Rapid and Simple Approaches to Multi-residue Pesticide Analysis in Fruits and Vegetables on both GC-MS/MS and LC-MS/MS

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Introduction

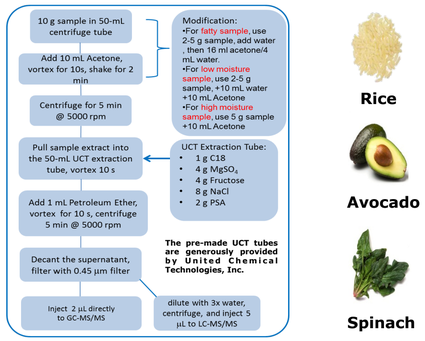
Tandem mass spectrometry coupled to chromatography, such as GC-MS/MS and LC-MS/MS, operated in MRM mode, has become the method of choice for targeted screening of multi-residue analysis in complex food matrix samples. A fast, easy and efficient sample preparation of food sample is the key to multi-residue pesticide MS analysis, which in fact still remains as a challenge. On the other hand, the multi-residue MRM method is labor-intensive and time-consuming. For production labs, it is always desired to have a ease-of-use software which integrates MRM method development flow to significantly speed up the method set-up.

In the current study, an improved QuEChERS sample preparation protocol as an alternative to the conventional QuEChERS is employed for vegetable matrix extraction. It is easy, fast, and has comparable recovery rate.[1] The exacted matrix can be diluted and directly shoot into GC/LC-MS for pesticide analysis which largely simplifies sample prep and saves time. We also demonstrate MSWS 8.1 software with Compound Based Screening (CBS) workflow for fast MRM method development using Bruker Scion GC-MS/MS and EVOQ LC-MS/MS system.

Figure 1. Bruker Scion™ GC-MS/MS with Scion 436 GC (left); EVOQ™ Elite LC-MS/MS with Bruker Advance™ UHPLC (right)

Methods

Three vegetable samples rice, avocado and spinach representing low moisture content, fatty content and high moisture content vegetable group were extracted using the following modified QuEChERS protocol recently developed at US FDA Lab at Irvine.[2]



Rice

Avocado

Spinach

30 pesticides were spiked in to the three extracted vegetable matrix. Calibration solutions were diluted using extracted blank matrix.

Scion GC-MS/MS analysis

Ionization mode: EI mode

Calibration: 1, 2, 5, 10, 20, 50, 100 ppb

Column: Bruker BR-5MS 30m x 0.25 mm, 0.25 µm

Run time: 36 min

EVOQ LC-MS/MS analysis

Ionization mode: ESI positive

Calibration: 0.1, 0.5, 1, 2, 5, 10, 20, 50, 100 ppb

Column: Phenomenex Synergi Hydro-RP, 100mm × 2.0 mm ID, 2.5 µm

Run time: 14 min

GC and LC-MS/MS MRM method

Compound name	GC-MS /MS		LC-MS /MS	
	MRM 1 (eV)	MRM 2 (eV)	MRM 1 (eV)	MRM 2 (eV)
Ametryn	212 > 94 (20)	212 > 122 (10)	228 > 186 (17)	228 > 68 (30)
Azaconazole	217 > 173 (15)	217 > 145 (25)	300 > 159 (15)	300 > 231 (15)
Azoxystrobin	344 > 156 (35)	344 > 329 (10)	404 > 372 (14)	404 > 344 (23)
Benalaxyl	206 > 162 (10)	206 > 132 (18)	326 > 148 (24)	326 > 208 (15)
Bromacil	205 > 162 (15)	205 > 188 (15)	261 > 205 (12)	261 > 188 (25)
Butralin	244 > 132 (20)	266 > 190 (10)	296 > 222 (15)	296 > 240 (12)
Carboxine	235 > 87 (20)	235 > 143 (20)	236 > 143 (16)	236 > 87 (27)
Clomazone	204 > 78 (30)	204 > 107 (20)	240 > 125 (23)	240 > 89 (30)
Coumaphos	362 > 109 (15)	362 > 226 (15)	363 > 227 (20)	363 > 211 (28)
Diethofencarb	267 > 197 (15)	267 > 225 (10)	268 > 180 (15)	268 > 226 (5)
Diniconazole	268 > 171 (20)	268 > 232 (10)	326 > 148 (23)	326 > 208 (14)
Fenamidone	238 > 103 (20)	268 > 180 (20)	312 > 236 (15)	312 > 92 (23)
Fenamiphos	303 > 154 (15)	303 > 228 (10)	304 > 217 (21)	304 > 202 (34)
Fenbuconazol	198 > 102 (25)	198 > 129 (15)	337 > 125 (29)	337 > 70 (25)
Fenothiocarb	160 > 72 (10)	160 > 106 (10)	254 > 160 (8)	254 > 72 (10)
Fenpropimorph	128 > 70 (10)	303 > 128 (10)	304 > 147 (29)	304 > 119 (30)
Flusilazole	233 > 152 (15)	315 > 233 (10)	316 > 247 (16)	316 > 165 (28)
Hexaconazole	214 > 152 (20)	214 > 159 (20)	314 > 70 (10)	314 > 159 (25)
Hexazinone	171 > 71 (15)	171 > 85 (15)	253 > 171 (16)	253 > 71 (25)
Imazalil	215 > 41 (20)	215 > 173 (10)	297 > 159 (23)	297 > 255 (12)
Isoprocarb	136 > 103 (25)	136 > 121 (10)	194 > 95 (10)	194 > 77 (25)
Myclobutanil	179 > 125 (15)	179 > 152 (10)	289 > 70 (10)	289 > 125 (25)
Napropamide	128 > 72 (5)	271 > 128 (10)	272 > 171 (19)	272 > 129 (18)
Pendimethalin	252 > 160 (10)	252 > 191 (10)	282 > 212 (5)	282 > 194 (15)
Pyriproxifen	136 > 41 (10)	136 > 96 (12)	322 > 185 (25)	322 > 134 (25)
Tebuconazole	250 > 125 (10)	250 > 163 (10)	308 > 125 (33)	308 > 70 (38)
Thiabendazole	201 > 130 (25)	201 > 174 (15)	202 > 175 (23)	202 > 131 (32)
Thiamethoxam	247 > 139 (15)	247 > 182 (10)	292 > 181 (15)	292 > 211 (15)
Tricyclazole	189 > 135 (20)	189 > 162 (10)	190 > 163 (20)	190 > 136 (27)
Triflumizole	206 > 179 (15)	278 > 73 (10)	346 > 43 (15)	346 > 73 (10)

Table 1. The MRM transitions of 30 pesticides by GC-MS/MS and LC-MS/MS system

Results

Compound based Screening (CBS) MRM method development workflow

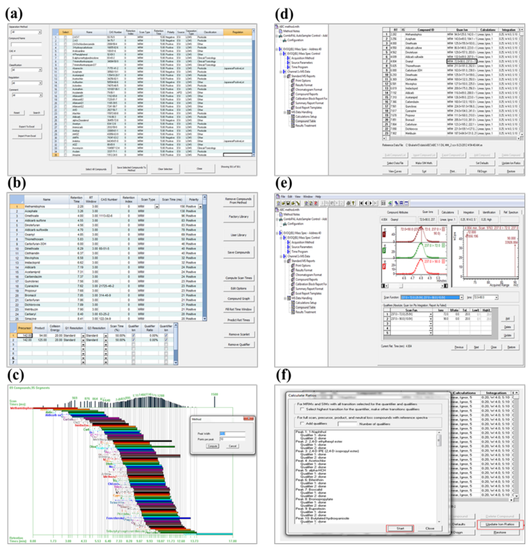


Figure 2. MRM method development workflow using CBS. a) select target pesticides from MRM library; b) export to CBS compound method editor; c) auto-calculate scan time for timed-MRM; d) "built-in" processing method; e) easy update of RT and method parameters; f) auto update Quan/Qual ion ratios from the result of a standard.

Sensitivity

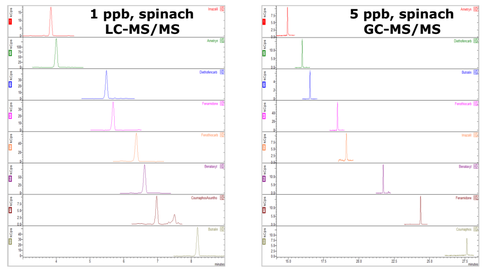


Figure 3. Total ion chromatogram of 1 ppb spiked-in pesticides in spinach QuCHERS matrix by LC-MS/MS (left) and 5 ppb spiked-in pesticides in spinach QuCHERS matrix by GC-MS/MS (right)

Linearity

Compound name	Control		Rice		Avocado		Spinach	
	GC-MS/MS 1 - 100 ppb	LC-MS/MS 0.1 - 100 ppb	GC-MS/MS 1 - 100 ppb	LC-MS/MS 0.1 - 100 ppb	GC-MS/MS 1 - 100 ppb	LC-MS/MS 0.1 - 100 ppb	GC-MS/MS 1 - 100 ppb	LC-MS/MS 0.1 - 100 ppb
Ametryn	0.998	0.999	1.000	0.994	0.999	0.993	1.000	0.998
Azaconazole	0.997	0.999	0.999	0.995	0.999	0.994	1.000	0.999
Azoxystrobin	0.995	0.987	0.999	0.999	0.999	0.997	0.999	0.997
Benalaxyl	0.998	0.997	1.000	0.999	0.999	0.988	1.000	0.991
Bromacil	0.997	0.997	0.999	0.997	0.999	0.992	1.000	0.999
Butralin	0.995	0.999	0.999	0.998	0.997	0.998	1.000	0.993
Carboxine	0.997	0.992	1.000	0.998	0.996	0.999	0.998	0.995
Clomazone	0.998	0.991	1.000	1.000	0.999	0.998	1.000	0.990
Coumaphos	0.994	0.997	1.000	0.987	0.998	0.998	1.000	0.993
Diethofencarb	0.997	0.997	0.999	0.999	0.999	0.995	1.000	0.989
Diniconazole	0.996	0.998	0.999	0.999	0.999	0.986	1.000	0.998
Fenamidone	0.996	0.996	1.000	1.000	0.999	0.999	1.000	0.997
Fenamiphos	0.995	0.993	1.000	1.000	0.999	0.998	1.000	0.993
Fenbuconazol	0.993	0.997	0.999	0.999	0.999	0.995	0.999	1.000
Fenothiocarb	0.997	0.998	0.999	0.995	0.999	0.992	1.000	0.997
Fenpropimorph	0.997	0.995	0.999	0.997	0.999	1.000	1.000	0.992
Flusilazole	0.997	0.998	0.999	1.000	0.999	1.000	1.000	0.998
Hexaconazole	0.995	0.996	0.999	0.999	0.999	0.996	1.000	0.999
Hexazinone	0.997	1.000	1.000	0.989	0.999	0.992	1.000	0.996
Imazalil	0.993	0.989	0.999	0.992	0.999	0.997	0.987	0.992
Isoprocarb	0.998	0.994	1.000	0.998	0.999	0.997	1.000	0.991
Myclobutanil	0.997	0.996	0.999	0.998	0.999	0.998	1.000	0.990
Napropamide	0.999	0.995	1.000	0.995	0.999	0.994	0.999	0.998
Pendimethalin	0.993	0.998	0.998	0.999	0.997	0.998	0.999	0.994
Pyriproxifen	0.997	0.999	0.999	1.000	0.999	1.000	1.000	0.997
Tebuconazole	0.995	0.994	1.000	0.999	0.999	0.993	1.000	0.997
Thiabendazole	0.983	1.000	0.999	0.997	0.995	0.996	0.999	1.000
Thiamethoxam	0.998	0.997	0.999	1.000	0.989	1.000	0.998	0.997
Tricyclazole	0.994	0.991	0.999	0.995	N/A	0.999	0.992	0.996
Triflumizole	0.996	0.996	0.999	0.998	0.999	0.993	1.000	0.997

Table 2. Calibration of pesticides in different matrices using GC-MS/MS and LC-MS/MS, shown above are R^2 values of calibration curve; excellent linearity was achieved in each matrix

References:

1. FDA/ORA/DFS, LIB# 4495, *Irvine Rapid Analytical Method: A rapid SPE Multiresidue Method for the Analysis of Polar and Nonpolar Pesticides in High Moisture Food products* by Olusegun Ajayi, et. al.

2. 2012 AOAC Conference Poster, *Los Angeles Micro Method: A Rapid SPE Multiresidue Method for the Analysis of Polar and Nonpolar Pesticides in High Moisture* by Olusegun Ajayi, et. al.

Conclusions

- The modified QuCHERS Method developed at FDA Irivine office is a simple, less expensive, and unified sample preparation for pesticide analysis on both GC-MS and LC-MS
- Compound-based Screening (CBS) work flow along with Bruker factory MRM libraries simply multi-residue method development on GC-MS/MS and LC-MS/MS system
- Good sensitivity of low ppb (1 ppb) on Scion TQ GC-MS/MS and sub-ppb (0.1 ppb) on EVOQ LC-MS/MS were demonstrated; great linearity was achieved on both instruments

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