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Analysis of Pesticides in Baby Foods Using a Triple-Quadrupole GC/MS/MS

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Laura Chambers, Richard Whitney, Ph.D.,
Nicole M. Lock, Zhuangzhi "Max" Wang, Ph.D.,
Clifford M. Taylor;
Shimadzu Scientific Instruments, Columbia, MD, USA

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Introduction

Contamination of food products with pesticides is a growing concern because of recognized adverse health effects, increasing world-wide usage of pesticides, and increasing imports of raw foodstuffs from foreign sources. The concern is particularly acute for baby foods because of the high vulnerability of babies to health effects from synthetic chemicals such as pesticides.
This poster presents analytical results for analysis of 36 pesticides from various chemical classes in a QuEChERS extract of baby food using the Shimadzu GCMS-TQ8030 triple quadrupole GC/MS/MS (Figure 1). Results were evaluated for calibration linearity, analytical precision, and accuracy in a baby food matrix. Selectivity as a function of variable mass spectral resolution settings on the two sets of quadrupoles, Q1 and Q3, is also discussed.

Figure 1: Shimadzu GCMS-TQ8030 triple quadrupole GC/MS/MS

Experimental

The analyses were conducted using a Shimadzu GCMS-TQ8030 triple quadrupole GC/MS/MS. The GCMS-TQ8030 was operated in the multiple reaction monitoring (MRM) mode, using the optimized MRM transitions and collision energies detailed in the Shimadzu GC/MS/MS Pesticide SmartMRM® Database. The GCMS-TQ8030 allows optimization of the collision energy for each MRM transition, providing ultimate sensitivity.
A sample of blended pears was used as the test sample matrix; an organic variety was selected so it would be free from background pesticide contamination. The sample matrix was extracted and subjected to cleanup using the QuEChERS procedure. Calibration was conducted using the matrix-matched internal standard procedure.

Results and Discussion

Chromatography

The total ion chromatogram (TIC) acquired in the MRM mode for the pesticide standard is shown in Figure 2, and illustrates the chromatographic separation of the target pesticides in this study. In the MRM mode, the TIC for each analyte is the sum of the signal for each MRM transition for that particular compound, so the appearance of the chromatogram is slightly different than a typical TIC acquired in the full-scan mode.

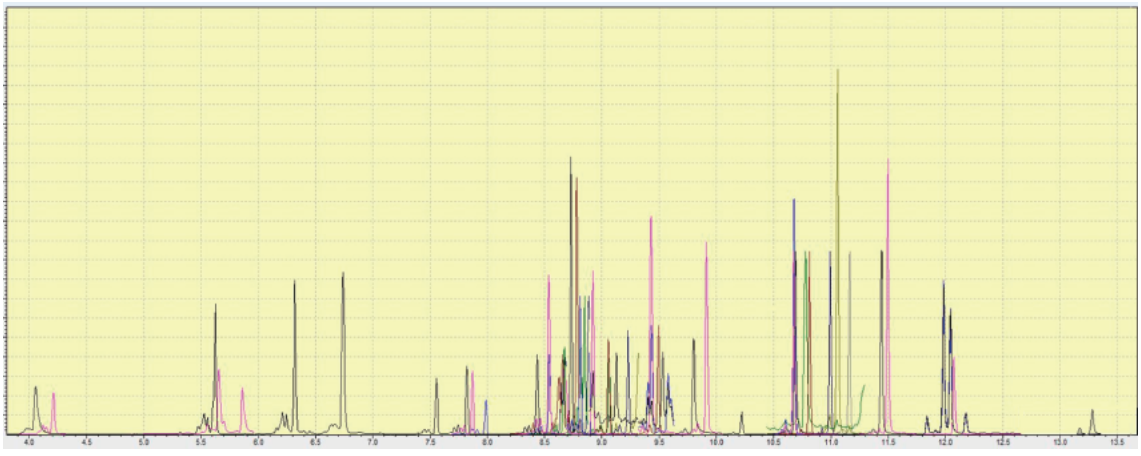

Figure 2: Total Ion Chromatogram (TIC) of a low-level Matrix-Matched Pesticide Standard Run in the MRM Mode

Matrix-Matched Calibration

Using the matrix-matched calibration approach, five calibration standards were prepared in a blended pears extract over the range of 1-200 ng/mL (ppb). Triphenylmethane was used as the internal standard (IS) and was held constant at 10 ng/mL; triphenyl phosphate was used as a surrogate standard (SS) at 20 ng/mL in all standards.

In many cases where the RSD for the response factors was greater than 20% (e.g. thiabendazole and imazalil), the presence of native pesticides in the matrix contributed to the signal for the lowest concentration standards and accounts for the high %RSD. When the low-level calibration standard is not included in the calculation, RSD is less than 20% overall (Table 1).

Analysis of Pesticides in Baby Foods Using a Triple-Quadrupole GC/MS/MS

Table 1: Matrix Matched Calibration, Precision, and Accuracy Results for Pesticides Analysis

Compound	Calibration Results			Matrix Blank	Precision and Accuracy			
					1.0 ppb		5.0 ppb	
	Mean RF	RF %RSD	r	ppb	Mean (ppb)	%RSD	Mean (ppb)	%RSD
Methamidophos	0.91	14	>0.999	0.29	0.93	10	3.93	6
Dichlorvos	0.38	6	>0.999	ND	0.84	17	5.46	6
Mevinphos	0.71	16	>0.999	ND	0.82	6	3.71	7
Acephate	0.53	17	>0.999	ND	0.65	13	2.85	13
2-Phenylphenol	0.90	18	0.999	0.60	1.05	8	3.14	5
Omethoate	1.34	9	0.999	ND	0.92	9	3.91	5
Dimethoate	0.33	20	>0.999	0.44	0.91	17	2.92	8
gamma-BHC (Lindane)	0.44	4	>0.999	ND	0.88	12	5.50	4
Diazinon	0.56	14	>0.999	0.02	0.92	14	5.26	6
Vinclozolin	0.23	15	>0.999	ND	0.75	41	6.05	9
Carbaryl	1.60	10	>0.999	ND	0.69	7	3.91	6
Metalaxyl	0.37	25	>0.999	ND	0.86	19	5.57	6
Methiocarb	1.92	21	>0.999	0.27	0.65	28	3.48	7
Pirimiphos-methyl	0.40	21	>0.999	ND	0.88	15	5.26	9
Malathion	1.14	8	>0.999	0.13	1.01	11	5.21	6
Fenthion	1.12	7	0.999	0.03	1.04	12	5.42	7
Chlorpyrifos	0.58	19	>0.999	0.06	0.84	17	5.29	5
Dicofol deg. (DCBP)	0.53	15	>0.999	ND	0.87	18	5.31	6
Triphenylmethane (IS)	N/A	N/A	N/A	NA	NA	5	NA	7
Cyprodinil	0.91	8	0.999	0.30	1.05	13	4.63	6
Thiabendazole	2.93	34	>0.999	0.89	0.86	5	1.81	6
Imazalil	0.83	27	>0.999	0.78	0.87	7	2.52	6
Myclobutanil	1.38	3	>0.999	0.19	1.01	4	4.71	7
Endrin	0.07	5	>0.999	ND	1.04	15	4.60	13
Phenhexamid	0.41	6	>0.999	0.23	0.82	20	4.31	12
Endosulfan sulfate*	0.05	34	>0.999	ND	ND	ND	3.60	26
p,p'-DDT	1.85	7	>0.999	ND	0.98	11	4.95	5
Triphenyl phosphate (SS)	N/A	N/A	N/A	19.80	19.71	4	19.24	7
Propargite*	1.24	12	>0.999	ND	0.83	32	2.27	15
Iprodione*	0.05	20	>0.999	ND	ND	ND	1.68	49
Bifenthrin	4.72	9	0.999	ND	0.96	8	4.01	3
Fenpropathrin	0.34	8	>0.999	ND	0.65	35	4.31	12
Phosalone	1.26	2	>0.999	0.08	0.96	10	4.43	6
Azinphos-methyl	1.64	9	>0.999	ND	1.01	12	4.01	7
Permethrin-1	0.76	15	>0.999	ND	0.91	12	5.64	17
Coumaphos	0.41	16	>0.999	0.05	0.80	17	4.47	5
Permethrin-2	0.52	2	>0.999	ND	0.50	14	2.79	8
Deltamethrin	0.16	16	0.999	ND	0.75	13	4.41	7

Note: for most compounds the low-level calibration standard was 1.0 ng/mL. For compounds indicated with an *, the low-level calibration standard was 5.0 ng/mL.

Selectivity as a Function of Mass Spectral Resolution

Resolution settings on the GCMS-TQ8030 are expressed using the FWHM (Full Width at Half Maximum) definition. Three resolution settings are available for each set of quadrupoles when operating in the MRM mode (Table 2), and the resolution can be defined independently for Q1 and Q3, using any combination of the three settings. In most cases, Unit resolution (0.8 u) for both Q1 and Q3 provides the best combination of sensitivity and selectivity, however Q1 and Q3 mass spectral resolution settings can be adjusted individually for each analyte to provide a customized method when needed. The resolution settings that are chosen can have an enormous impact on signal intensity, noise levels, compound detection limits, and selectivity against background interferences. This principle is illustrated using 10 replicate injections of an octafluoronaphthalene (OFN) standard, as shown in Table 3.

Table 2: Resolution Settings for Q1 and Q3 on the GCMS-TQ8030

Resolution	FWHM
High	0.6 u
Unit	0.8 u
Low	3.0 u

Table 3: Effect of Resolution Settings on Signal Intensity and SNR (10 replicate injections of OFN)

Q1 = Low, Q3 = Low			Q1 = Unit, Q3 = Unit		
Run #	Peak Area	SNR	Run #	Peak Area	SNR
1	172,178	67	1	46,829	32,867
2	191,542	83	2	45,518	49,634
3	183,778	76	3	41,580	39,014
4	169,255	69	4	39,213	46,252
5	168,489	73	5	41,723	36,260
6	179,107	65	6	43,647	33,482
7	200,396	86	7	40,716	26,709
8	176,782	69	8	37,946	34,634
9	169,624	72	9	44,807	52,017
10	169,073	72	10	40,602	40,126
Average	178,022	73	Average	42,658	41,100
%RSD	6.1		%RSD	6.8	

Perhaps even more important than signal and noise considerations, is the impact mass spectral resolution can have on analyte selectivity against co-eluting matrix interferences. When a low resolution setting is used (e.g. 3.0 u), the *m/z* range of ion fragments that are allowed to strike the detector is broad, and allows non-specific fragments from compounds other than the target analyte (i.e. matrix interferences) to be included in the measurement. Narrowing the *m/z* range to Unit (0.8 u) or High (0.6 u) resolution minimizes the potential of there being close-eluting contaminants with similar *m/z* fragments. Compound specificity is achieved by using unique MRM transitions with customized resolution settings for each compound, and provides clean MRM chromatograms even in the presence of matrix interferences with common precursor or product ions. This principle is illustrated in Figure 3.

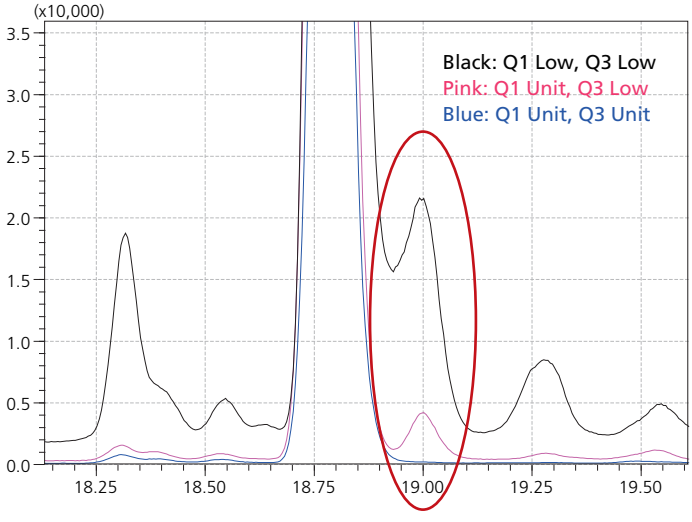

Figure 3: One MRM Transition, 158 → 130, Analyzed Using Three Different Resolution Settings for Q1 and Q3: Low/Low (Black), Unit/Low (Pink), and Unit/Unit (Blue) illustrates the effect of quadrupole resolution on compound selectivity.

Analysis of Pesticides in Baby Foods Using a Triple-Quadrupole GC/MS/MS

The effect of resolution settings on compound selectivity can also be seen in the matrix-matched pesticide standards used for the baby food project. Figure 4 shows the overlaid MRM chromatograms for mycyclobutanil (1.0 ng/mL) at three different resolution settings for Q1 and Q3: Low/Low, Unit/Low, and Unit/Unit. When using the Low/Low resolution setting, background interference from the baby food matrix is clearly evident, and produces interferences which prevent proper integration and confirmation of compound identity using peak ratios. The Unit/Unit resolution setting narrowed the *m/z* range on both Q1 and Q3 to eliminate the fragments from close-eluting matrix interference, and prevent them from contributing to the signal. The peak was easily and accurately integrated, and peak area ratios for the three individual transitions can be used for confirmation of compound identity.

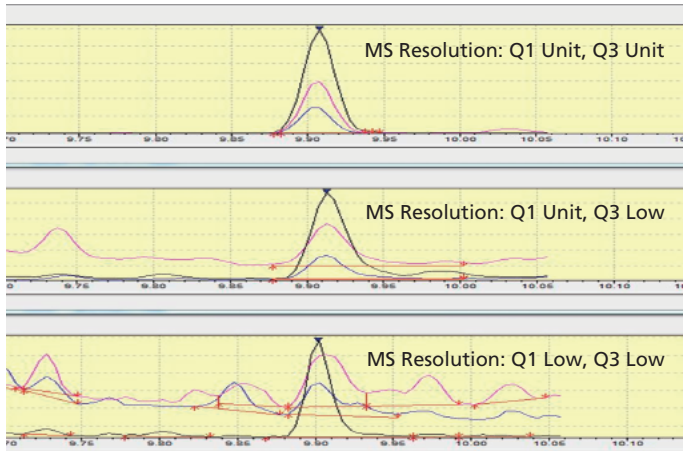

Figure 4: MRM Chromatograms for Mycyclobutanil at Three Settings of MS Resolution

Summary and Conclusions

Detection of pesticides was demonstrated at single-digit ng/mL (ppb) levels in a complex sample matrix, and linear calibration was confirmed from 1-200 ng/mL in matrix-matched standards. The concentration range used in this study covers the Maximum Residue Levels (MRL) for many pesticides, and validates the utility of the MRM mode for analysis of pesticides in complex food matrices.

For most analyses, the Unit/Unit resolution settings for Q1 and Q3 provide the best combination of sensitivity and selectivity. Lower resolution settings (Unit/Low or Low/Low) allow matrix contaminants to interfere with quantitation, and are not recommended. Higher resolution settings (e.g. High/Unit or High/High) which narrow the *m/z* range to 0.6 u on one or both sets of quadrupoles can also be used when matrix interference is severe. In this case, signal intensity will be reduced, but interference will be minimized or eliminated, and quantitation accuracy will be improved. A powerful feature of the Shimadzu GCMS-TQ8030 is the ability to adjust the Q1 and Q3 resolution settings individually to customize the method.

A Shimadzu GCMS-TQ8030 system operated in the MRM mode was shown to be a rapid, sensitive, and selective technique for analysis of various classes of pesticides in baby foods in the range required for many regulatory MRLs. Reliable, precise measurements were obtained for 36 pesticides. The Shimadzu GC/MS/MS Pesticide SmartMRM Database simplified development of the MRM method.

For further information

For a more complete discussion of the topics described here, including detailed analytical results, please send request for SSI Application Note GCMS-1402 to www.ssi.shimadzu.com.

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