Fast Pesticide Residue Analysis Using a Novel Benchtop Time-of-Flight Mass Spectrometer

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Introduction

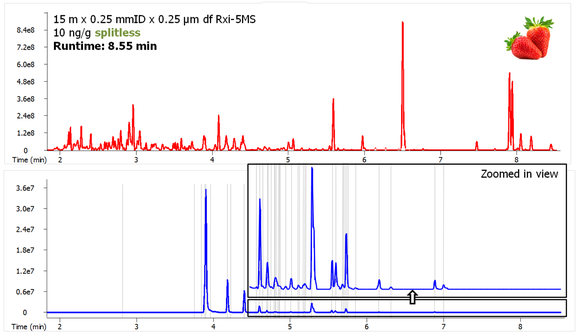
- Primary objective was to maximize throughput without introducing a significant number of additional chromatographic coelutions not separable by deconvolution, while transitioning from a standard 30 m column to a 15 m column.
- LECO's proprietary NonTarget Deconvolution™ (NTD)™ was leveraged to maintain exceptional peak fidelity of the qualitative analysis, while the Target Analyte Find data processing feature was utilized for robust quantitation and to establish method detection limits for organonitrogen pesticides spiked in QuEChERS strawberry extracts.

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. The instrument conditions used are shown in the table below.

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 mmID 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



Analytical ion chromatograms (AIC) of a fortified strawberry QuEChERS extract; (Red, top) for analytes reported using NonTarget Deconvolution (NTD) and (Blue, bottom) analytes reported using Target Analyte Find. The intense peaks in the Blue trace represent analytes that were incurred in the matrix in addition to the 10 ppb spiked. Spiked pesticides and their LODs are shown in Table I.

Excellent Linearity and Low LODs in Matrix

Calibration curves for four representative pesticides in strawberry.

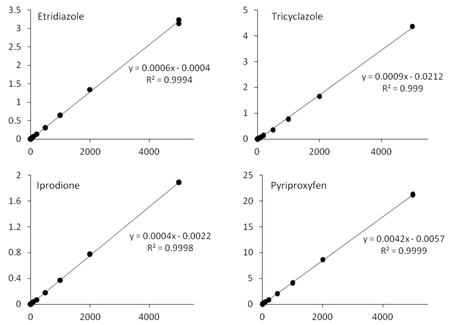


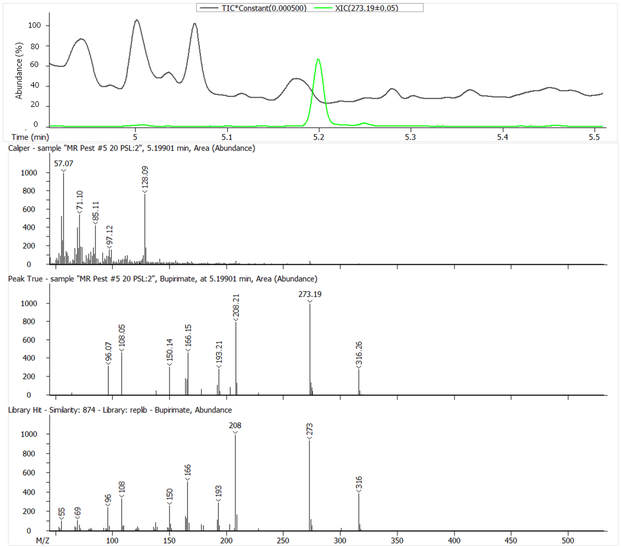
Table I. Calibration curve linearity and LODs for organonitrogen pesticides in strawberry from 0.10 to 5000 ng/g using Target Analyte Find on a Rxi-5ms, 15 m x 0.25 mm ID x 0.25 µm df column.

Name	CAS #	R.T. (min)	R²	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	0.20	ng/g
Terbacil	5902-51-2	3.963	0.9995	0.50	ng/g
Vinclozoline	50471-44-8	4.225	0.9992	0.20	ng/g
MGK 264	113-48-4	4.635	0.9992	0.20	ng/g
MGK 264 isomer	113-48-4	4.708	0.9993	5.00	ng/g
Penconazole	66246-88-6	4.748	0.9999	0.20	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	0.20	ng/g
Flutriafol	76674-21-0	5.012	0.9996	0.50	ng/g
Fludioxonil	131341-86-1	5.100	0.9997	0.20	ng/g
Tricyclazole	41814-78-2	5.118	0.9991	1.00	ng/g
Myclobutanil	88671-89-0	5.165	0.9998	0.10	ng/g
Flusilazole	85509-19-9	5.183	0.9996	0.20	ng/g
Bupirimate	41483-43-6	5.198	0.9994	0.10	ng/g
Lenacil	2164-08-1	5.602	0.9997	0.50	ng/g
Hexazinone	51235-04-2	5.675	0.9998	0.20	ng/g
Tebuconazole	107534-96-3	5.693	0.9998	0.50	ng/g
Propargite	2312-35-8	5.713	0.9991	2.00	ng/g
Iprodione	36734-19-7	5.848	0.9994	0.20	ng/g
Pyriproxyfen	95737-68-1	6.146	0.9998	0.50	ng/g
Fenarimol	60168-88-9	6.312	0.9998	0.20	ng/g
Etofenprox	80844-07-1	6.885	0.9996	0.20	ng/g
Fluridone	59756-60-4	6.998	0.9992	0.10	ng/g

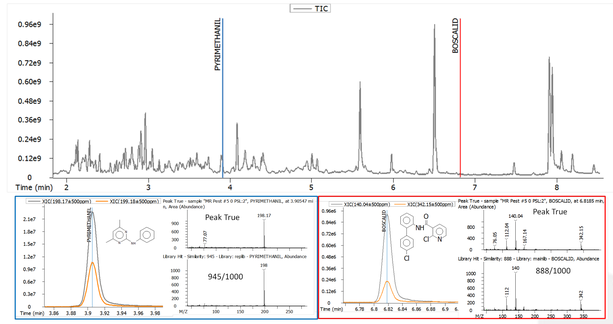
Note: Captan, captafol, chlorfenapyr, folpet, cyprodinil, pyrimethanil, triadimefon, triadimenol, and triflumizole were incurred in the strawberry matrix or had chemical interferences that effected the low end of their calibration curves, so their linearity and LOD were not reported even though they were spiked and detected.

Non-Target Full Mass Spectra All the Time

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 column demonstrating the software's ability to accurately identify analytes at low concentration in matrix.

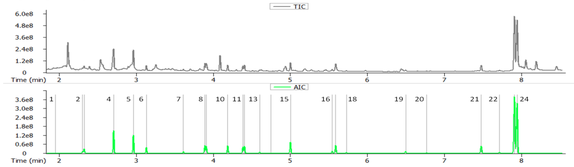


Examples of incurred pesticides in strawberry identified using NTD.



NonTarget Deconvolution

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



Representative list of putatively identified peaks from the above figure.

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

Qualitative analysis may be used to screen for additional pesticides or to tentatively identify and characterize other aspects of the sample (e.g. in this case, flavor and fragrance characteristics of strawberries).

Conclusions

- The Pegasus BT delivers a superior combination of quantitative and qualitative information in the same sample injection without sacrificing sensitivity.
- 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.
- LECO's industry-leading spectral deconvolution software provides uncontaminated mass spectra with unsurpassed spectral fidelity for library searching.

Delivering the Right Results