表9 高濃度標準液（落花生用）（オリエンタル酵母㈱）添加食材の落花生タンパク質の測定

| 食材[a] | 落花生タンパク質 添加量[b] (μg/tube) | モリナガFASPEK落花生測定キット | | | FASTKITエライザVer.II落花生 | | |
		測定値 (μg/tube)	回収率 (%)	RSD (%)	測定値 (μg/tube)	回収率 (%)	RSD (%)
食材なし	0	0.00	–	–	0.00	–	–
（高濃度標準液のみ）	9.12	7.34	80.5	0.5	7.77	85.2	2.1
クッキー1	0	0.00	–	–	0.00	–	–
	9.12	7.92	86.8	1.8	12.18	133.6	1.2
クッキー2	0	0.00	–	–	0.00	–	–
	9.12	7.75	85.0	6.4	11.11	121.8	3.5
せんべい	0	0.00	–	–	0.00	–	–
	9.12	10.23	112.2	4.3	19.72	216.2	6.2
ラーメン	0	0.00	–	–	0.00	–	–
	9.12	8.20	89.9	2.1	13.72	150.4	3.7
おかゆ	0	0.00	–	–	0.00	–	–
	9.12	6.91	75.8	4.9	8.58	94.1	3.3

添加量 9.12は 2測定の平均、添加量 0 は 1測定
a 食材はそれぞれ 1g を分取
b 高濃度標準液（落花生用）（オリエンタル酵母㈱）の表示量から計算

表10 落花生高濃度標準液のタンパク質濃度

測定法	2-D Quant Kit	モリナガFASPEK落花生測定キット		FASTKITエライザVer.II落花生	
	測定値(A)	測定値(B)	回収率[b]	測定値(C)	回収率[c]
試料	(μg/mL)	(μg/mL)	(%)	(μg/mL)	(%)
高濃度標準液(落花生用)(オリエンタル酵母)	228[d]	184	80.4	194	85.2
自家製落花生高濃度標準液[a]	187[e]	197	105.3	136	72.6

a 自家製落花生一次標準粉末0.4 g に 0.5% SDS、2% Mercaptoethanol および0.5M塩化ナトリウムを含む20mM Tris-HCl(pH7.5) 20mLを加え、一晩振とうして抽出後、通知に従って20倍希釈して調製

b B/A×100

c C/A×100

d 表示値(オリエンタル酵母(株)での測定値)

e 2-D Quant Kitによる落花生標準品原液の測定値から計算

表11 自家製落花生高濃度標準液の添加回収および安定性試験

	保存期間	落花生タンパク質添加量[b]	モリナガFASPEK落花生測定キット			FASTKITエライザVer.II 落花生		
	(week)	添加量[b] (μg/tube)	測定値 (μg/tube)	回収率 (%)	RSD (%)	測定値 (μg/tube)	回収率 (%)	RSD (%)
自家製 高濃度標準液 添加	保存前		4.37	116.8	4.5	3.44	92.0	3.9
	1	3.74	3.95	105.6	2.2	3.63	97.1	2.4
	4		4.25	113.6	2.9	4.32	115.5	2.0
クッキー2[a]	12		4.19	112.0	3.1	4.22	112.8	5.1

a クッキー2を1g取り高濃度標準液を添加後、-20℃で保存、1時点につき3検体測定

b 2-D Quant Kit による落花生標準品原液の測定値から計算

表12 自家製落花生一次標準粉末添加試料の添加回収および安定性試験

測定キット	試料	タンパク質 添加量[a] (μg/tube)	保存前 測定値 (μg/tube)	保存前 回収率 (%)	保存前 RSD (%)	-20℃ 1週間保存後 測定値 (μg/tube)	-20℃ 1週間保存後 回収率 (%)	-20℃ 1週間保存後 RSD (%)	-20℃ 1か月保存後 測定値 (μg/tube)	-20℃ 1か月保存後 回収率 (%)	-20℃ 1か月保存後 RSD (%)	-20℃ 3か月保存後 測定値 (μg/tube)	-20℃ 3か月保存後 回収率 (%)	-20℃ 3か月保存後 RSD (%)
モリナガ FASPEK落花生 測定キット	CMC懸濁液	0	0	-	-	0	-	-	0	-	-	0	-	-
		5	5.15	103.0	1.3	4.88	97.6	1.0	4.98	99.6	1.4	4.83	96.6	0.9
		8	7.70	96.3	1.2	7.10	88.8	0.8	7.36	92.0	1.1	7.29	91.1	2.2
	あん	0	0	-	-	0	-	-	0	-	-	0	-	-
		5	5.71	114.2	3.8	5.17	103.4	1.4	5.61	112.2	0.2	5.38	107.6	3.4
		8	8.69	108.6	2.7	8.22	102.8	0.3	8.37	104.6	1.7	8.08	101.0	1.7
FASTKIT エライザVer.II	CMC懸濁液	0	0	-	-	0	-	-	0	-	-	0	-	-
		5	3.38	67.6	2.6	3.72	74.4	2.9	4.04	80.7	4.8	4.17	83.4	1.1
		8	5.45	68.1	2.8	5.91	73.9	0.0	6.60	82.5	8.0	6.52	81.5	8.3
	落花生 あん	0	0	-	-	0	-	-	0	-	-	0	-	-
		5	6.12	122.4	1.9	6.40	128.0	1.8	7.51	150.2	5.9	7.45	149.0	4.1
		8	9.83	122.9	1.6	10.39	129.9	2.4	13.65	170.6	4.2	12.42	155.3	2.7

CMC懸濁液：タンパク質添加量5および8μg/gは2測定の平均、添加量0は1測定
あん：タンパク質添加量5および8μg/gは3測定の平均、添加量0は1測定
a 落花生標準原液の2-D Quant Kitによる測定値から推定

表13 自家製高濃度標準液*の測定値を指標としたアッセイ間の再現性

| 測定時点(week) | 測定値(μg/tube) | | | | RSD |
	0	1	4	12	(%)
モリナガFASPEK小麦測定キット	8.34	8.93	9.05	8.85	3.6
モリナガFASPEKそば測定キット	5.34	5.06	5.01	5.12	2.8
モリナガFASPEK落花生測定キット	3.94	3.70	3.95	4.11	4.3
FASTKITエライザVer.Ⅱ小麦	4.67	4.97	5.15	4.81	4.2
FASTKITエライザVer.Ⅱそば	7.79	6.81	8.33	9.36	13.2
FASTKITエライザVer.Ⅱ落花生	2.71	2.78	3.20	3.40	11.0

*　　小麦はハルユタカ抽出液を使用
　　自家製高濃度標準液は、-80℃で保存した

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研究成果に関する刊行物一覧表

研究成果の刊行に関する一覧

書籍

著者氏名	論文タイトル名	書籍全体の編集者名	書籍名	出版社名	出版地	出版年	ページ
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研究成果に関する刊行物

論文発表

RESIDUES AND TRACE ELEMENTS

Simultaneous Analysis of 260 Pesticide Residues in Agricultural Products by Gas Chromatography/Triple Quadrupole Mass Spectrometry

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A method for simultaneous analysis of about 260 pesticides by gas chromatography coupled to tandem mass spectrometry (GC/MS/MS) with a triple quadrupole analyzer (QqQ) has been studied. The pesticides were extracted with acetonitrile and cleaned up by a bilayer cartridge. A single injection method was developed for the monitoring of all of the targeted pesticides. Two MS/MS transitions were selected for each analyte using the intensity ratio obtained from them as a confirmatory parameter. By using matrix-matched standards, 260 pesticides could be determined in most matrixes with recoveries of 70-120% and a standard deviation of ≤20 at 2 different fortification levels of 0.02 and 0.1 µg/g. The developed method was applied to the monitoring of 173 agricultural product samples from local market. The sensitivities of this method were lower than with most of selective GC detectors, such as flame photometric or single MS. The selectivity of QqQ gives a very clean chromatogram, making compound identification and confirmation easy. The quick and reliably monitoring was achieved by combination with rapid extraction and cleanup.

In Japan, all agricultural chemicals are regulated under the uniform limit (0.01 µg/g) except maximum residue levels (MRLs), which have been set for about 800 pesticides and veterinary drugs in 2006 (1). This system does not require analyzing all pesticides before distribution, but the demands of quality evaluation of commodities are increasing for various pesticides. These demands require a great amount of analytical labour. Until now, many multiresidue methods were developed to achieve effective analysis (2-7). These methods used gas chromatography (GC) that coupled with selective detectors and/or single mass spectrometry (MS) for determination of pesticides. Numerous target pesticides required more than one analysis by GC/MS or several kind of detectors. Recently, GC coupled to tandem mass spectrometry

(GC/MS/MS) has been used for the determination of agricultural chemicals (8-14). The MS/MS analysis is superior to single MS analysis. In the process, a narrow range of target masses is selected from all ions like selected ion monitoring (SIM) mode. Then, this selected range of masses is fragmentized and the product ions are monitored. A fragmentation depends on the chemical structure of analytes and provides superior selectivity to SIM mode and other conventional detections. An ion trap detector (ITD) allows product ion scan analysis in the MS/MS mode. On the other hand, a triple quadrupole (QqQ) analyzer can operate in the multiple reaction monitoring (MRM) mode, which monitors a few product ions/analyte. In these MS/MS measurements, the number of compounds that can be determined simultaneously is limited by the scan speed of the mass filters and data points of chromatographic peaks. It takes a very short time to monitor 1 or 2 product ions compare to that required for the product scan mode. Because of this advantage, QqQ could monitor approximately 50 MRM ions/s while ITD could analyze several product scans. Some research papers have been published about pesticide residue analysis by GC/ITD/MS (8-11) and GC/QqQ/MS (12-14). These reports determined from 50 to 130 pesticides with 1 or 2 injections. To achieve quick and effective monitoring, a large number of pesticides should be determined in a short time. The sensitivity and selectivity of QqQ have great potential that enables efficient screening. The aim of this work was to develop a method for the simultaneous analysis of more than 250 pesticide residues by GC/QqQ/MS with 1 injection.

Experimental

Apparatus

(a) *GC/QqQ/MS instrument.* — The extracts were analyzed with a Waters/Micromass (Manchester, UK) Quattro Micro GC QqQ instrument coupled with an Agilent (Little Falls, DE) 6890 gas chromatograph. The mass spectrometer was used in the MRM mode with electron impact ionization. The system was equipped with a split/splitless injection inlet, electronic pressure control, and 7683B autosampler. MassLynx and TargetLynx software were used for instrument control and data analysis respectively.

(b) *Capillary column.* — DB-5ms capillary column, 30 m, 0.25 mm i.d., 0.25 µm film thickness (Agilent, Folsom, CA).

Table 1. Conditions of the MRM transitions

Pesticide	F[a]	RT[b]	MRM1	MRM2
			Precursor > product ion (m/z)[c]	
			Collision energy (eV)	
Methamidophos	1	6.10	141 > 95 (6)	141 > 79 (18)
Dichlorvos	1	6.25	185 > 93 (10)	187 > 93 (12)
Allidochlor	1	6.70	132 > 56 (4)	134 > 56 (4)
Diphenyl	1	7.85	154 > 153 (10)	154 > 152 (22)
Mevinphos	1	8.21	192 > 127 (8)	193 > 127 (4)
Acephate	1	8.27	136 > 94 (10)	136 > 42 (6)
Propham	1	8.64	179 > 137 (4)	179 > 93 (10)
Metolcarb	1	8.68	108 > 107 (12)	108 > 79 (12)
Methacrifos	1	9.09	208 > 180 (4)	240 > 180 (8)
2-Phenylphenol	1	9.44	170 > 169 (16)	170 > 141 (20)
Isoprocarb	1	9.59	136 > 121 (6)	121 > 103 (10)
Molinate	1	9.73	187 > 126 (4)	126 > 55 (14)
XMC	1	9.92	122 > 107 (8)	122 > 121 (14)
Omethoate	2	10.29	156 > 110 (8)	110 > 79 (10)
Tecnazene	2	10.33	261 > 203 (8)	215 > 179 (6)
Xylylcarb	2	10.38	122 > 107 (10)	107 > 77 (12)
Fenobucarb	2	10.49	121 > 77 (18)	150 > 121 (10)
Propoxur	2	10.51	110 > 64 (14)	152 > 110 (5)
Propachlor	2	10.52	196 > 120 (6)	169 > 120 (6)
Diphenylamine	3	10.80	169 > 168 (10)	168 > 167 (10)
Ethoprophos	3	10.89	158 > 114 (6)	200 > 158 (6)
Ethalfluralin	3	11.00	276 > 202 (12)	316 > 276 (6)
Chlorpropham	3	11.16	213 > 171 (6)	213 > 127 (12)
Trifluralin	3	11.21	306 > 264 (6)	306 > 160 (18)
Benfluralin	3	11.28	292 > 264 (6)	292 > 206 (10)
Bendiocarb	3	11.33	166 > 151 (10)	223 > 166 (6)
Dioxabenzofos	3	11.36	216 > 138 (10)	216 > 137 (20)
Monochlotophos	3	11.43	127 > 109 (10)	192 > 127 (10)
Cadusafos	4	11.55	159 > 97 (12)	158 > 114 (4)
Promecarb	4	11.59	150 > 135 (8)	135 > 115 (10)
Pencycuron	4	11.60	180 > 125 (8)	125 > 89 (14)
Phorate	4	11.65	260 > 75 (8)	231 > 203 (4)
BHC, α-	4	11.77	219 > 183 (6)	181 > 145 (12)
Thiometon	4	11.96	88 > 60 (6)	246 > 88 (6)
Dicloran	4	12.07	206 > 176 (8)	208 > 178 (8)
Dimethoate	4	12.07	229 > 87 (6)	125 > 79 (6)
Carbofuran	5	12.22	164 > 149 (10)	164 > 131 (16)
Furilazole	5	12.22	262 > 220 (4)	264 > 222 (6)
Simazine	5	12.26	201 > 173 (4)	201 > 138 (10)
Atrazine	5	12.37	215 > 200 (4)	200 > 122 (8)
BHC, β-	5	12.39	219 > 183 (6)	181 > 145 (12)
Dimethipin	5	12.39	124 > 76 (4)	118 > 58 (2)
Clomazone	5	12.47	125 > 89 (12)	204 > 107 (16)
Quintozene	5	12.47	249 > 214 (10)	295 > 237 (16)
BHC, γ-	6	12.62	219 > 183 (6)	181 > 145 (12)
Cyanophos	6	12.72	243 > 109 (10)	243 > 127 (6)
Terbufos	6	12.72	231 > 175 (10)	288 > 231 (4)
Propyzamide	6	12.80	173 > 145 (12)	173 > 109 (22)
Diazinon	6	12.88	199 > 93 (16)	304 > 179 (12)
Pyrimethanil	7	13.00	199 > 198 (8)	198 > 118 (26)

Table 1. (continued)

Pesticide	F[a]	RT[b]	MRM1	MRM2
			Precursor > product ion (m/z)[c]	
			Collision energy (eV)	
Chlorothalonil	7	13.01	264 > 168 (18)	266 > 170 (18)
Flufenoxuron	7	13.08	268 > 241 (14)	331 > 276 (16)
Disulfoton	7	13.16	274 > 88 (5)	186 > 142 (5)
Terbacil	7	13.16	161 > 88 (16)	160 > 76 (10)
Isazophos	7	13.19	257 > 162 (4)	257 > 119 (16)
Tefluthrin	7	13.24	177 > 127 (14)	197 > 141 (10)
Etrimfos	7	13.29	292 > 181 (6)	292 > 153 (16)
BHC, δ-	7	13.33	219 > 183 (6)	181 > 145 (12)
Tri-allate	7	13.35	268 > 184 (16)	270 > 186 (16)
Pirimicarb	8	13.49	238 > 166 (6)	166 > 96 (12)
Iprobenfos	8	13.55	204 > 91 (6)	204 > 122 (10)
Benoxacor	8	13.62	259 > 120 (12)	261 > 120 (10)
Formothion	8	13.67	198 > 170 (4)	170 > 93 (6)
Ethiofencarb	8	13.70	168 > 107 (8)	168 > 77 (30)
Phosphamidon	9	13.85	264 > 127 (10)	227 > 127 (6)
Benfuresate	9	13.89	256 > 163 (8)	163 > 121 (4)
Dichlofenthion	9	13.91	279 > 223 (12)	223 > 205 (12)
Dimethenamid	9	13.93	230 > 154 (8)	232 > 154 (8)
Propanil	9	13.95	217 > 161 (8)	161 > 99 (22)
Acetochlor	9	14.03	224 > 148 (8)	223 > 146 (6)
Chlorpyrifos-methyl	9	14.06	286 > 93 (16)	286 > 271 (10)
Bromobutide	9	14.07	232 > 176 (8)	232 > 114 (6)
Metribuzin	9	14.07	198 > 82 (10)	198 > 110 (8)
Vinclozolin	10	14.17	285 > 212 (8)	214 > 174 (10)
Parathion-methyl	10	14.23	263 > 109 (10)	263 > 246 (4)
Alachlor	10	14.25	189 > 131 (18)	189 > 160 (8)
Simeconazole	10	14.25	195 > 75 (10)	211 > 121 (12)
Tolclofos-methyl	10	14.25	265 > 250 (12)	265 > 93 (22)
Simetryn	11	14.35	213 > 170 (8)	213 > 185 (6)
Carbaryl	11	14.39	144 > 115 (20)	144 > 116 (8)
Metalaxyl	11	14.44	206 > 132 (14)	206 > 162 (6)
Ametryn	11	14.46	227 > 185 (4)	227 > 170 (8)
Heptachlor	11	14.46	272 > 237 (12)	274 > 239 (14)
Fenchlorphos	11	14.50	285 > 270 (10)	287 > 272 (12)
Prometryn	11	14.53	226 > 184 (6)	241 > 184 (8)
Dithiopyr	11	14.57	354 > 306 (6)	354 > 286 (12)
Pirimiphos-methyl	12	14.79	290 > 151 (14)	305 > 180 (6)
Terbutryn	12	14.85	241 > 185 (4)	170 > 128 (6)
Fenitrothion	12	14.86	277 > 260 (4)	277 > 109 (14)
Methiocarb	12	14.90	168 > 153 (6)	153 > 109 (6)
Ethofumesate	12	14.92	207 > 161 (6)	207 > 137 (10)
Bromacil	12	14.93	205 > 188 (12)	207 > 190 (20)
Probenazole	12	14.96	159 > 130 (6)	159 > 103 (20)
Esprocarb	12	15.09	222 > 91 (12)	162 > 91 (6)
Malathion	12	15.09	173 > 127 (6)	173 > 99 (10)
Thiazopyr	12	15.12	327 > 277 (24)	381 > 361 (6)
Quinoclamine	12	15.14	207 > 172 (8)	209 > 172 (10)
Metolachlor	13	15.22	238 > 162 (10)	238 > 133 (24)
Chlorpyrifos	13	15.26	314 > 258 (12)	316 > 260 (12)
Diethofencarb	13	15.31	267 > 225 (8)	267 > 168 (16)

Table 1. (continued)

Pesticide	F[a]	RT[b]	Precursor > product ion (m/z)[c] Collision energy (eV)	
			MRM1	MRM2
Dimethylvinphos	13	15.31	295 > 109 (16)	297 > 109 (16)
Thiobencarb	13	15.31	100 > 72 (4)	125 > 89 (12)
Aldrin	13	15.37	263 > 193 (22)	263 > 191 (24)
Chlorthal-dimethyl	13	15.37	299 > 221 (18)	301 > 223 (18)
Cyanazine	13	15.37	225 > 189 (10)	225 > 198 (8)
Fenthion	13	15.38	278 > 109 (16)	278 > 169 (14)
Parathion	14	15.46	291 > 109 (10)	291 > 137 (4)
Fenpropimorph	14	15.47	128 > 110 (6)	128 > 70 (8)
Tetraconazole	14	15.52	336 > 218 (12)	336 > 204 (24)
Triadimefon	14	15.54	208 > 181 (6)	208 > 127 (10)
Nitrothal-isopropyl	14	15.65	236 > 194 (6)	236 > 148 (14)
4,4'-dichloro-benzophenone (Dicofol decomposed)	14	15.66	250 > 139 (8)	250 > 215 (4)
Fthalide	14	15.70	243 > 215 (14)	241 > 213 (14)
Pirimiphos-ethyl	14	15.80	304 > 168 (10)	318 > 166 (12)
Bromophos	14	15.81	331 > 316 (10)	329 > 314 (12)
Diphenamid	14	15.83	239 > 167 (4)	167 > 165 (16)
Fosthiazate	14	15.86	195 > 103 (6)	195 > 139 (4)
Pendimethalin	15	16.08	252 > 162 (8)	252 > 191 (8)
Chlorfenvinphos α	15	16.09	323 > 267 (12)	325 > 269 (12)
Cyprodinil	15	16.12	225 > 224 (8)	224 > 208 (16)
Fipronil	15	16.18	367 > 213 (22)	367 > 255 (18)
Penconazole	15	16.25	248 > 157 (18)	248 > 192 (10)
Dimethametryn	15	16.26	212 > 122 (8)	212 > 94 (18)
Isofenphos	15	16.31	213 > 121 (14)	213 > 185 (6)
Heptachlor-epoxide	15	16.34	353 > 263 (12)	355 > 265 (12)
Pyrifenox Z	15	16.34	262 > 200 (14)	262 > 91 (14)
Chlorfenvinphos β	15	16.36	323 > 267 (12)	325 > 269 (12)
Bioallethrin	16	16.46	123 > 81 (6)	168 > 123 (6)
Phenthoate	16	16.49	274 > 121 (8)	274 > 125 (16)
Quinalphos	16	16.52	146 > 118 (10)	146 > 91 (22)
Captan	16	16.58	149 > 105 (2)	149 > 70 (12)
Procymidone	16	16.58	283 > 96 (6)	283 > 68 (16)
Triadimenol	16	16.60	168 > 70 (8)	128 > 65 (18)
Dimepiperate	16	16.63	145 > 112 (6)	145 > 69 (12)
Triflumizole	16	16.63	206 > 179 (12)	278 > 73 (6)
Methidathion	17	16.86	145 > 85 (6)	145 > 58 (12)
Hexythiazox	17	16.94	184 > 149 (4)	227 > 149 (6)
Propaphos	17	16.94	220 > 140 (8)	304 > 220 (10)
Chinomethionat	17	16.97	234 > 206 (8)	206 > 148 (14)
Pyrifenox E	17	16.98	262 > 200 (14)	262 > 91 (14)
Tetrachlorvinphos	17	17.01	329 > 109 (18)	331 > 109 (18)
Paclobutrazol	17	17.07	236 > 125 (10)	236 > 167 (8)
Butachlor	17	17.09	237 > 160 (8)	176 > 146 (20)
Fenothiocarb	17	17.14	160 > 72 (6)	161 > 72 (6)
Endosulfan α	18	17.28	241 > 206 (12)	195 > 160 (8)
Butamifos	18	17.29	286 > 202 (12)	286 > 185 (22)
Flutriafol	18	17.36	219 > 123 (10)	123 > 75 (22)

Table 1. (continued)

Pesticide	F[a]	RT[b]	Precursor > product ion (m/z)[c] Collision energy (eV)	
			MRM1	MRM2
Fenamiphos	18	17.41	303 > 195 (4)	303 > 288 (6)
Napropamide	18	17.43	271 > 128 (4)	271 > 72 (10)
Flutolanil	18	17.47	281 > 173 (10)	173 > 145 (14)
Metominostrobin E	18	17.54	191 > 160 (8)	238 > 210 (10)
Fludioxonil	18	17.55	248 > 127 (22)	248 > 154 (16)
Hexaconazole	18	17.57	214 > 159 (16)	256 > 159 (16)
Prothiofos	18	17.58	267 > 239 (8)	309 > 239 (12)
Isoprothiolane	19	17.62	290 > 118 (10)	290 > 204 (2)
Pretilachlor	19	17.62	262 > 202 (10)	162 > 147 (10)
Profenofos	19	17.69	337 > 267 (12)	339 > 269 (12)
DDE,pp'-	19	17.80	246 > 176 (26)	248 > 176 (26)
Oxadiazon	19	17.80	258 > 175 (4)	175 > 112 (8)
Thifluzamide	19	17.80	449 > 429 (10)	194 > 125 (18)
Uniconazole P	19	17.81	234 > 165 (6)	234 > 137 (12)
Flamprop-methyl	19	17.84	276 > 105 (4)	230 > 170 (12)
Tribuphos	19	17.87	202 > 147 (4)	202 > 113 (12)
Myclobutanil	19	17.90	179 > 125 (14)	179 > 152 (6)
Oxyfluorfen	20	17.92	300 > 223 (12)	361 > 300 (10)
Dieldrin	20	17.94	263 > 193 (22)	263 > 191 (24)
Flusilazole	20	17.94	233 > 165 (16)	233 > 152 (14)
Bupirimate	20	17.95	273 > 193 (4)	273 > 108 (14)
Buprofezin	20	17.97	172 > 57 (12)	105 > 104 (8)
Kresoxim-methyl	20	17.98	206 > 116 (4)	206 > 131 (10)
Metominostrobin Z	20	18.03	191 > 160 (8)	238 > 210 (10)
Diclobutrazol	20	18.06	270 > 159 (8)	272 > 161 (8)
Iprovalicarb	20	18.11	116 > 98 (4)	158 > 116 (2)
Chlorfenapyr	20	18.19	247 > 227 (10)	247 > 200 (22)
Cyflufenamid	21	18.23	223 > 203 (10)	294 > 237 (4)
Isoxathion	21	18.28	177 > 130 (6)	313 > 177 (6)
Cyproconazole	21	18.32	222 > 125 (18)	222 > 82 (8)
Fenoxanil	21	18.37	293 > 155 (16)	189 > 125 (8)
Endrin	21	18.46	263 > 193 (22)	263 > 191 (24)
Pyriminobac-methyl Z	21	18.56	302 > 256 (12)	302 > 230 (12)
Chlorobenzilate	21	18.59	251 > 139 (12)	253 > 141 (10)
Fensulfothion	21	18.66	293 > 125 (12)	293 > 97 (18)
Endosulfan β	21	18.71	241 > 206 (12)	195 > 160 (8)
Oxadixyl	21	18.78	163 > 132 (8)	233 > 146 (10)
Ethion	22	18.83	231 > 175 (10)	231 > 129 (18)
DDD,pp'-, DDT,op'-	22	18.86	235 > 165 (18)	237 > 165 (16)
Fluacrypyrim	22	19.00	189 > 129 (10)	204 > 129 (18)
Mepronil	22	19.15	269 > 119 (10)	269 > 210 (6)
Triazophos	22	19.19	161 > 134 (6)	257 > 162 (4)
Sulprofos	22	19.22	322 > 156 (8)	322 > 139 (12)
Carfentrazone-ethyl	22	19.36	340 > 312 (8)	330 > 310 (8)
Benalaxyl	22	19.39	266 > 148 (8)	204 > 176 (4)
Norflurazon	22	19.49	303 > 145 (14)	305 > 145 (18)
Cyanofenphos	23	19.51	303 > 141 (12)	303 > 169 (4)
Trifloxystrobin	23	19.51	222 > 130 (8)	190 > 130 (6)
Edifenphos	23	19.56	173 > 109 (6)	310 > 173 (10)

Table 1. (continued)

Pesticide	F[a]	RT[b]	Precursor > product ion (m/z)[c] — Collision energy (eV) — MRM1	MRM2
Propiconazole	23	19.56	259 > 69 (8)	259 > 173 (12)
Quinoxyfen	23	19.59	237 > 208 (22)	272 > 237 (10)
Diofenolan	23	19.61	300 > 186 (6)	186 > 157 (14)
Pyriminobac-methyl E	23	19.61	302 > 256 (12)	302 > 230 (12)
Lenacil	23	19.65	153 > 136 (12)	153 > 82 (14)
Pyraflufen-ethyl	23	19.69	412 > 349 (8)	349 > 307 (10)
Clodinafop-propargyl	23	19.73	349 > 266 (6)	349 > 238 (12)
DDT,pp'-	23	19.75	235 > 165 (18)	237 > 165 (16)
Hexazinoe	24	19.85	171 > 71 (12)	171 > 85 (12)
Thenylchlor	24	19.96	288 > 141 (10)	127 > 59 (6)
Tebuconazole	24	20.08	250 > 125 (14)	252 > 127 (14)
Diclofop-methyl	24	20.09	253 > 162 (12)	340 > 253 (8)
Diflufenican	24	20.12	394 > 266 (8)	266 > 246 (10)
Propargite	24	20.12	135 > 107 (10)	173 > 135 (14)
Captafol	24	20.28	150 > 79 (6)	313 > 79 (18)
Pyributicarb	25	20.54	181 > 108 (8)	181 > 93 (20)
Pyridaphenthion	25	20.66	340 > 199 (6)	340 > 109 (16)
Iprodione	25	20.67	314 > 245 (10)	316 > 247 (10)
Carbosulfan	25	20.69	160 > 104 (8)	118 > 76 (6)
Phosmet	25	20.87	160 > 77 (18)	160 > 133 (10)
Bifenthrin	25	20.91	181 > 166 (10)	181 > 165 (20)
EPN	25	20.94	169 > 141 (8)	169 > 77 (20)
Piperophos	25	20.97	320 > 122 (8)	140 > 98 (8)
Bromopropylate	26	20.97	341 > 185 (12)	343 > 185 (12)
Picolinafen	26	20.99	376 > 239 (10)	376 > 238 (16)
Fenoxycarb	26	21.03	186 > 109 (12)	255 > 186 (6)
Cloquintocet-1-methylhexyl	26	21.07	192 > 162 (18)	192 > 127 (28)
Etoxazole	26	21.10	300 > 270 (20)	204 > 176 (8)
Methoxychlor	26	21.10	227 > 169 (22)	227 > 141 (32)
Fenpropathrin	26	21.14	265 > 210 (10)	265 > 89 (26)
Tebufenpyrad	26	21.28	333 > 171 (16)	276 > 171 (8)
Anilofos	26	21.30	226 > 184 (4)	226 > 157 (12)
Bifenox	26	21.31	341 > 310 (6)	341 > 189 (16)
Furametpyr	27	21.43	298 > 123 (16)	157 > 76 (18)
Clomeprop	27	21.45	288 > 169 (12)	323 > 288 (4)
Furathiocarb	27	21.50	325 > 194 (4)	163 > 107 (10)
Tetradifon	27	21.59	354 > 159 (8)	356 > 159 (8)
Phenothrin	27	21.64	123 > 81 (5)	183 > 153 (12)
Phosalone	27	21.74	367 > 182 (8)	182 > 138 (6)
Azinphos-methyl	27	21.84	160 > 77 (12)	160 > 104 (6)
Cyhalothrin	28	21.95	208 > 181 (8)	197 > 141 (10)
Pyriproxyfen	28	21.97	136 > 96 (8)	136 > 78 (18)
Cyhalofop-butyl	28	22.02	256 > 120 (6)	357 > 256 (8)
Mefenacet	28	22.05	192 > 136 (12)	193 > 137 (12)
Lactofen	28	22.19	344 > 223 (12)	344 > 300 (6)
Acrinathrin	28	22.39	209 > 181 (6)	290 > 93 (8)
Pyrazophos	28	22.42	221 > 193 (6)	232 > 204 (6)
Fenarimol	28	22.45	251 > 139 (14)	219 > 107 (10)
Pyraclofos	28	22.80	360 > 194 (8)	360 > 139 (14)

Table 1. (continued)

Pesticide	F[a]	RT[b]	Precursor > product ion (m/z)[c] — Collision energy (eV) — MRM1	MRM2
Bitertanol	29	23.15	170 > 141 (18)	170 > 115 (28)
Fluquinconazole	29	23.39	340 > 298 (14)	340 > 286 (20)
Permethrin	29	23.40	183 > 168 (12)	183 > 153 (12)
Pyridaben	29	23.45	309 > 147 (14)	147 > 117 (18)
Prochloraz	29	23.47	310 > 70 (14)	308 > 70 (14)
Butafenacil	29	23.60	331 > 180 (14)	333 > 182 (14)
Cafenstrole	29	23.81	100 > 72 (4)	188 > 119 (18)
Etobenzanid	29	23.81	179 > 149 (6)	179 > 121 (10)
Fenbuconazole	29	23.91	198 > 129 (8)	129 > 102 (12)
Cyfluthrin	29	24.05	163 > 127 (4)	226 > 206 (12)
Halfenprox	29	24.45	263 > 117 (10)	265 > 117 (10)
Cypermethrin	29	24.49	163 > 127 (4)	165 > 127 (4)
Flucythrinate	29	24.57	199 > 157 (8)	199 > 107 (20)
Silafluofen	29	24.96	286 > 258 (10)	286 > 207 (12)
Pyrimidifen	30	25.28	184 > 169 (16)	186 > 171 (18)
Flumioxazin	30	25.47	287 > 259 (10)	354 > 326 (4)
Fluvalinate	30	25.69	250 > 55 (14)	250 > 200 (18)
Fenvalerate	30	25.83	167 > 125 (6)	225 > 119 (14)
Difenoconazole	30	26.19	323 > 265 (12)	325 > 267 (12)
Indoxacarb-MP	30	26.39	203 > 134 (10)	218 > 203 (6)
Deltamethrin	30	26.65	253 > 174 (8)	253 > 93 (14)
Tralomethrin	30	26.65	253 > 174 (8)	253 > 93 (14)
Flumiclorac-pentyl	30	26.86	423 > 318 (6)	423 > 308 (12)
Azoxystrobin	30	26.90	344 > 329 (10)	388 > 345 (14)

[a] F = Function number.

[b] RT = Retention time, min.

[c] m/z = Mass-to-charge ratio.

(c) **Solid-phase extraction (SPE) cartridge.**— Double-layer cartridge with 500 mg graphitized carbon black (GCB) and 500mg primary secondary amine (PSA) was obtained from Supelco (Bellefonte, PA) as ENVI-Carb II/PSA. The cartridge was preconditioned with 30 mL acetonitrile-toluene (3:1).

(d) **Food processor and homogenizer.**— A Toshiba (Tokyo, Japan) QS-7 food processor was used to comminute fruit and vegetable samples. A Hitachi (Tokyo, Japan) HG30 homogenizer was used to blend sample and acetonitrile in the extraction step.

(e) **Tube and centrifuge.** — For the extraction step, Becton Dickinson (Franklin Lakes, NJ) BLUE MAX 50 mL polypropylene conical tubes were used. A Hitachi Himac SCR 20B centrifuge was used for these tubes.

(f) **Analytical balance.** — A Sartorius (Westbury, NY) BP2100S top-loading balance was used to weigh the chopped samples and solid reagents.

(g) **Solvent evaporator.** — An Iwaki (Asahi Techno Glass, Chiba, Japan) REN-1000 and REN-1 rotary evaporators were used to concentrate eluates.
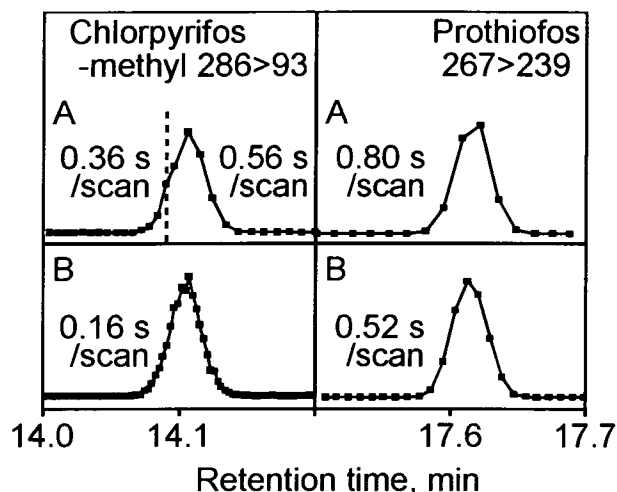
Figure 1. Peak shapes of the pesticide with the lowest scan rate. A: 0.20–0.80 s/scan, B: 0.04–0.52 s/scan.

Reagents

(a) Chemicals. — Acetonitrile, toluene, acetone and n-hexane were of pesticide analysis grade; anhydrous magnesium sulfate and sodium chloride were of analytical grade (Wako Pure Chemical Industries, Osaka, Japan).

(b) Pesticide standard. — Pesticide standards certified (Wako; Kanto Chemical Co., Inc., Tokyo, Japan; Riedel-de-Haën, Seelze, Germany; Hayashi Pure Chemical, Osaka, Japan; Ehrenstorfer Laboratories GmbH, Augsburg, Germany). Each compound was dissolved in acetone to make a 1 mg/mL stock standard solution. Mixed-compound intermediate solutions were prepared from stock solutions at concentrations ranging from 40 to 100 µg/mL. Two groups of spiking solutions were prepared from intermediate solutions containing approximately 140 compounds at the concentration of 5 µg/mL. Spiking solutions were used for fortifying the samples and also for the calculation after appropriate dilution.

Extraction and Cleanup Procedure

The sample was extracted according to our previous report (7). An aliquot of 10 g of sample was homogenized with 20 mL acetonitrile. The homogenate was shaken with 4g MgSO4 and 1 g NaCl to separate the sediment and water from the acetonitrile. An aliquot of 16 mL of the acetonitrile layer was loaded into a GCB/PSA SPE cartridge, and 30 mL acetonitrile-toluene (3 + 1) was used to elute the retained pesticides. The eluate was evaporated, and the residue was dissolved in 8 mL acetone-hexane (1 + 9) for GC/QqQ/MS analysis. The concentration of the sample represented by the test solution was 1 g/mL.

Fortifications

In recovery studies, 40 or 200 µL of 2 spiking solutions were added to each 10 g carrot, banana, and grapefruit

individually. The tubes containing fortified sample were left for 30 min to give them time to interact with the matrix.

Preparation of Matrix-Matched Calibration Standards

Calibration was achieved by preparing matrix-matched calibration standards from the extracts of blank samples in order to compensate for the matrix effects (15). Analytes were quantified by using from 3 to 6 points of matrix-matched calibration standards.

Analysis

GC/QqQ/MS analysis was conducted under the following conditions: column, DB-5ms; helium carrier gas flow, 1.5 mL/min; injector temperature, 250°C; injection volume, 1 µl (splitless); MS interface temperature, 250°C; ion source temperature, 250°C; oven temperature program: 60°C for 1 min, then 20°C/min to 140°C and 8°C/min to 300°C, and held for 5 min. The total run time was 30 min. The MRM parameters were summarized in Table 1. MRM1 was used for quantification, and the intensity ratio of MRM1 and 2 was used as the confirmatory parameter.

Crosscheck Analysis

GC with a flame photometric detector (GC/FPD), GC/ITD/MS, and GC/MS analyses were conducted according to earlier papers (6,7).

Results and discussion

GC/QqQ/MS Method Development

An MS/MS measurement method is usually constructed by some groups of MRM ions, which is called "function" by the system software. Start and end time of each function can be defined individually. More than 2 functions can operate simultaneously. A measurement method can be constructed with 1 to 32 functions that can monitor up to 32 MRM ions. It is calculated that 1024 MRM ions (32 × 32) could be measured in one analysis. Practically, the chromatographic
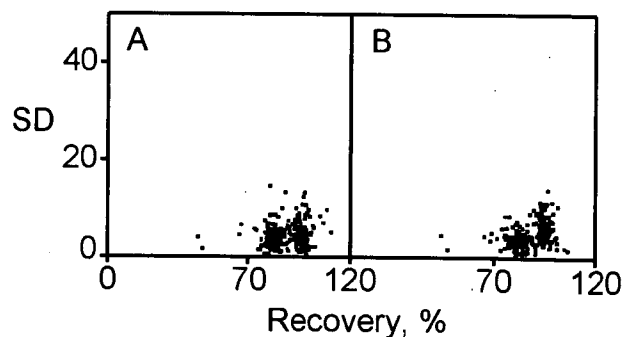

Figure 2. Summary of recovery tests in carrot measured by 2 different scan speeds. A: 0.20-0.80 s/scan, B: 0.04-0.52 s/scan.

Table 2. The list of final time window

Function No.	No. of MRM ions	Start time, min	End time, min
1	26	5.00	10.1
2	12	10.10	10.7
3	22	10.70	11.6
4	16	11.30	12.30
5	16	12.10	12.60
6	10	12.50	13.00
7	20	12.80	13.55
8	10	13.40	13.90
9	18	13.70	14.25
10	10	14.10	14.40
11	16	14.25	14.75
12	22	14.60	15.30
13	18	15.05	15.60
14	22	15.30	16.05
15	18	16.00	16.60
16	18	16.40	16.80
17	18	16.70	17.30
18	20	17.15	17.70
19	20	17.50	18.05
20	20	17.80	18.40
21	20	18.05	19.00
22	18	18.60	19.70
23	22	19.40	19.90
24	14	19.70	20.45
25	14	20.45	21.10
26	24	20.80	21.50
27	14	21.20	22.00
28	18	21.85	23.00
29	27	22.80	25.10
30	18	25.10	28.00

peak shape, which depends on scan speed, restricts the number of simultaneous analysis.

Reported measurements with GC/ITD/MS targeted less than 100 pesticides (8-11), and other methods using GC/QqQ/MS analyzed less than 130 pesticides simultaneously (12-14). Some of these methods needed 2 injections. In the beginning of our experiments, the retention time and MRM transitions of 270 pesticides were determined to construct the GC/QqQ/MS method. Two MRM transitions were selected for determination and confirmation of each pesticide. All compounds were sorted by their retention times and divided into 30 groups corresponding to 30 functions. Each function monitored 10 to 27 MRM ions. Some functions overlapped with neighbors. In these periods, 26 to 40 MRM ions were monitored simultaneously. The dwell time of all

MRM ions was set for 0.01 s, and another 0.01 s was needed for inter channel delay time. In this method, the scan speeds of MRM ions ranged from 0.20 to 0.80 s/scan (low speed). To evaluate the effect of scan speed, this GC/QqQ/MS method was divided into 2 analysis methods that monitored 140 compounds each. In these methods, the scan speeds were reduced to from 0.04 to 0.52 s/scan (high speed).

Extraction procedure has been investigated in our previous reports (6,7). The features of the extraction procedure were a rapid process and effective cleanup. The concentration of extract and the injection volume were less than those of other reports (8-14). It was calculated that our method injected 10 - 50 times less sample equivalents into the instrument than other methods. The extraction procedure showed good recoveries and precision in our previous work. Three parallel trials of recovery tests were conducted in carrot for 270 compounds at a level of 100 ng/g to confirm reliability of the analytical method. The spiked samples and matrix-matched standards were measured by low and high speed methods, and the recovery results were calculated. Figure 1 shows the typical chromatograms of spiked pesticides measured by the low and high speed methods. The peak of prothiofos appeared in the most crowded period in the chromatogram and was indicated with 6 points at 0.80 s/scan. There were no differences in the recovery between 2 scan speeds as shown in the following results: chlorpyrifos-methyl (A; low speed) $83 \pm 4\%$, (B; high speed) $82 \pm 3\%$; prothiofos (A) $94 \pm 3\%$, (B) $93 \pm 4\%$. Figure 2 shows the results of the recovery tests. Almost all of the compounds were recovered in the range of 70 to 120% with low standard deviations (SDs) of ≤ 20. It was concluded that the simultaneous analysis of 270 compounds had good precision and was feasible for monitoring. Table 2 shows the final time window for 270 compounds.

Further recovery tests were conducted with carrot, banana, and grapefruit at levels of 20 and 100 ng/g, and all compounds were measured simultaneously (Table 3). Typical calibration graphs and chromatograms of MRM transitions are shown in Figure 3. TargetLynx software reported the limits of detection values that were calculated based on a signal-to-noise) ratio of 3 with the matrix-matched standard analyses. The results of 222 pesticides indicated an acceptable range of recovery between 70 and 120% and SD values of ≤ 20 in all cases. Another 38 compounds showed good results but failed in 1 or 2 samples. The remaining 10 pesticides gave poor results. The standard of dicofol gave 2 peaks in the chromatograms for the original and decomposed. In the recovery tests, decomposed dicofol gave high recoveries, and no original dicofol was detected. Chinomethionat and chlorothalonil were retained by PSA in the SPE cleanup. In total, 260 pesticides showed sufficient recoveries and low SDs. Moreover, the proposed method could detect most pesticides at lower levels than the uniform limit (0.01 μg/g) required by legislation.

Table 3. Mean recovery, precision, and limit of detection values

Pesticide	Recovery, % and SD												LOD, ng/g
	Carrot (n = 4, 3)[a]				Banana (n = 3)				Grapefruit (n = 5)				
	20 ng/g		100 ng/g		20 ng/g		100 ng/g		20 ng/g		100 ng/g		
Acephate	95	11	79	6	81	3	72	10	31	18	37	11	6.5
Acetochlor	85	4	82	4	100	4	99	5	83	16	96	3	2.8
Acrinathrin	96	17	100	8	84	13	63	4	NC[b]	—[c]	120	13	10.7
Aldrin	79	6	84	8	80	6	90	2	94	13	92	7	3.3
Allidochlor	88	3	83	7	88	6	89	4	88	7	87	4	0.8
Ametryn	90	7	79	3	96	5	95	4	80	8	89	4	2.4
Anilofos	98	3	97	5	110	5	92	3	100	9	112	7	1.5
Atrazine	85	6	85	5	96	6	94	3	90	4	89	5	1.6
Azinphos-methyl	105	7	95	2	110	5	80	6	89	8	105	3	1.9
Azoxystrobin	84	6	98	4	106	3	78	1	81	15	92	8	3.7
Benalaxyl	86	4	76	3	98	3	90	8	95	5	108	6	1.0
Bendiocarb	85	7	82	6	97	6	93	3	90	4	98	5	1.9
Benfluralin	96	5	93	4	95	5	89	3	84	6	93	4	2.6
Benfuresate	89	5	96	5	109	4	96	2	96	5	96	3	1.4
Benoxacor	99	4	96	7	101	4	96	3	92	6	100	4	1.4
BHC, α-	103	9	93	5	90	5	90	2	90	5	95	5	0.7
BHC, β-	105	17	93	6	91	6	94	3	101	6	103	3	0.9
BHC, γ-	101	2	90	3	92	2	88	2	96	8	98	2	0.9
BHC, δ-	102	9	90	5	89	4	94	2	91	10	98	2	0.3
Bifenox	94	17	100	2	103	20	98	12	110	24	108	3	4.1
Bifenthrin	87	2	84	4	91	2	94	6	94	11	102	1	1.5
Bioallethrin	90	8	86	4	91	11	86	15	91	30	82	7	2.2
Bitertanol	89	2	78	5	104	6	98	5	88	9	100	4	2.9
Bromacil	100	5	94	9	104	2	100	3	92	12	91	4	3.6
Bromobutide	94	11	101	5	106	7	85	5	95	22	95	5	2.5
Bromophos	93	6	92	6	99	1	93	2	97	6	95	2	1.0
Bromopropylate	94	3	85	5	93	5	97	6	95	10	110	4	1.8
Bupirimate	79	10	81	4	84	11	93	6	102	13	97	5	2.2
Buprofezin	97	9	80	4	89	8	90	2	102	17	102	12	2.3
Butachlor	89	7	80	5	86	3	91	6	104	13	99	6	2.7
Butafenacil	79	4	79	5	89	1	92	3	91	9	108	6	2.5
Butamifos	85	6	99	5	108	4	102	11	108	9	104	4	2.4
Cadusafos	91	5	96	3	110	5	95	3	89	7	95	2	1.3
Cafenstrole	94	4	97	4	106	7	89	5	87	6	93	6	2.1
Carbaryl	88	13	80	1	90	9	96	6	82	7	96	4	2.4
Carbofuran	88	3	102	6	111	8	107	6	106	17	103	7	2.9
Carfentrazone-ethyl	77	8	97	3	111	2	97	6	108	9	109	3	3.2
Chlorfenapyr	98	10	90	5	107	7	92	6	29	41	95	3	2.2
Chlorfenvinphos α	93	3	85	3	98	2	93	2	93	5	96	5	1.7
Chlorfenvinphos β	87	10	83	6	93	4	96	2	87	7	96	2	1.7
Chlorobenzilate	90	5	83	4	98	3	98	4	100	7	113	3	1.1
Chlorpropham	88	7	76	2	94	3	98	2	98	3	91	5	1.7

Table 3. (continued)

Pesticide	Recovery, % and SD											LOD, ng/g
	\multicolumn{4}{c}{Carrot (n = 4, 3)[a]}	\multicolumn{4}{c}{Banana (n = 3)}	\multicolumn{4}{c}{Grapefruit (n = 5)}	
	\multicolumn{2}{c}{20 ng/g}	\multicolumn{2}{c}{100 ng/g}	\multicolumn{2}{c}{20 ng/g}	\multicolumn{2}{c}{100 ng/g}	\multicolumn{2}{c}{20 ng/g}	\multicolumn{2}{c}{100 ng/g}	
Chlorpyrifos	90	7	83	2	90	6	96	6	100	9	96	4	2.1
Chlorpyrifos-methyl	101	6	83	4	96	4	88	3	86	4	94	4	2.1
Chlorthal-dimethyl	94	6	95	5	107	5	101	3	91	6	94	5	1.2
Clodinafop-propargyl	39	6	66	7	92	8	91	12	97	12	112	10	3.0
Clomazone	93	5	97	2	101	4	96	2	91	7	93	2	1.4
Clomeprop	79	6	80	15	101	7	98	10	124	67	133	18	2.2
Cloquintocet-1-methylhexyl	96	3	96	5	101	1	97	0	96	10	105	3	2.7
Cyanazine	80	10	83	4	96	3	94	4	95	16	98	8	2.5
Cyanofenphos	83	5	81	4	90	8	88	8	101	23	109	9	1.9
Cyanophos	92	3	83	3	89	4	93	3	93	6	99	2	1.4
Cyflufenamid	82	7	96	5	111	1	100	5	82	12	102	7	2.1
Cyfluthrin	97	5	96	3	82	5	91	2	95	7	98	6	0.8
Cyhalofop-butyl	89	3	96	4	102	5	108	1	103	9	107	3	1.4
Cyhalothrin	87	4	82	7	86	5	94	4	97	5	110	5	1.6
Cypermethrin	96	9	97	3	92	6	93	5	94	14	102	5	0.5
Cyproconazole	91	9	96	4	107	8	103	3	86	12	98	5	2.3
Cyprodinil	83	7	81	3	93	7	94	3	87	5	94	1	1.7
DDD,pp'-, DDT,op'-	87	5	82	4	91	1	95	6	92	4	98	3	1.1
DDE,pp'-	90	5	83	5	85	4	95	5	85	6	91	3	0.6
DDT,pp'-	83	4	82	5	95	5	93	6	90	2	96	2	1.9
Deltamethrin	89	3	89	6	69	2	88	2	101	9	96	2	1.5
Diazinon	99	18	83	1	93	5	101	4	85	9	91	7	1.7
Dichlofenthion	90	3	95	5	103	5	96	2	91	5	96	1	1.0
Dichlorvos	76	3	89	2	91	11	69	8	123	9	118	5	1.9
Diclobutrazol	94	6	85	4	97	4	98	3	99	8	113	5	3.3
Diclofop-methyl	77	6	83	5	93	5	95	6	104	7	106	4	1.6
Dicloran	99	4	93	2	102	2	96	3	85	8	98	5	1.6
Dieldrin	85	32	100	10	88	11	96	8	102	14	119	10	2.5
Diethofencarb	79	8	76	2	90	7	101	5	89	12	94	6	2.7
Difenoconazole	93	9	95	1	89	3	86	1	89	7	102	2	2.7
Diflufenican	89	2	96	3	105	1	94	0	96	11	108	5	2.0
Dimepiperate	88	4	83	5	90	1	95	4	94	5	98	4	1.8
Dimethametryn	87	3	81	4	94	2	95	4	90	4	96	3	0.9
Dimethenamid	92	5	94	6	101	7	95	2	90	4	98	4	1.7
Dimethipin	111	8	92	4	98	6	101	6	88	16	85	6	2.0
Dimethoate	114	14	111	5	119	10	107	4	90	23	87	13	3.7
Dimethylvinphos	87	8	85	1	90	8	94	1	85	6	96	5	2.3
Diofenolan	83	11	97	5	109	4	96	1	99	10	109	3	5.3
Dioxabenzofos	95	13	97	1	100	7	88	2	98	8	93	6	1.7
Diphenamid	83	5	83	1	96	4	94	3	96	7	96	4	0.9
Diphenyl	66	6	89	1	87	2	69	5	74	4	72	4	1.8
Diphenylamine	83	6	95	3	145	22	88	1	87	3	89	3	2.3

Table 3. (continued)

Pesticide	Carrot (n = 4, 3)[a]				Banana (n = 3)				Grapefruit (n = 5)				LOD, ng/g
	20 ng/g		100 ng/g		20 ng/g		100 ng/g		20 ng/g		100 ng/g		
Disulfoton	83	11	90	6	87	5	93	6	97	10	89	11	1.5
Dithiopyr	90	3	93	8	105	4	95	1	84	6	88	3	1.8
Edifenphos	97	2	97	2	104	6	97	3	95	3	108	2	1.7
Endosulfan α	94	13	96	1	118	9	100	8	86	5	101	8	2.5
Endosulfan β	104	23	97	12	113	14	97	7	115	29	109	8	2.2
Endrin	83	11	91	5	91	4	99	8	87	20	102	5	1.5
EPN	90	9	83	5	NC	—	NC	—	104	17	111	4	4.7
Esprocarb	87	6	95	9	108	2	93	2	88	9	95	3	1.6
Ethalfluralin	88	12	89	6	115	11	90	2	91	13	94	4	1.5
Ethiofencarb	82	8	94	2	104	3	95	3	77	7	107	7	1.7
Ethion	86	6	86	4	92	5	94	6	93	5	101	5	1.8
Ethofumesate	89	7	81	2	99	2	96	3	87	7	92	2	1.7
Ethoprophos	108	8	89	3	89	2	93	3	96	9	91	3	0.8
Etobenzanid	90	5	98	4	86	5	79	2	96	13	101	4	2.1
Etoxazole	73	5	82	6	98	9	92	7	97	11	95	5	2.3
Etrimfos	84	4	82	3	88	6	94	2	95	6	95	4	1.2
Fenamiphos	79	11	77	2	101	10	101	7	101	12	104	5	4.3
Fenarimol	97	3	95	3	106	2	101	3	99	13	105	4	2.3
Fenbuconazole	80	3	79	4	95	1	95	5	82	5	91	6	2.4
Fenchlorphos	90	6	85	1	91	3	92	3	89	5	95	2	1.9
Fenitrothion	103	5	92	7	102	4	98	5	98	8	108	3	1.9
Fenobucarb	85	10	84	3	91	5	95	3	90	7	95	4	0.6
Fenothiocarb	106	9	83	2	93	3	93	3	96	9	103	3	2.7
Fenoxanil	84	7	78	8	99	5	102	7	83	10	91	8	1.9
Fenoxycarb	91	4	79	6	90	5	92	4	95	18	116	11	2.2
Fenpropathrin	83	7	82	4	88	7	91	6	88	19	106	3	1.9
Fenpropimorph	88	6	84	3	101	6	95	2	87	11	93	3	1.8
Fensulfothion	85	11	80	3	92	18	91	9	97	4	108	11	2.9
Fenthion	93	1	97	4	93	4	94	1	91	10	96	4	1.1
Fenvalerate	93	3	90	3	77	3	93	2	87	6	107	4	1.6
Fipronil	90	7	79	3	88	0	87	4	93	6	100	4	2.8
Flamprop-methyl	91	7	84	2	93	6	95	2	95	9	112	5	3.0
Fluacrypyrim	89	3	97	2	114	13	100	5	99	8	99	2	1.7
Flucythrinate	84	9	91	3	86	3	92	4	94	8	99	4	1.4
Fludioxonil	92	5	95	6	106	11	105	7	89	8	97	4	1.3
Flumiclorac-pentyl	73	14	98	8	107	14	57	1	95	21	94	7	9.0
Flumioxazin	83	5	99	2	100	5	70	5	79	17	96	11	2.3
Fluquinconazole	87	7	82	3	79	1	75	6	95	9	100	3	2.3
Flusilazole	88	2	96	5	106	9	94	2	88	7	96	5	1.8
Flutolanil	85	4	81	4	94	1	98	5	97	5	103	2	1.8
Flutriafol	92	4	95	4	103	7	100	6	90	10	93	7	2.5
Fluvalinate	84	5	97	5	71	1	84	2	100	22	100	2	1.6