the TIC for the GCxGC equivalent run. The black dots indicate the location of each target pesticide.

Example Workflow

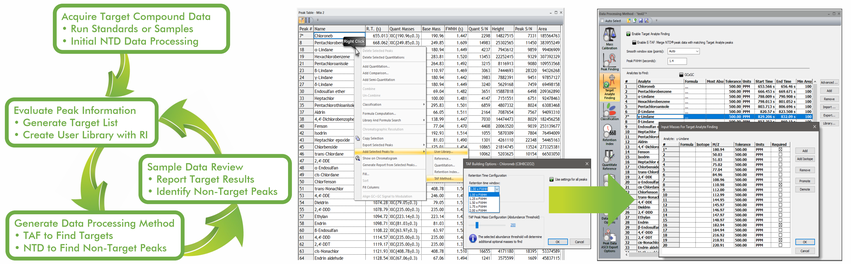

Figure 2. Simplified workflow for creating and maintaining a data processing method for both target and non-target analytes.

The entire target list can be easily created with just a few mouse clicks directly from an automatically generated Peak Table. The peak information, including the full, deconvoluted spectrum and RI information, can be similarly stored in a user library. Additional emerging targets can be added to the target list and user library as they are detected and identified. This simplified process allows users to update their methods, and curate target list and library as they go, eliminating the need to manually generate a large target list all at once.

Targeted and Non-Targeted Peak Find in a Single Method

By combining target screening and traditional peak deconvolution in a single method analysts can quickly filter, find, and report the targeted compounds. With the full mass range data and ChromaTOF's deconvolution algorithms you may also interrogate the same sample file for important, untargeted compounds

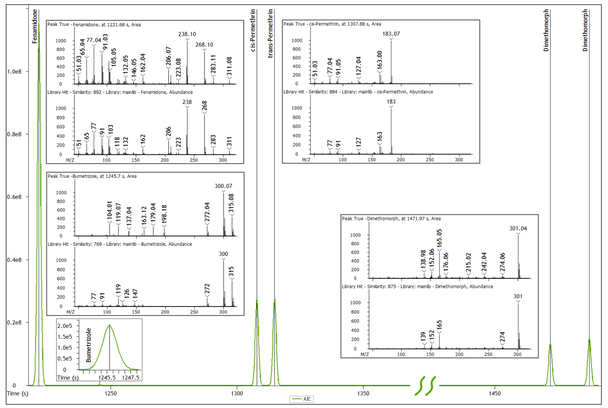

Figure 3. Two fungicides (Fenamidone and Dimethomorph), and the two isomers of Permethrin, a common insecticide, found in the spinach blank extract. Bumetrizole, a common UV stabilizer in plastics (likely from the QUeChERS tube), is also present. Now that these incurred compounds have been found they can be quickly added to the targeted section of the method for future screens.

Delivering the Right Results

Sensitive Target Screening - Traditional, 1D Separation

Table 1. Linearity data for halogenated pesticides in spinach extract. The Limit of Quantitation is the lowest standard in which the calculated concentration is within ±20% of the expected concentration. Ion ratio(s) at all levels are within ±30% of established targets. Chloroneb and Endrin Aldehyde had chemical interferences so their linearities are not reported even though they were spiked and detected in matrix.

Target Analyte	Correlation Coefficient	Curve Order	Limit of Quantitation in Matrix ng/g	Target Analyte	Correlation Coefficient	Curve Order	Limit of Quantitation in Matrix ng/g
Chloroneb	0.99919	1	1.0	cis-Chlordane	0.99979	1	0.5
Pentachlorobenzene	0.99787	1	0.2	Chlorfenson	0.99873	1	5.0
α-Lindane	0.99962	1	1.0	trans-Nonachlor	0.99936	1	0.2
Hexachlorobenzene	0.99944	1	0.2	4,4'-DDE	0.99984	1	0.2
Pentachloroanisole	0.99922	1	0.5	Dieldrin	0.99895	1	5.0
β-Lindane	0.99941	1	1.0	2,4'-DDD	0.99959	1	1.0
γ-Lindane	0.99984	1	5.0	Ethylan	0.99992	1	0.5
δ-Lindane	0.99961	1	5.0	Endrin	0.99954	1	5.0
Endosulfan ether	0.9994	1	1.0	β-Endosulfan	0.99976	1	5.0
Heptachlor	0.99951	1	5.0	4,4'-DDD	0.99987	1	5.0
Pentachlorothioanisole	0.99941	1	0.5	2,4'-DDT	0.99572	1	5.0
Aldrin	0.99946	1	1.0	cis-Nonachlor	0.99927	1	0.5
DCBP	0.99977	1	1.0	Methoxychlor olefin	0.99952	1	1.0
Fenson	0.99983	1	5.0	Endosulfan sulfate	0.99942	1	1.0
Isodrin	0.99953	1	1.0	4,4'-DDT	0.99772	1	5.0
Heptachlor epoxide	0.99964	1	1.0	o,p'-Methoxychlor	0.99795	1	0.5
trans-Chlordane	0.99994	1	0.5	Endrin ketone	0.9987	1	5.0
2,4'-DDE	0.99856	1	1.0	Tetradifon	0.99952	1	5.0
α-Endosulfan	0.99837	1	5.0	Mirex	0.99964	1	0.5

Improved GCxGC Separation

By leveraging GCxGC's superior chromatographic resolution you can often separate target analytes from matrix interferences or other target compounds. In Figure 4 below, you can see the 1D and GCxGC quantitation curves for Chloroneb. Thanks to the improvements from GCxGC peak focusing and chromatographic resolution, Chloroneb is separated from the nearby matrix interference. This results in dramatic improvements in overall sensitivity, linearity, and quantitation accuracy.

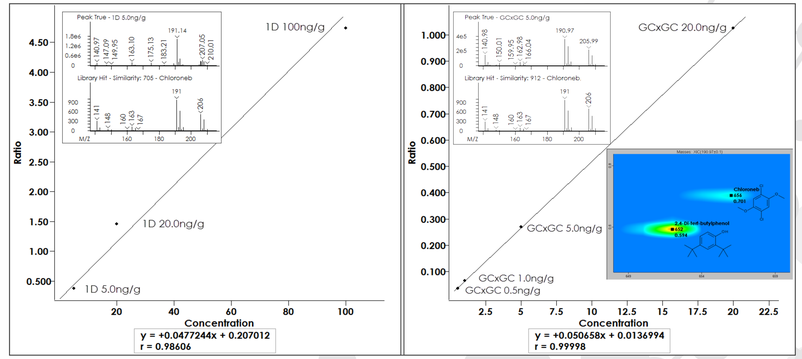

Figure 4. Comparison of the 1D and GCxGC quantitation curves for Chloroneb. Spectra for the 5.0 ng/g standards are shown in their respective plots. Traditional peak searching could not find the Chloroneb in the 1D data. A manually added, background subtracted spectra is shown instead. Obvious matrix influences in mass accuracies and ion ratios can be seen in the 1D spectrum compared to the high fidelity, GCxGC spectrum.

Conclusions

- The Pegasus BT 4D delivers a superior combination of quantitative and qualitative information in the same sample injection without sacrificing sensitivity
- Target Analyte Find lists are easy to setup and maintain
- LECO's industry-leading NonTarget Deconvolution® (NTD®) feature software provides clean mass spectra with unsurpassed spectral fidelity for library searching
- GCxGC allows for improved chromatographic resolution, peak detection, and sensitivity