Significant Improvement in GCMS Screening of Pesticides by Use of a High Efficiency Ion Source and Spectral Deconvolution

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Introduction

Routine pesticide residue analysis in environmental and food samples requires low-level detection with confident identification, which may be accomplished by the use of GCMS in full scan mode and spectral deconvolution with a program such as AMDIS. Improved full scan screening capability is made possible by the use of a mass spectrometer equipped with a High Efficiency Source (HES), which increases the number of ions that are created and transferred into the quadrupole analyzer. This increase in response translates into better sensitivity and thus more targets found with good NIST library matches. Identification in food samples at 10 ng/g is now possible for many residues using scan mode as was demonstrated by analysis of tomato extract spiked with over 200 pesticides.

Method

Sample Preparation: Extraction/Partitioning (AOAC)

Refer to GC/MS/MS "Pesticide Analysis Reference Guide", Agilent Technologies publication 5991-2389EN.

2 g of homogenized tomato, 2 ceramic homogenizers
2 mL ACN (1% HAc), vortex
1 g of Agilent Bond Elut AOAC salts; shake and centrifuge

Dispersive SPE:

Transfer 1 mL of extract to 2 mL Agilent Bond Elut dSPE: General fruit & veg [PSA] or Universal [PSA, C18, GCB]
vortex and centrifuge
transfer 250 uL to vial for analysis

QC samples were fortified with a 1 µg/mL pesticide stock solution (>200 pesticides) yielding concentrations of 10 and 100 ng/g.

Analysis by GC/MS Pesticides Analyzer

Analysis was performed using the Agilent 5977B GC/MSD equipped with the High Efficiency Source (HES) operated in scan mode. The instrument was set up and operated as a GC/MS Pesticides Analyzer. The 7890 GC was equipped with a split-splitless inlet and an HP-5MSUI column, 30m x 250µm x 0.25µm, which was ramped from 70°C to 280°C over a 42 minute analysis. Backflushing was accomplished using a Purged Ultimate Union controlled by an Aux EPC module. The source temperature was 250°C and the quadrupole was 150°C. The instrument was autotuned. Following analysis with the HES, the source was replaced with a standard extractor source (also autotuned) and the analysis repeated for comparison.

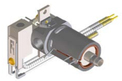
Method, cont.

New 5977B High Efficiency Source

5977B High Efficiency Source, magnet removed

More intense electron beam x Longer path length for electron beam/effluent interaction

= Up to 20x More Ions Produced



5977A Extractor Source

Spectral deconvolution was by Deconvolution Reporting Software (DRS) which utilizes AMDIS. A Minimum Match Factor of 80 was set for searches against a custom library, and NIST hits (reverse match) were reported as well. An excerpt of an example report is shown below; note that this particular analysis was not quantitative and so the "amount" column is ignored.

Example MSD Deconvolution Report, 10 ng/g in tomato

MSD Deconvolution Report
Sample Name: 10ppb_tomato_HES_9-1-15_03
Data File: C:\Users\michurley\Desktop\F\El - pesticides 2015\9.2.15 HES 250 tomato sequence\10ppb_tomato_HES_9-1-15_01.D
Date/Time: 11:29:59 AM Thursday, September 03, 2015

Adjacent Peak Subtraction = 1
Resolution = Medium
Sensitivity = High
Shape Requirements = Medium

The NIST library was searched for the components that were found in the AMDIS target library.

			Amount (ng)		AMDIS		NIST	
R.T.	Cas #	Compound Name	Chem station	AMDIS	Match	R.T. Diff sec	Reverse Match	Hit Num.
3.503	108952	Phenol	1.22					
5.8156	62737	Dichlorvos			85	-0.9	79	1
6.7388	1194656	2,6-Dichlorobenzonitrile			92	-0.6	91	2
7.0875	92524	Biphenyl			88	-1.0	84	2
8.5873	33704619	Cashmeran			81	-2.0	71	21
8.9269	608935	Pentachlorobenzene	0.32		80	-1.2	78	1
9.9753	84662	Diethyl phthalate	2.99		97	1.0	95	1

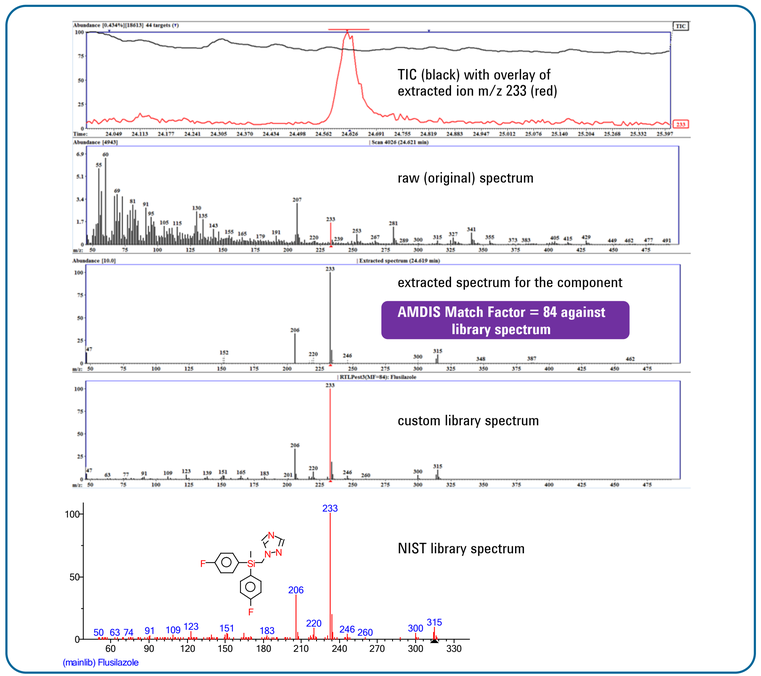
(continued)

27.0060	50293	p,p'-DDT			81	1.4	76	2
28.5167	732116	Phosmet			83	0.9	72	1
28.6428	18181801	Bromopropylate			83	1.6	90	1
28.8626	82657043	Bifenthrin			82	1.4	89	1
29.555	131983727	Triticonazole	0.05					
29.6703	117817	Bis(2-ethylhexyl)phthalate	0.95		88	1.3	82	6
29.7404	21609905	Leptophos			81	0.7	58	1
29.8441	2385855	Mirex			84	0.5	81	1
31.5375	96489713	Pyridaben	0.77		86	0.8	87	1
31.6493	136426545	Fluquinconazole			80	-0.4	68	1
13.722		Phenanthrene-d10	10					

Classical Spectra With Excellent Library Match Scores

Analysis of 10 pg flusilazole in tomato injected using DRS/AMDIS

The HES allows for classical spectra which are easily searched within NIST libraries. Analysis of flusilazole in tomato using AMDIS consists of a TIC with an overlay of diagnostic mass ion *m/z* 233. Note the good signal strength based on S/N when only 10 pg is injected (red trace). Below this, it is seen that identification would not be possible based on the raw, or un-cleaned, spectrum due to extraneous masses from the matrix and background. However, when a component is identified in AMDIS based on how well individual mass ion profiles match up based on exact retention time, S/N, peak shape, and component width setting or resolution, a spectrum is reconstructed for that component. This spectrum, designated as an extracted spectrum, is then searched against a library such as a custom, in-house library or that from NIST. In the case of flusilazole presented here, the match score against a custom library is 84 and the NIST reverse match score is 73.



More Targets Identified With the High Efficiency Source

The table below shows the number of AMDIS targets identified in tomato spiked at 10 and 100 ng/g using the extractor source and the HES using a Minimum Match Factor of 80. The amount of pesticides injected is 10 and 100 pg, respectively. The NIST hit number breakdown (distribution) is given for categories 1st, 2nd and ≥3 hit. Identified targets that were not spiked into tomato but had an AMDIS match score ≥ 80 and NIST hit # ≤3 are also listed.

	5977A Extractor source		5977B High Efficiency Source	
	10 ng/g	100 ng/g	10 ng/g	100 ng/g
Number of targets with AMDIS score ≥ 80	0	91	38	164
NIST hit breakdown:				
#1 hits	0	63	26	144
#2 hits	0	12	7	14
hits ≥ #3	0	16	5	6
Not spiked, with hit# ≤ 3	2*	4**	2*	8***

*diethyl phthalate, benzophenone

** benzilamide, benzophenone, quintozene metabolite (pentachlorophenyl methyl sulfide), indoxacarb and dioxacarb decomposition product [Phenol, 2-(1,3-dioxolan-2-yl)-]

*** diethyl phthalate, benzophenone, fonofos, phenol, phthalic acid, di(oct-3-yl) ester, phthalimide, quintozene metabolite (pentachlorophenyl methyl sulfide), indoxacarb and dioxacarb decomposition product [Phenol, 2-(1,3-dioxolan-2-yl)-]

Conclusions

Fast and accurate screening of pesticides is improved with the Agilent Pesticide DRS Screening GC/MSD Analyzer, which can now be configured with the new 5977B GC/MSD with the High Efficiency Source. When combined with Deconvolution Reporting Software, positive identification in full scan mode for many targets in food at a concentration of 10 ng/g was made possible.

References

1. NIST Standard Reference Database 1A, NIST/EPA/NIH Mass Spectral Library (NIST 14) and NIST Mass Spectral Search Program (Version 2.2), User's Guide: http://www.nist.gov/srd/upload/NIST1aVer22Man.pdf

2. Philip L. Wylie, "Screening for 926 Pesticides and Endocrine Disruptors by GC/MS with Deconvolution Reporting Software and a New Pesticide Library," Agilent Technologies publication 5989-5076EN.