Fast Pesticide Residue Analysis in Food with a New Benchtop GC-TOFMS: Pegasus® BT

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Key Words: Pesticide Residue Analysis, *Pegasus* BT, Quantitative Analysis, Qualitative Analysis, High Throughput

1. Introduction

Sample throughput including data processing is an important factor to consider when performing routine analyses. In this application note we used the speed and power of TOFMS to shorten the runtime of a standard pesticide residue analysis by using a 15 m column instead of a standard 30 m column without loss of analytical performance. The Restek EZGC Method Translator suggested parameters for the 15 m column which significantly shortened the analysis time when coupled with version 5.0 of LECO's ChromaTOF® brand software to perform concurrent qualitative and quantitative analysis. One objective was to maximize throughput without introducing a significant number of additional chromatographic coelutions not separable by deconvolution. The goal was for the same number of spiked pesticides to be detected under both analytical methods. LECO's proprietary deconvolution algorithm, embodied as NonTarget Deconvolution™, was leveraged to maintain exceptional peak fidelity of the qualitative analysis, while the Target Analyte Find feature was utilized for robust quantitation and to establish method detection limits for organonitrogen pesticides spiked in QuEChERS strawberry extracts.

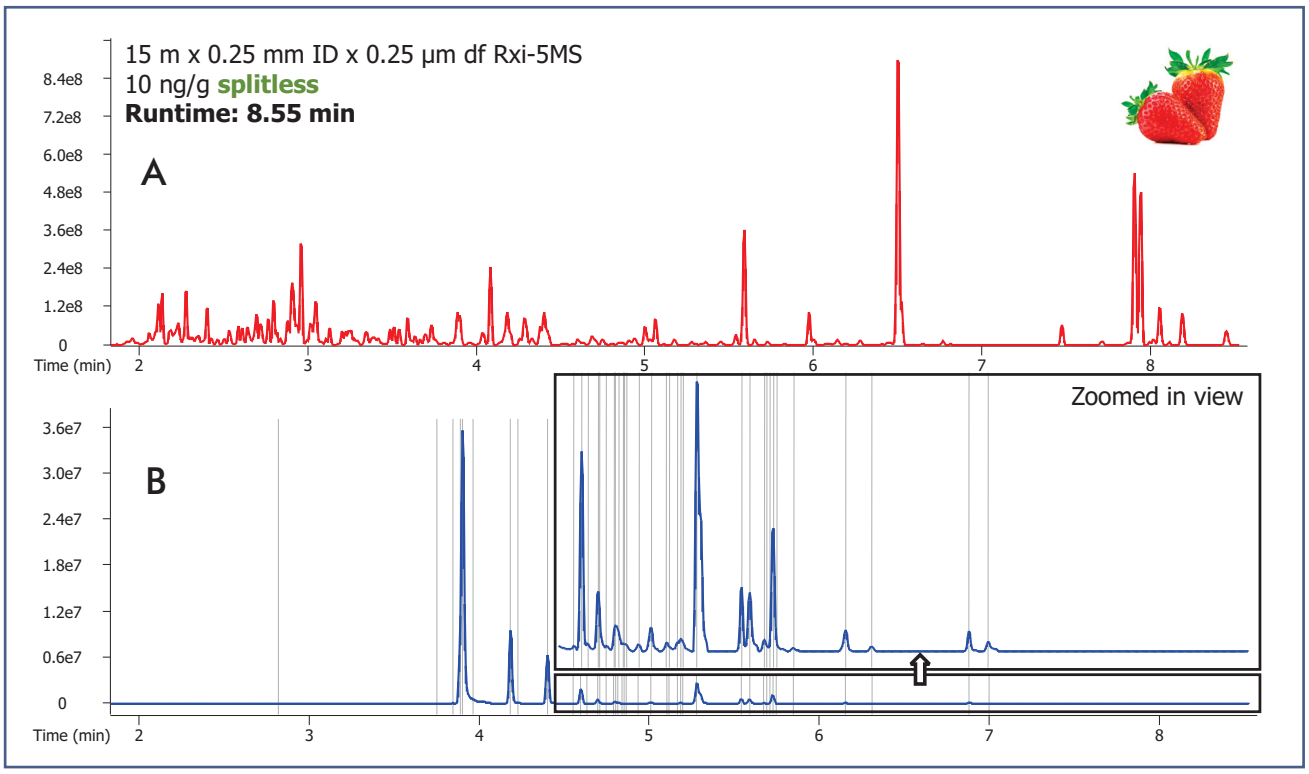

Figure 1. Analytical ion chromatograms (AIC) of a fortified strawberry QuEChERS extract; (A) for analytes reported using Peak Find (non-target), and (B) analytes reported using Target Analyte Find. The intense peaks in the target trace represent analytes that were incurred in the matrix in addition to the 10 ppb spiked. The pesticides and their LODs are shown in Table 2.

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2. GC Method for Fast Run Time

A bulk extract of strawberries purchased from a local grocery store was generated using methods described elsewhere (http://www.restek.com/pdfs/GNAN1097A.pdf). A dilution series from 5000 ng/g to 0.10 ng/g of GC Multiresidue Pesticide Mix #5 (Restek) in the bulk extract was prepared in duplicate for GC-MS analysis, as well as a raw extract unfortified and without cleanup to investigate the occurrence of incurred pesticides.

Table 1. GC-TOFMS (*Pegasus* BT) Conditions

Gas Chromatograph	**LECO L-PAL3 Autosampler, Agilent 7890B GC**
Injection	1 µL pulsed splitless, 20 psi for 0.7min, GC injector @ 250°C
Carrier Gas	He @ 2.0 mL/min, Constant Flow
Column	Rxi-5ms, 15 m x 0.25 mm ID x 0.25 µm df (Restek, Bellefonte, PA, USA)
Oven Program	70°C (0.7 min), to 150°C @ 60°C/min, to 330°C @ 30°C/min (0.5 min)
Transfer Line	300°C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	225°C
Mass Range	45-650 m/z
Acquisition Rate	10 spectra/s

3. Excellent Linearity and Lower Limits of Detection in Matrix

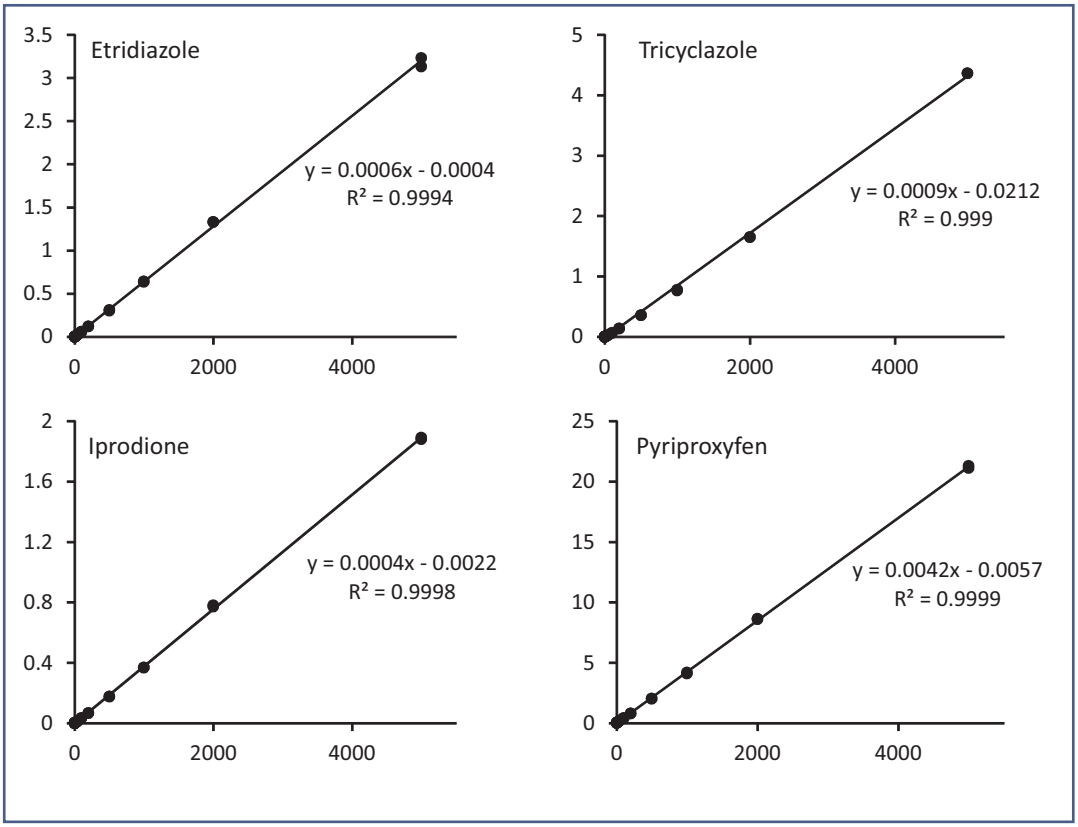

Figure 2. Calibration curves of four representative pesticides in strawberry from their LOD to 5000 ng/g.

Table 2. Calibration curve linearity and limits of detection for organonitrogen pesticides in strawberry from 0.10 to 5000 ng/g using Target Analyte Find on a Rxi-5ms, 15 m x 0.25 mm ID x 0.25 µm df column.

Name	CAS	R.T. (min)	R^2	LOD	Units
Etridiazole	2593-15-9	2.818	0.9994	0.50	ng/g
Atrazine	1912-24-9	3.750	0.9992	0.20	ng/g
Terbuthylazine	5915-41-3	3.843	0.9996	0.10	ng/g
Terbacil	5902-51-2	3.963	0.9995	0.10	ng/g
Vinclozoline	50471-44-8	4.225	0.9992	0.10	ng/g
MGK 264	113-48-4	4.635	0.9992	0.10	ng/g
MGK 264 isomer	113-48-4	4.708	0.9993	5.00	ng/g
Penconazole	66246-88-6	4.748	0.9999	0.10	ng/g
Fipronil	120068-37-3	4.793	0.9997	0.10	ng/g
Procymidone	32809-16-8	4.853	0.9998	0.20	ng/g
Paclobutrazol	76738-62-0	4.935	0.9994	0.10	ng/g
Flutriafol	76674-21-0	5.012	0.9996	0.10	ng/g
Fludioxonil	131341-86-1	5.100	0.9997	0.10	ng/g
Tricyclazole	41814-78-2	5.118	0.9990	1.00	ng/g
Myclobutanil	88671-89-0	5.165	0.9998	0.10	ng/g
Flusilazole	85509-19-9	5.183	0.9996	0.10	ng/g
Bupirimate	41483-43-6	5.198	0.9994	0.10	ng/g
Chlorfenapyr	122453-73-0	5.282	0.9991	0.10	ng/g
Lenacil	2164-08-1	5.602	0.9997	0.10	ng/g
Hexazinone	51235-04-2	5.675	0.9998	0.10	ng/g
Tebuconazole	107534-96-3	5.693	0.9998	0.10	ng/g
Propargite	2312-35-8	5.713	0.9991	2.00	ng/g
Iprodione	36734-19-7	5.848	0.9998	0.10	ng/g
Pyriproxyfen	95737-68-1	6.146	0.9999	0.10	ng/g
Fenarimol	60168-88-9	6.312	0.9998	0.20	ng/g
Etofenprox	80844-07-1	6.885	0.9996	0.10	ng/g
Fluridone	59756-60-4	6.998	0.9994	0.10	ng/g

Note: Captan, captafol, folpet, cyprodinil, pyrimethanil, triadimefon, triadimenol, and triflumizole were incurred in the strawberries, so their linearity and LOD were not reported even though they were spiked into the matrix and detected.

The LOD was ≤ 0.1 ppb for 74% of the pesticides in Table 2, with all but two of the pesticides having an LOD less than 1.0 ppb in strawberry. The coefficient of determination (R^2) was greater than 0.999 for all of the pesticides in this study. The combination of excellent linearity over greater than 4 orders of magnitude of dynamic range and sub ppb detection limits in matrix demonstrate that the *Pegasus* BT is a powerful tool for quantitative pesticide residue analysis.

4. Identify More Peaks with Confidence Using *NonTarget Deconvolution*

The automated deconvolution (Peak Find) example in Figure 3 (shown below) demonstrates the software's ability to accurately identify analytes at low concentration in matrix. The library score for bupirimate was 874 (out of 1000) at a concentration of 20 ng/g.

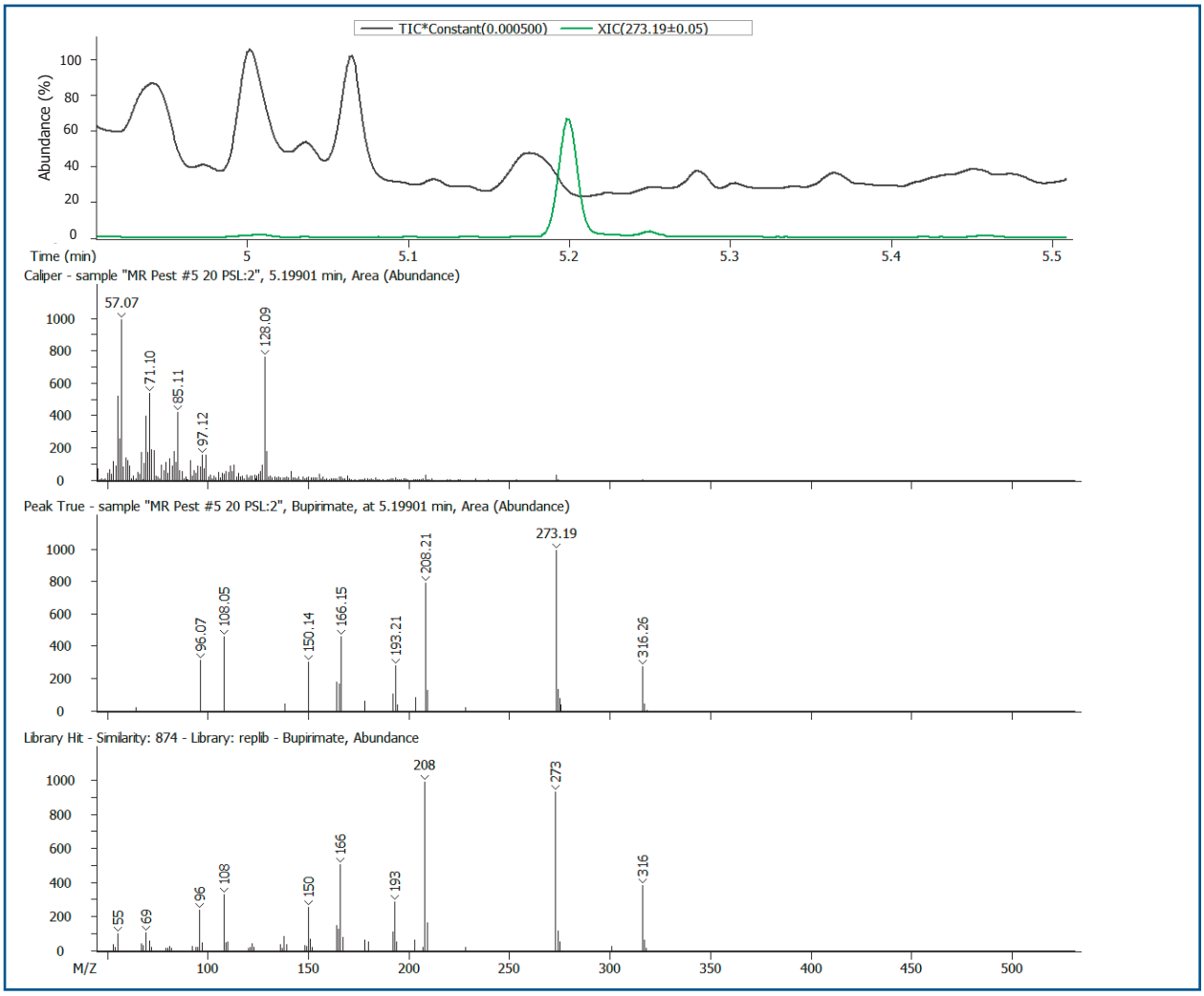

Figure 3. Analysis of 20 pg on column of bupirimate in strawberry on a 15 m x 0.25 mm ID x 0.25 µm df Rxi-5MS. (A) Overlay of the scaled total ion chromatogram (TIC, gray) and extracted ion chromatogram (XIC, green) of m/z 273.19 ±0.05; (B) mass spectrum of the raw data at the apex of the green trace; (C) deconvoluted mass spectrum using the NonTarget Deconvolution feature in ChromaTOF; (D) library spectrum from NIST 14 with an excellent similarity score.

Figure 4 and Table 3 on the following page show *NonTarget Deconvolution* for the qualitative analysis of naturally occurring flavor and fragrance compounds in strawberry, as well as incurred pesticides and spiked internal standards with library similarity scores greater than 900 (out of 1000). Qualitative analysis may be used to screen for additional pesticides not included in the list of calibration standards, which may be subsequently semi-quantified, or to tentatively identify and characterize other aspects of the sample, in this case, flavor and fragrance characteristics of strawberries.

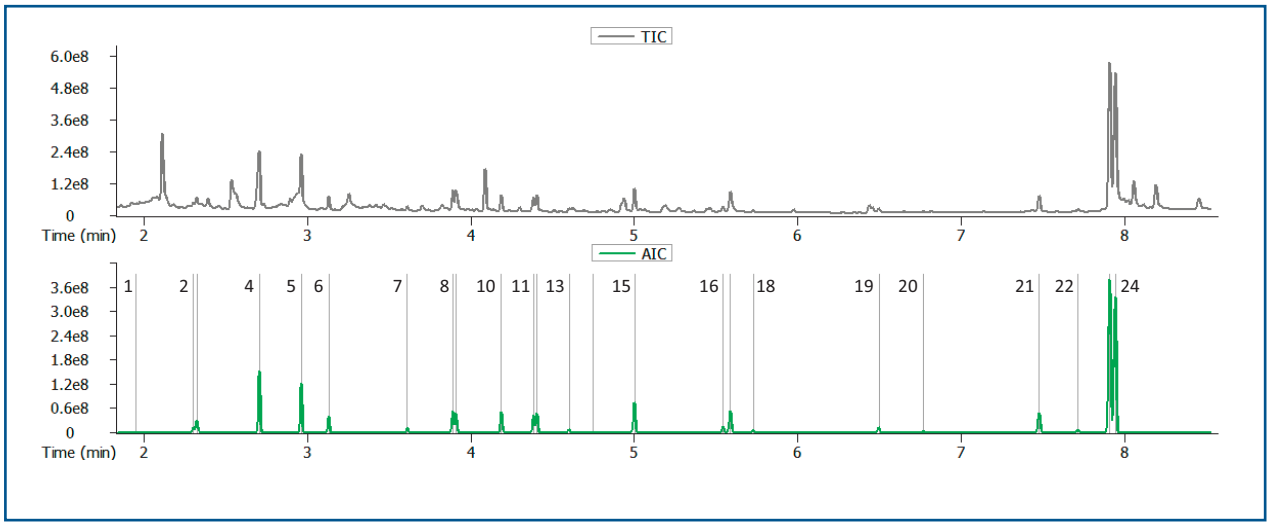

Figure 4. Non-target analysis of a strawberry QuEChERS extract without cleanup and with instrument performance standards spiked at 500 pg. TIC and AIC highlighting peaks with a NIST library similarity score > 900.

Table 3. Tentative identifications for the peaks numbered in Figure 4.

#	Name	CAS	Formula	R.T. (min)	Similarity	Type	S/N
1	N-Nitrosodimethylamine	62-75-9	$C_2H_6N_2O$	1.949	958	Non-Target	86
2	p-Methylcatechol	452-86-8	$C_7H_8O_2$	2.301	949	Non-Target	1006
3	Salicylic acid	69-72-7	$C_7H_6O_3$	2.322	932	Non-Target	1138
4	trans-Cinnamic acid	140-10-3	$C_9H_8O_2$	2.705	937	Non-Target	1143
5	2,5-Di-tert-butylphenol	5875-45-6	$C_{14}H_{22}O$	2.962	918	Non-Target	4461
6	Nerolidol	7212-44-4	$C_{15}H_{26}O$	3.130	930	Non-Target	633
7	Indole-3-acetaldehyde	2591-98-2	$C_{10}H_9NO$	3.611	901	Non-Target	1265
8	PCB 18	38444-73-4	$C_{12}H_7Cl_3$	3.890	933	Spiked	1518
9	Pyrimethanil	53112-28-0	$C_{12}H_{13}N_3$	3.909	947	Incurred	2668
10	PCB 28	55712-37-3	$C_{12}H_7Cl_3$	4.187	937	Spiked	1827
11	n-Hexadecanoic acid	57-10-3	$C_{16}H_{32}O_2$	4.384	946	Non-Target	808
12	PCB 52	41464-47-5	$C_{12}H_6Cl_4$	4.404	919	Spiked	1686
13	Triphenylmethane	519-73-3	$C_{19}H_{16}$	4.601	915	Spiked	862
14	Cyclic octaatomic sulfur	10544-50-0	S_8	4.745	910	Non-Target	98
15	Octadecanoic acid	57-11-4	$C_{18}H_{36}O_2$	5.001	953	Non-Target	1069
16	TDCPP	13674-87-8	$C_9H_{15}Cl_6O_4P$	5.544	944	Spiked	940
17	9-Octadecenamide, (Z)-	301-02-0	$C_{18}H_{35}NO$	5.589	905	Non-Target	1382
18	Triphenyl phosphate	115-86-6	$C_{18}H_{15}O_4P$	5.729	915	Spiked	837
19	Stearic acid 1-monoglyceride	123-94-4	$C_{21}H_{42}O_4$	6.498	909	Non-Target	283
20	Supraene	7683-64-9	$C_{30}H_{50}$	6.772	903	Non-Target	290
21	Vitamin E	59-02-9	$C_{29}H_{50}O_2$	7.479	929	Non-Target	2721
22	Campesterol	474-62-4	$C_{28}H_{48}O$	7.718	914	Non-Target	549
23	Sitosterol	83-46-5	$C_{29}H_{50}O$	7.911	911	Non-Target	1611
24	Isofucosterol	481-14-1	$C_{29}H_{48}O$	7.944	924	Non-Target	2329

Delivering the Right Results

5. Conclusions

The *Pegasus* BT delivers a superior combination of quantitative and qualitative information in the same sample injection. With TOFMS, all of the masses are collected all the time without compromising sensitivity and without mass spectral skewing, resulting in unsurpassed spectral fidelity. LECO's industry-leading spectral deconvolution software, *ChromaTOF,* leverages this high-quality mass spectral information to provide uncontaminated mass spectra for compound identification by means of commercial library databases or for spectral interpretation. Additionally, Target Analyte Find was demonstrated to quantitate across more than 4 orders of magnitude in food matrix and up to 100 times lower than the regulatory guideline of 10 ng/g for the majority of pesticides in this study with a run time of less than 9 minutes.

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