

# The GC/MS/MS Analyzer and the Pesticides and Environmental Pollutants MRM Database

# **Application Note**

Food Safety and Environmental

## Abstract

Based on an Agilent 7890A GC System and an Agilent 7000 Series Triple Quadrupole GC/MS, these GC/MS/MS Multiresidue Analyzers were developed to simplify a lab's startup process. The database has an average of eight MRM transitions with relative intensities for each compound to provide alternative measurements for minimizing matrix interferences. Easy-to-use tools, as well as tutorial videos are included in the database to build an MRM acquisition method based on your list of compound CAS numbers in less than 5 minutes.

# Introduction

Pesticide residue analysis is a complex task requiring the analyst to search for dozens, or even hundreds, of compounds in a wide variety of crop or environmental matrices. Triple Quadrupole GC/MS (GC/MS/MS) provides excellent sensitivity and selectivity in analyzing complex matrices. Agilent Technologies offers several preconfigured and pretested GC/MS/MS analyzers to simplify a lab's startup process. The analytical capability of a lab, however, is largely determined by the completeness of the MS/MS MRM transitions in an acquisition method. Agilent Technologies developed an MS/MS MRM Pesticides and Environmental Pollutants Database (G9250AA) of over 1,070 compounds to address many of the limitations most labs are facing. This database is in the form of a spreadsheet for ease-of-use. Significant efforts were invested to acquire multiple transitions (eight on average, with relative intensities) of each compound in the database to work around matrix interferences.



## Author

Chin-Kai Meng Agilent Technologies, Inc. 2850 Centerville Road Wilmington, DE 19808 USA Key features of the MS/MS MRM Database include:

- Allows users to build acquisition methods without buying all compound standards, thus saves time and money
- Includes retention times for either constant flow or constant pressure methods; corresponding retention index (RI) values are also included for easy migration to other GC oven programs
- Has multiple MS/MS transitions, eight on average, for each compound which provides alternatives to work around matrix interferences
- Shows relative intensity of each MS/MS transition within a compound that facilitates transition selection
- Allows a quick sort according to compound category (phthalates, PAHs, organophosphorus, fungicides, or semivolatile pollutants and so forth, see Appendix A), CAS number, molecular formula, or molecular weight and so forth.

Using the tools in the database, an MRM acquisition method, based on a list of compound CAS numbers, can be easily created from a subset of MS/MS transitions in the database in less than 5 minutes.

### **Experimental Conditions**

### **Sample Preparation**

Without proper extraction and cleanup procedures, it is difficult to detect trace levels of analytes in complex matrices. The QuEChERS sample preparation technique was first introduced for pesticide analysis in foods by USDA scientists in 2003 [1]. It has been rapidly accepted worldwide for multiresidue pesticide analysis due to its special features known as Quick, Easy, Cheap, Effective, Rugged, and Safe. The QuEChERS extracts can be analyzed by LC and GC combined with MS to determine a wide range of pesticide residues. Agilent's QuEChERS extraction kits and dispersive SPE cleanup kits have demonstrated excellent recoveries for the frequently used pesticides in different food matrices [2, 3]. The sample extracts used in this study were prepared using the QuEChERS technique as described in an application note by Zhao, L. *et al* [4].

### **GC/MS/MS** Analyzer

The Multiresidue GC/MS/MS Analyzer is configured with Agilent's proprietary Capillary Flow Technology (CFT), enabling rugged, reliable GC column backflushing. Backflushing the GC column shortens run times, extends column life, reduces chemical background, provides consistent retention times and spectra, and keeps the MS ion source clean. A Multi-Mode Inlet (MMI) provides the flexibility to inject samples in cold, hot, or solvent-vent modes. Each analyzer system is tested with a 17-compound mixture and retention-time locked at the factory.

Two hardware configurations are available to meet different lab needs (see Figure 1):

- G3445A option 411: This configuration is based upon constant pressure mode method with post-column backflushing. It provides the flexibility to add GC detectors and can be easily scaled for shorter run times.
- G3445A option 412: This configuration is based upon constant flow mode method with mid-column backflushing. This method provides ultimate performance and shorter cycle times with reduced carrier gas consumption.

Both configurations (option 411 and option 412) are interchangeable by changing the column and adding or removing a capillary flow-restrictor. A Quick Start Guide for each analyzer discusses the retention time locking, checkout method results and report for your specific system, a list of supplies, and some troubleshooting tips.





Figure 1. System configurations of Agilent GC/MS/MS Multiresidue Analyzers.

#### Methods

There are three sets of method parameters included with the database. Some of the method highlights are shown in Table 1.

 Table 1.
 Method Parameters Included with the Databases

	Method 1	Method 2	Method 3
Run time	40.5 min	41.867 min	19.75 min
Column flow	Constant flow mode	Constant pressure mode	Constant flow mode
Feature	Allowing many more transitions in an analysis than Method 3	MS/MS Analyzer G3445A option # 411	MS/MS Analyzer G3445A option # 412
Column(s)	Agilent J&W HP-5ms UI 0.25 mm × 15 m, 0.25 μm (two each)	Agilent J&W HP-5ms UI 0.25 mm × 30 m, 0.25 µm (one each)	Agilent J&W HP-5ms UI 0.25 mm × 15 m, 0.25 μm (two each)
Oven program	Initial at 60 °C, hold for 1 min 40 °C/min to 120 °C, hold for 0 min 5 °C/min to 310 °C, hold for 0 min	Initial at 70 °C, hold for 2 min 25 °C/min to 150 °C, hold for 0 min 3 °C/min to 200 °C, hold for 0 min 8 °C/min to 280 °C, hold for 10 min	Initial at 60 °C, hold for 1 min 40 °C/min to 170 °C, hold for 0 min 10 °C/min to 310 °C, hold for 2 min
Locking compound and RT	Chlorpyrifos-methyl locked to 18.111 min	Chlorpyrifos-methyl locked to 16.593 min	Chlorpyrifos-methyl locked to 9.143 min
MS source temperature	300 °C	300 °C	300 °C
Quad temperature	Q1 = Q2 = 180 °C	Q1 = Q2 = 180 °C	Q1 = Q2 = 180 °C
Backflush	Mid-column, post-run	Post-column, post-run	Mid-column, post-run

Additional method details for each method are listed on individual pages (tabs) in the database.

The retention times (RTs) and retention indexes (RIs) corresponding to these three sets of methods are included for all compounds in the database. Therefore, you can either use one of the above prescribed methods (use RTs in the database) or your existing lab method (convert database RIs to expected RTs for your method). The database RIs were calculated using retention times of straight-chain hydrocarbons from C-8 to C-35. An RI\_to\_RT conversion tool is included with the database, so you can calculate expected retention times of your analytes based on the RIs in the database and RTs of hydrocarbon markers (C-8 to C-35) from your existing GC method. If your existing method uses HP-5ms UI column of the same phase ratio as a 0.25 mm, 0.25 µm column, you will see the smallest difference between the expected and actual retention times for your analytes.

#### **Backflush**

Food or environmental extracts after cleanup are usually still very complex containing various matrix residues such as highboiling compounds. The extracts used in GC/MS analyses can cause contamination and deterioration of the analytical column and MS ion source, affecting data quality due to poor peak shape and loss of responses of active analytes. It also leads to a shorter lifetime of the analytical columns and frequent MS maintenance. Therefore, it is necessary to use best techniques and supplies to achieve reliable results and to protect the analytical column and MS ion source.

Column backflushing can be beneficial for the analysis of complex extracts because it significantly reduces analysis time and reduces both column head trimming and MSD ion source cleaning frequency [5]. Agilent CFT makes column backflushing routine [6, 7].

#### **Database Overview**

The G9250AA MRM Database is in Microsoft Excel format for easy searching and filtering. Compounds are separated by color bands for clarity. The following basic compound information is included for each compound:

- Common name
- · Molecular formula
- · Molecular weight (averaged)
- · Molecular weight (mono-isotopic)
- · CAS number, without dashes for easy sorting
- Classification 1 (see Appendix A)
- Classification 2 (see Appendix A)
- Retention times (RT) and retention indexes (RI) for constant flow and constant pressure methods (total three methods)
- Relative intensity of each transition within a compound
- · Chinese name and Japanese name where available

In addition, information is included for building MassHunter MRM acquisition methods:

- · CAS number, standard format with dashes
- Method RT
- · Common name
- · ISTD (true or false)
- · Precursor ion
- MS1 resolution
- · Product ion
- MS2 resolution
- Dwell time
- Collision energy (Voltage)
- Retention time window (used in the MassHunter Compound List Assistant tool)

Figures 2 and 3 give an overview of the database layout. Using the Excel filtering tool, it is easy to display the table array according to the criteria chosen in any column. Figure 4 shows the database after using Excel filtering in column AE to hide all transitions except the top two (Q0 and Q1). This flexibility allows the user to build methods according to compound categories, (for example, PAHs, Phthalates, or PCBs), or regulatory methods and so forth. Two groups of compound classifications in the Database are listed in Appendix A as a reference.

-	<b>. . . .</b>	• 🖪 🕅 🔹				GS	250AA_Databa	se.xlsm - Micros	soft Excel								- * *
_	Home	Insert Page Layout Formulas	Data Review	View Deve	loper Add-In:												@ - ¤
	🔏 Cut	Calibri - 11 - A	· ^ = = =	-	fext Ger	neral	-	Do	tabacok	hac R	Te (a	nd RI	c) + c	ho u	boo	with	throo
Paste	Copy Copy	B Z H Z H Z AZ		E SE SEAterne	& Captar 7	- 9/ • • • 0	Conditional	Da	itabase i	105 11	15 (a	nu m	sju	, ne n	seu	vvitii	unee
-	I Format F	ainter			a center 5	70 × 00 ÷	Formatting *	* CC	mother		: <u>/</u> 0,	nin (	N D	0 min	000		20 min
	Clipboard	6 Font	9	Alignment	Gr [	Number	9 <u> </u>	ן טע	, methot	ມລັງປະເ	-401	iiiii, u	F -4		, an	u 66-	20 11111
	C1									-					~		
	С	D		E	F	G	Н	1	)		ι.	M	N	0	P	Q	R
						Molecular				/							
					Molecular	Weight	CAS #	(		RT - CF						User Field	
1	Com	non Nama		Molecular	Weight	(mono-	(for corting	Incrification 1	Classification	screening (40.5	RI - CF	RT - opt 411	RI- opt	RT - opt 412	RI- opt	(Method	(format 1) Com
4447	CCD Cont	non wante	10		(averagin)	150t0p - 1	101 301111 -	assincation	classificatio( - )		streening .	[41.07 mil -	-	10.72	-12	None)	(tormaci) - jeonn
4447	563 Capt	10		C9H8CI3NO25	300.6	298.9341323	133062	fungicide	Thiophthalimide	21.43	2077	21.23	2064	10.73	2105		133-06-2 Capta 133-06-2 Capta
4449	563 Capt	an an		C9H8CI3NO2S	300.6	298.9341323	133062	fungicide	Thiophthalimide	21.43	2077	21.23	2064	10.73	2105		133-06-2 Capta
4450	563 Capt	an		C9H8CI3NO2S	300.6	298,9341323	133062	fungicide	Thiophthalimide	21.43	2077	21.23	2064	10.73	2105		133-06-2 Capta
4451	563 Capt	an		C9H8CI3NO2S	300.6	298.9341323	133062	fungicide	Thiophthalimide	21.43	2077	21.23	2064	10.73	2105		133-06-2 Capta
4452	563 Capt	an		C9H8CI3NO2S	300.6	298.9341323	133062	fungicide	Thiophthalimide	21.43	2077	21.23	2064	10.73	2105		133-06-2 Capta
4453	563 Capt	in		C9H8CI3NO2S	300.6	298.9341323	133062	fungicide	Thiophthalimide	21.43	2077	21.23	2064	10.73	2105		133-06-2 Capta
4454	564 Fluo	anthene		C16H10	202.3	202.0782503	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4455	564 Fluo	anthene		C16H10	202.3	202.0782503	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4456	564 Fluo	anthene		C16H10	202.3	202.0782503	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4457	564 Fluo	anthene		C16H10	202.3	202.0782503	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4458	564 Fluo	anthene		C16H10	202.3	202.0782503	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4459	564 Fluo	anthene		C16H10	202.3	202.0782503	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4460	564 Fluo	anthene		C16H10	10.3	26230202365	206440	pollutant	PAH	21.23	2066	20.85	2050	10.73	2106		206-44-0 Fluor
4401	565 Trioc	imenol		C14H18CIN3O2	Ave	rade	-5219053 (ii	ide, breakdown	Triadimeton	21.04	2088	21.08	2080	10.73	2100		55219-65-3 Triad
4402	565 Triac	imenol		C14H18CIN3O2	,	rugo	55219653	de breakdown	Triadimeton	21.04	2000	21.00	2080	10.75	2100		55219-65-2 Triad
4464	565 Triac	imenol		C14H18CIN3O2	and	exact	\$5219653 (	ide breakdown	Triadimeton	21.64	2088	21.68	2080	10.73	2106		55219-65-3 Triad
4465	565 Triac	imenol		C14H18CIN3O2			\$5219653 in	ide, breakdown	Triadimefon	21.64	2088	21.68	2080	10.73	2106		55219-65-3 Triad
4466	565 Triac	imenol		C14H18CIN3O2	Mo	lecular	55219653 (i	ide, breakdown	Triadimefon	21.64	2088	21.68	2080	10.73	2106		55219-65-3 Triad
4467	566 Pher	thoate		C12H17O4PS2	101	6 a	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4468	566 Pher	thoate		C12H17O4PS2	VVe	ight	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4469	566 Pher	thoate		C12H17O4PS2		-	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4470	566 Pher	thoate		C12H17O4PS2	320.4	320.0305869	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4471	566 Pher	thoate		C12H17O4PS2	320.4	320.0305869	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4472	566 Pher	thoate		C12H17O4PS2	320.4	320.0305869	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4473	566 Pher	thoate		C12H17O4PS2	320.4	320.0305869	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen
4474	566 Pher	thoate		C12H17O4PS2	320.4	320.0305869	2597037	insecticide	Organophosphorus	21.66	2089	21.74	2082	10.73	2106		2597-03-7 Phen 2597-02-7 Phen
4475	567 Quin	alphor		C12H1704P52	320.4	202.05003009	12592029	insecticide	Organophosphorus	21.00	2005	21.74	2082	10.75	2100		12592-03-7 Prier
4470	567 Quin	alphos		C12H15N2O3P5	298.3	298.0540996	13593038	insecticide	Organophosphorus	21.63	2000	21.00	2079	10.73	2100		13593-03-8 Quin
4478	567 Quin	alphos		C12H15N2O3PS	298.3	298.0540996	13593038	insecticide	Organophosphorus	21.63	2088	21.66	2079	10.73	2106		13593-03-8 Quin
4479	567 Quin	alphos		C12H15N2O3PS	298.3	298.0540996	13593038	insecticide	Organophosphorus	21.63	2088	21.66	2079	10.73	2106		13593-03-8 Quin
4480	567 Quin	alphos		C12H15N2O3PS	298.3	298.0540996	13593038	insecticide	Organophosphorus	21.63	2088	21.66	2079	10.73	21/6		13593-03-8 Quin
14 4 1	MRM T	ble DATABASE DE Compound	My Target	Compound List 📝	CF, 40-min Met	nod (CP. 40-m	in Method (	F Comin Mathe	d / ubst is 10 Offi	UP / 🗩		_		_		(7) (1) 10 m	
Ready	10					Feel		h a u na d	in l							LU HU 100%	0.0
						Eaci	1 com	pound	IS								
						1.1	100.00	· · · ·									
						clas	sified	in two	ways								

Figure 2. Layout of the Database 1: molecular weights, classifications, and three RTs and RIs.

8	Home	r 💁 ∰ = Insert Page Layout Fe	MassH	unt	er forn	nat f	or		⊉atabase.xlsm	n - Micros	oft Excel	The	scale	and	relative			_ = ×
Past	Cut Lin Copy	Calibri • 11	building	g ac	quisiti	ion n	netho	ods	Sitional Form	Norm at Norm	ial 2 nal	inte	nsitie	s of	transitions	S e Form	Σ AutoSum * A	T 🕅
	Clipboard	G Font	6	Alig	nment	6	Number	G Par	Farring , as rap			Captan				10.00	Editing	er · select ·
	(Calar Social) Orange depetes strong intensity and blue																	
	Color Scale): Orange denotes strong intensity and blue										u blue							
	N.						~		-	~~~	-		der	iotes w	eak intensity am	ong ALL	transitions.	
									Dwell			Response	Relative	Quant		China GB		
	CAS #		Method		Precursor N	4S1	Product	MS2	Time		RT	Scaled within	Intensit of	Q0) and	USER	Method		
1	(format 1) 💌	Common Name	💌 RT 💽 I	STD 📔	🔹 Ion 💽 R	esolution	• Ion 💽	Resolution	• (ms) •	CE (V) 💌	Windo	the Databa	Tran itior	Qual	FIELD Chinese Name	Group 💌	Japanese Name	<b>•</b>
4447	133-06-2	Captan	10.73	false	151.0	LowRes	80.0	LowRes	10	5	0.1	470	100%	Q0	3 克薗丹	E	キャプタン	-
4448	133-06-2	Captan	10.73	false	149.0	LowRes	79.1	LowRes	10	10	0.1	320	68%	Q1	3 克薗丹	E	キャプタン	
4449	133-06-2	Captan	10.73	false	151.0	LowRes	79.0	LowRes	10	15	0.1	300	64%	Q2	3 克薗丹	E	キャプタン	
4450	133-06-2	Captan	10.73	false	149.0	LowRes	70.0	LowRes	10	15	0.1	220	47%	Q3	3 克薗丹	E	キャプタン	
4451	133-06-2	Captan	10.73	false	116.9	LowRes	82.0	LowRes	10	30	0.1	160	34%	Q4	3 克薗丹	E	キャプタン	
4452	133-06-2	Captan	10.73	false	149.0	LowRes	77.1	LowRes	10	30	0.1	130	28%	QS	3 兄園丹	E	R R 7 9 2	
4453	133-06-2	Captan	10.73	false	263.8	LowRes	79.0	LowRes	10	15	0.1	40	9%	Q6	3 兄園村	E	*****	-
4454	206-44-0	Fluorantnene	10.73	false	201.1	LOWKES	200.1	LOWKES	10	15	0.1	4510	100%	QU	4			
4455	200-44-0	Fluoranthene	10.73	false	202.1	LOWRES	152.1	LOWRES	10	30	0.1	1000	2276	01	4			
4450	200-44-0	Fluoranthene	10.73	false	202.1	LowRes	176.0	LowRes	10	30	0.1	570	2270	42	4			
4457	200-44-0	Fluoranthene	10.73	falco	200.1	LowRes	1/4.0	LowRes	10	20	0.1	530	1.44/0	04	4			
4450	206-44-0	Fluoranthene	10.73	falco	200.1	LowRos	175.0	LowRos	10	30	0.1	320	12/6	05	4			
4455	206-44-0	Fluoranthene	10.73	falco	201.1	LowRes	177.0	LowRes	10	20	0.1	150	396	06	4			
4461	55219-65-3	Triadimenol	10.73	false	128.0	LowRes	65.0	LowRes	10	25	0.1	750	100%	00	5 三唑酸	c	トリアジメノール	
4462	55219-65-3	Triadimenol	10.73	false	168.0	LowRes	70.0	LowRes	10	10	0.1	540	72%	01	5 三唑醇	c	トリアジメノール	
4463	55219-65-3	Triadimenol	10.73	false	128.0	LowRes	100.0	LowRes	10	10	0.1	370	49%	02	5 三唑醇	c	トリアジメノール	
4464	55219-65-3	Triadimenol	10.73	false	129.9	LowRes	65.0	LowRes	10	25	0.1	270	36%	Q3	5 三唑醇	с	トリアジメノール	
4465	55219-65-3	Triadimenol	10.73	false	112.0	LowRes	58.0	LowRes	10	10	0.1	230	31%	Q4	5 三唑醇	с	トリアジメノール	
4466	55219-65-3	Triadimenol	10.73	false	129.9	LowRes	102.0	LowRes	10	15	0.1	120	16%	Q5	5 三唑醇	с	トリアジメノール	1
4467	2597-03-7	Phenthoate	10.73	false	274.0	LowRes	121.0	LowRes	10	10	0.1	730	100%	Q0	6 稻丰散	E	フェントエート	
4468	2597-03-7	Phenthoate	10.73	false	274.0	LowRes	125.0	LowRes	10	15	0.1	620	85%	Q1	6 稻丰散	E	フェントエート	
4469	2597-03-7	Phenthoate	10.73	false	121.0	LowRes	77.0	LowRes	10	25	0.1	610	84%	Q2	6 稻丰散	E	フェントエート	
4470	2597-03-7	Phenthoate	10.73	false	274.0	LowRes	93.0	LowRes	10	15	0.1	430	59%	Q3	6 稻丰散	E	フェントエート	
4471	2597-03-7	Phenthoate	10.73	false	157.0	LowRes	93.0	LowRes	10	10	0.1	370	51%	Q4	6 栢丰散	E	72712-1	
4472	2597-03-7	Phenthoate	10.73	false	121.0	LowRes	51.0	LowRes	10	45	0.1	350	48%	Q5	5 伯牛凯 6 松士粉	E	フェントエート	
4473	2597-03-7	Phenthoate	10.73	false	246.0	LOWKES	120.9	LOWKES	10	5	0.1	260	36%	Q6	6 伯平郎	E .	フェントエート	
4474	2597-03-7	Phenthoate	10.73	falco	240.0	LowRes	92.9	LowRes	10	15	0.1	130	18%	08	6 松主教	E	フチントエート	
4475	12592.02.9	Quinalphos	10.73	false	146.0	LowRes	119.0	LowRes	10	20	0.1	2290	100%	00	7 國家研究	L .	キナルホス	
4470	13593-03-8	Quinalphos	10.73	falco	146.0	LowRes	91.0	LowRes	10	30	0.1	1230	36%	01	7 時間	2	キナルホス	
4478	13593-03-8	Quinalphos	10.73	false	157.0	LowRes	129.1	LowRes	10	15	0.1	730	22%	<b>X</b>	7 嘧硫磷	A	キナルホス	
4479	13593-03-8	Quinalphos	10.73	false	157.0	LowRes	102.0	LowRes	10	30	0.1	590	17%	T	7 喹硫磷	A	キナルホス	
4480	13593-03-8	Quinalphos	10.73	false	192.9	LowRes	129.0	LowRes	10	10	0.1	310	9%	64	7 喹硫磷	A	キナルホス	
н .	H MRM Ta	ble DATABASE DE Com	oound List 🖉 My Tar	get Comp	iound List 📈 CF	, 40-min Met	thod / CP, 4	10-min Metho	od 📈 CF, 20-	min Metho	d 🖉 what	B LOOKID		4				
Read	Y 🔛														(00)			(*)
													One (	luan	t (00) and	Seve	eral	
													Qualit	icati	ion ions fo	r eac	h compo	hund
													Quali	iout	10113 10	- cau	n compt	Junu

*Figure 3.* Layout of the Database 2: MassHunter format for building acquisition methods, multiple transitions, and relative intensities.

9	Home	Insert Page Layout Formulas	Data	Revie	w Vie	ew Develop	er Add-In	5	G9250AA_I	Database.xlsn	n - Micr	Use	e the f	filteri	na fu	ncti	on to d	uick	lv		
	j ∦ Cut				20						8 m	1.1		0		1		1.0	utoSum - A	7 (1)	
	Copy	Calion VII A	A _			wrap tex	G	neral		<b>1</b> 39 - <b>1</b> 3		sel	ect a	Uuan	t (UU	) an	d a Uu	alifie	r Z	ara	
Pas	🧳 Format F	ainter B I U · 🖾 · 💁 · 🗛				Merge &	Center • \$	* % *	to to Form	attional Form hatting * as Tab	ole - Ne	·	4 - L	11. L. L.		í			léar * Filte	a Find a	
	Clipboard	6 Font	6		Align	ment	6	Number	6		_	ION	to bu	illd ar	1 acq	uisit	tion me	ethoc	Editing		
	C1	$\bullet$ (9 $f_x$									_										2
- 1	R	S		Т	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	-
	C 4 5 #							Decidination		Dwell		or	Response	Relative	Quant (OO) and			China GB			
1	(format 1)	Common Namo	Met	hod	TD T	Precursor	MS1 Recolution	Product	MS2 Recolution	Time	CE DO D	KI Windo x	Scaled within	Intensity of	(QU) and		Chinere Name	Group	Japanoro Namo		
1	(10mmat 1) *	Control Name	- INI -	10.72	false.	100 151 0	Lew0ee	Pilon (*)	LewDer	* ((ms)   * )	CE (V)	- Twindol +	the Databa +	1005	Qual	PIELU •	古世口	Group	japanese Name    まやプタン		
4447	122.06.2	: Captan		10.75	false	1/10	LowRes	79.1	LowRes	10		0 0.1	. 470	1003	01	2	元四八 古世兵	-	キャプタン		
4454	206-44-0	Fluoranthene		10.73	false	201.1	LowRes	200.1	LowRes	10	1	5 0.1	4510	1005	00	4	300071			-	
4455	206-44-0	Fluoranthene		10.73	false	202.1	LowRes	152.1	LowRes	10	3	0 0.1	1000	229	01	4					
4461	55219-65-3	Triadimenol		10.73	false	128.0	LowRes	65.0	LowRes	10	2	5 0.1	750	1005	Q0	5	三唑醇	С	トリアジメノール」		
4462	55219-65-3	Triadimenol		10.73	false	168.0	LowRes	70.0	LowRes	10	1	0 0.1	. 540	729	Q1	5	三唑醇	с	トリアジメノール」		
4467	2597-03-7	Phenthoate		10.73	false	274.0	LowRes	121.0	LowRes	10	1	0 0.1	730	1009	Q0	6	稻丰散	E	フェントエート		
4468	2597-03-7	Phenthoate		10.73	false	274.0	LowRes	125.0	LowRes	10	1	5 0.1	620	859	Q1	6	稻丰散	E	フェントエート		
4476	13593-03-8	Quinalphos		10.73	false	146.0	LowRes	118.0	LowRes	10	1	0 0.1	3380	1009	Q0	7	喹硫磷	А	キナルホス		
4477	13593-03-8	Quinalphos		10.73	false	146.0	LowRes	91.0	LowRes	10	3	0 0.1	1230	365	Q1	7	喹硫磷	А	キナルホス		
4483	38379-99-6	2,2',3,5',6-Pentachlorobiphenyl (B2	Z #:	10.73	false	325.9	LowRes	255.9	LowRes	10	2	5 0.1	2300	1005	Q0	8					
4484	38379-99-6	2,2',3,5',6-Pentachlorobiphenyl (BZ	Z #: :	10.73	false	253.9	LowRes	184.0	LowRes	10	3	5 0.1	2300	1005	Q1	8				_	- 1
4494	60-09-3	Aminoazobenzene, 4-		10.74	false	92.0	LowRes	65.0	LowRes	10	1	0 0.1	. 1350	1009	Q0	9					- 1
4495	60-09-3	Aminoazobenzene, 4-		10.74	false	120.0	LowRes	92.1	LowRes	10		5 0.1	730	549	Q1	9				L	
4501	73575-56-1	2,2',3,5,6-Pentachlorobiphenyl (BZ	2 #9	10.74	false	253.9	LowRes	184.0	LowRes	10	3	5 0.1	2420	1005	Q0	0					
4502	73575-56-1	2,2',3,5,6-Pentachlorobiphenyl (BZ	2 #9	10.74	false	290.9	LowRes	255.9	LowRes	10	1	5 0.1	2380	985	Q1	0	医黄疸		22 K & L - L		
4512	61432-33-1	Dimepiperate		10.75	false	119.0	LowRes	91.0	LowRes	10	1	0 0.1	. 3520	1007	01	1	版單具	Č.	ジメビュレート		
4513	1096 02 9	Dimepiperate		10.75	false	272.0	LowRes	227.0	LowRes	10	1	0 0.1	2380	100	00	1	9次-平-7丁 0字:南田書	C C	226.00	-	-
4519	1086-02-8	Pyridinitril		10.75	falco	273.0	LowRes	202.0	LowRes	10	3	0 0.1	420	1007	01	2	喧菌語				
4529	7700-17-6	Crotovyphos		10.75	false	104.0	LowRes	78.0	LowRes	10	1	5 0.1	510	1005	00	3	巴畫礎	B			
4530	7700-17-6	Crotoxyphos		10.75	false	104.0	LowRes	103.0	LowRes	10	1	5 0.1	300	595	01	3	巴毒磷	в			
4537	55215-17-3	2.2'.3.4.6-Pentachlorobiphenyl (BZ	7 #8	10.75	false	325.9	LowRes	255.9	LowRes	10	2	5 0.1	3320	1005	00	4				-	
4538	55215-17-3	2,2',3,4,6-Pentachlorobiphenyl (BZ	2 #8	10.75	false	253.9	LowRes	184.0	LowRes	10	3	5 0.1	2260	689	01	4					
4548	57646-30-7	Furalaxyl		10.78	false	242.0	LowRes	95.0	LowRes	10	1	5 0.1	1860	1009	Q0	5	呋霜灵	E			
4549	57646-30-7	Furalaxyl		10.78	false	94.9	LowRes	67.0	LowRes	10	1	5 0.1	. 590	329	Q1	5	呋霜灵	Е			
4556	56558-18-0	2,3',4,5',6-Pentachlorobiphenyl (BZ	Z #1 : :	10.81	false	253.9	LowRes	184.0	LowRes	10	3	5 0.1	2220	1005	Q0	6					
4557	56558-18-0	2,3',4,5',6-Pentachlorobiphenyl (BZ	Z#: :	10.81	false	325.9	LowRes	255.9	LowRes	10	3	0 0.1	2050	929	Q1	6					
4567	89269-64-7	Ferimzone		10.81	false	123.0	LowRes	96.0	LowRes	10	1	0 0.1	. 120	1009	Q0	7	嘧菌腙		フェリムゾン		
4568	89269-64-7	Ferimzone	1	10.81	false	123.0	LowRes	95.0	LowRes	10	2	0 0.1	. 90	759	Q1	7	嘧菌腙		フェリムゾン		
4573	32809-16-8	Procymidone	1	10.84	false	96.0	LowRes	67.1	LowRes	10	1	0 0.1	3710	1005	Q0	8	腐霉利	Α	プロショドン		
4574	32809-16-8	Procymidone		10.84	false	96.0	LowRes	53.1	LowRes	10	1	5 0.1	1120	305	Q1	8	周寧利	A	フロシミドン	_	
4580	133-07-3	Folpet		10.84	false	259.8	LowRes	130.1	LowRes	10	1	5 0.1	. 940	1009	Q0	9	火菌片	A	*****		
4581	133-07-3	able DATABASE Discourse interest	st /	10.84 My Taro	Talse et Compo	261.8 und List C	LowRes F. 40-min Met	130.1 hod CP.	LowRes 40-min Metho	10 of CE, 20-	min Meth	od what	550	599 2	Q1	9	火菌片	A	JUNE Y P		
Rand	2149 of 954	records found		, rury			.,											10			

Figure 4. Using Excel filter to hide all transitions except the top two of each compound.

Table 2 gives a breakdown of the compounds included in the database.

#### Table 2. Compounds Included in the Database

	Total number
Pesticides (fungicides, herbicides, insecticides, rodenticides, and others)	675
Breakdown products	42
Deuterated compounds	6
Polybrominated Diphenyl Ether (PBDE)	4
Polybrominated Biphenyl (PBB)	1
Polychlorinated Biphenyl (PCB)	209
Polycyclic Aromatic Hydrocarbon (PAH)	26
Phthalates	17
Additional semivolatile pollutants	94

A complete list of compounds can be found on the **DB Compound List** tab in the database.

There are three videos included with the database to help the user learn the database:

- An overview of the content and layout of the database.
   → Each individual column and tab is explained in the video.
- A tutorial of building an MRM acquisition method based on your list of compound CAS numbers.
  - → An MRM acquisition method, based on your list of CAS numbers, can be easily and quickly created from a subset of MS/MS transitions in the database.
- A tutorial showing how to add new compounds to the database.

The database ReadMe file shows a few Excel shortcuts to use with the database and a few additional ways of using the database. For example, it shows how to find all nitrogen containing compounds in the database, or how to select all PCB congeners, or the 14 most toxic PCB planar congeners in the database.

## **Results and Discussion**

### **Chemical Background from the Matrix**

Figure 5 shows four MRM total ion chromatograms (TICs) of pepper, spinach, orange, and pear extracts acquired using method 3 described on page 3. Thirty-five analytes at 10 ppb each were spiked in each matrix. Seven transitions of each analyte were used in the acquisition method. The TICs showed that the chemical background from the four matrices was quite different and sizeable. In this study, pear extract showed the highest background response in terms of number of peaks and intensity. The TIC from the orange extract was the cleanest among the four chromatograms. These different and high background responses all came from the matrix. To understand the matrix effect, we need to evaluate the chemical background in each individual transition.



Figure 5. Total ion chromatograms (TICs) of pepper, spinach, orange, and pear extracts including 35 analytes spiked at 10 ppb each.



Figure 6. Top two transitions of methamidophos (at 10 pg) in three matrices.



Figure 7. Two alternative methamidophos transitions with minimum matrix interference.

A typical MRM database or acquisition method has two MRM transitions for each analyte. Figure 6 shows extracted ion chromatograms (EICs) of the top two transitions of methamidophos (at 10 pg) in three matrices. The retention time of methamidophos is about 4.6 minutes. The transitions are arranged in the descending order of responses with the larger one on top. Figure 6 shows the obvious issues of getting inaccurate quantitation results due to medium or strong matrix interference. For orange matrix, an overlapping peak in the second transition marked by a blue arrow, affected integration results and the qualifier ion ratio. For pear matrix, an overlapping peak in the first transition, marked by a green arrow, which is typically used for quantitation, gave higher and inaccurate quantitation results.

If a user only has two MRM transitions available for each analyte, it is difficult to work around the matrix effect as seen in Figure 6. The G9250AA database has an average of eight transitions for each compound. This allows the user to choose alternative transitions easily when matrix interference affects peak shape and integration results.

Figure 7 shows EICs of two alternative methamidophos transitions in the database. Both transitions showed minimum matrix interferences in orange and pear matrices. In fact, the EICs of these two transitions showed minimum matrix interference in all four matrices. Although these two transitions do not provide the highest responses, they are suited for a universal or screening MRM method. It is always best to evaluate the chemical background of an analyte's multiple transitions in different matrices before selecting the most appropriate transitions in a particular matrix.



Signal-to-Noise Ratio Comparison for MRM Transitions in Spinach and Orange

Figure 8. Comparison of area counts and signal-to-noise ratios of four analytes MRM transitions in spinach and orange matrices.

#### Signal-to-Noise Ratios

Evaluating the signal-to-noise ratios (S/N) of MRM transitions is another way to identify matrix effects. Some pesticides showed consistent MRM responses in different matrices, but many pesticides had different MRM responses in different matrices due to either matrix enhancement or matrix suppression.

Figure 8 shows responses, or area counts, and S/N's of several MRM transitions for four analytes in spinach and orange matrices. The orange dashed line and dark green dotted line represent area counts from four or five MRM transitions of each analyte in these two matrices. The solid blue and green lines represent the S/N from the same MRM transitions in these two matrices. The dashed and dotted lines, signifying area counts, superposed tightly. However, the solid lines, S/N, showed significant variations for some transitions within each analyte. Using atrazine as an example, the area count for transition 215→58 was about the same (approximately 7,000) for both matrices, but the S/N for this transition in spinach was about 40% higher than the S/N in orange matrix. In contrast, for transition 200→122, the S/N in orange matrix was almost double the S/N in spinach, even though the area counts in both matrices were about the same (approximately 4,000). This matrix effect was not unique to atrazine. The S/N variations from some of the MRM transitions of dichlorvos and lindane were more pronounced even though the area counts were comparable in both matrices. Again, if the number of MRM transitions available for each analyte is limited to two or three, it is difficult to select optimal MRM transitions suited for the matrix analyzed.

The multiple transitions available in the G9250AA database allow users to choose several selective transitions to achieve accurate confirmation and quantitation results. This study showed that MRM transitions should be chosen according to matrix to achieve optimal and reliable quantitation results. It is important to use matrix-matched calibrations and low background transitions to achieve accurate quantitation results.

### Conclusion

Based on the Agilent 7890A GC and 7000 Series Triple Quadrupole GC/MS, the GC/MS/MS Multiresidue Analyzers were developed to simplify a lab's startup process. A special feature of the analyzer is the comprehensive and flexible MRM database of over 1,070 pesticides and environmental pollutants. The analyzer also includes CFT backflush for superior system robustness during routine operations.

Matrix can cause quantitation interference, lower responses, or poor peak shape. Each matrix has a different matrix effect. Therefore, it is critical to choose the most selective transitions for a particular matrix and use matrix-matched calibration curves to achieve accurate and reliable quantitation results. The G9250AA MRM Database has an average of eight MRM transitions with relative intensities for each compound to provide alternative measurements to minimize matrix interference. Easy-to-use tools as well as tutorial videos are also included in the database to build an MRM acquisition method based on your list of compound CAS numbers in less than 5 minutes.

### References

- M. Anastassiades and S.J. Lehotay, "Fast and Easy Multiresidue Method Employment Acetonitrile Extraction/Partitioning and 'Dispersive Solid-Phase Extraction' for the Determination of Pesticide Residues in Produce", J. AOAC Int., 2003, 86, 412- 431.
- L. Zhao, D. Schultz, and J. Stevens, "Analysis of Pesticide Residues in Apple Using Agilent SampliQ QuEChERS AOAC Kits by GC/MS", Agilent Technologies publication 5990-4068EN.
- L. Zhao and J. Stevens, "Analysis of Pesticide Residues in Spinach Using Agilent SampliQ QuEChERS AOAC Kits by GC/MS", Agilent Technologies publication 5990-4305EN.
- L. Zhao and C.-K. Meng, "Quantitative and Repeatability Analysis of Trace Level Pesticides in Plantation Food by GC/MS/MS", Agilent Technologies publication 5990-9317EN.
- M.J. Szelewski and B. Quimby, "New Tools for Rapid Pesticide Analysis in High Matrix Samples", Agilent Technologies publication 5989-1716EN.
- C-K. Meng, "Improving Productivity and Extending Column Life with Backflush", Agilent Technologies publication 5989-6018EN.
- P.L. Wylie and C-K. Meng, "A Method for the Trace Analysis of 175 Pesticides Using the Agilent Triple Quadrupole GC/MS/MS", Agilent Technologies publication 5990-3578EN.

### **For More Information**

For more information on our products and services, visit our Web site at www.agilent.com/chem.

# Appendix A

### List of First Compound Classification in the Database

algicide	herbicide safener	insecticide, plant growth regulator
bird repellent	herbicide, algaecide	microbiocide
breakdown	herbicide, microbiocide	microbiocide, fungicide
defoliant, plant growth regulator	herbicide, plant growth regulator	molluscicide
deuterated	insect attractants	nematicide
fragrance	insect growth regulator	plant growth regulator
fumigant	insect repellent, synergist	plant growth regulator, herbicide
fungicide	insecticide	pollutant
fungicide, insecticide	insecticide, fungicide	rodenticide
fungicide, microbiocide	insecticide, insect repellent	synergist
fungicide, plant growth regulator	insecticide, molluscicide	wood preservative, microbiocide
herbicide	insecticide, nematicide	

### List of secondary compound classification in the Database

1,3-Indandione	Dinitrophenol derivative	Phthalate
2,6-Dinitroaniline	Diphenyl ether	Phthalic acid
Amide	Dithiocarbamate	Picolinic acid
Anilide	Folpet	Pyrazole
Anilinopyrimidine	Formamidine	Pyrethroid
Aromatic	Formamidine	Pyrethroid ester
Aryl phenyl ketone	Fumigant	Pyridazine
Arylalanine	Halogenated organic	Pyridazinone
Aryloxyphenoxy propionic acid	Hydrobenzonitrile	Pyridine
Auxins	Hydroxybenzonitrile	Pyridinecarboxylic acid
Benzamide	Imidazolinone	Pyrimidinamine
Benzimidazole	Juvenile hormone mimics	Pyrimidine
benzofuranyl alkylsulfonate	Keto-enol	Pyrimidine organothiophosphate
Benzoic acid	Mercaptobenzothiazole	Pyrimidinyloxybenzoic acid
Benzothiazole	Morphactins	Pyrrole
Botanical	Morpholine	Quinoline
Bridged diphenyl	Naphthalene acetic acid derivative	Quinone
Carbamate	Neonicotinoid	Quinoxaline
Carbanilate	Nitrophenyl ether	SemiVOC
Carbofuran	N-Methyl carbamate	Strobin
Carboxamide	Organochlorine	Substituted benzene
Chitin synthesis inhibitor	Organophosphorus	Sulfite ester
Chlorinated phenol	Oxadiazolone	Thiadiazole
Chloroacetanilide	PAH	Thiocarbamate

#### List of secondary compound classification in the Database

Chlorophenoxy acid or ester	PBB	Thiophthalimide
Conazole	PBDE	Triadimefon
Coumarin	PCB	Triazine
Cyclic dithiocarbamate	Phenol	Triazinone
Cyclodiene	Phenoxyacetic	Triazole
Cytokinins	Phenoxybutyric	Triazolone
Defoliant	Phenoxypropionic	Uracil
Deuterated PAH	Phenylsulfamide	Urea
Deuterated semiVOC	Phosphoramidate	Xylylalanine
Dicarboximide	Phosphorodiamide	

#### www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2011 Printed in the USA November 10, 2011 5990-9453EN

