JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Automated QuEChERS Tips for Analysis of Pesticide Residues in Fruits and Vegetables by GC-MS

Pakritsadang Kaewsuya,[†] William E. Brewer,[*,†] Jon Wong,[§] and Stephen L. Morgan[†]

[†]Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208, United States

[§]Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, Room 2E-014, HFS-717, 5100 Paint Branch Parkway, College Park, Maryland 20740-3835, United States

ABSTRACT: This paper reports the development of an automated method of QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) using pipet tips fitted with filtration screens and containing primary−secondary amine, magnesium sulfate, and graphitized carbon black. These tips are referred to as "QuEChERS Tips". Using loosely contained sorbent, dispersive solid phase extraction (dSPE) cleanup was performed with the QuEChERS Tips and automation. The main advantage of the QuEChERS Tips is that they are readily automated because this dSPE method does not require centrifugation. High recoveries (70−117%) and good reproducibilities (<12%) are shown for over 200 pesticides using automated QuEChERS Tips and GC-MS in various sample matrices.

KEYWORDS: *QuEChERS, pesticides, GC-MS, DPX*

■ INTRODUCTION

Pesticides are extensively used worldwide to increase yields in agricultural production. They are utilized to detroy weeds, kill insects, and prevent the spread of molds or bacteria. Exposure to low levels of pesticides in foods and agriculture products in our daily life is unavoidable, and exposure can be a risk to human health. Thus, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) gave authority to the Environmental Protection Agency (EPA) to regulate pesticides.[1,2]

The analysis of pesticides in fruits and vegetables is very important in the field of food safety. A routine testing for contaminated pesticides in fruits and vegetables must be performed to ensure toxic pesticides are below tolerance levels and foods are safe for consumption. The most time-consuming part of this analysis is the sample preparation. Liquid−liquid extraction has been previously used for sample preparation, but these methods are too time-consuming and use large quantities of solvents.[3−6]

Solid-phase extraction (SPE) has essentially replaced liquid−liquid extraction due to the minimization of large volumes of organic solvent.[7−12] However, the selectivity in conventional SPE has made it impossible to develop a comprehensive method for pesticide residue analysis. The chemistries of the various pesticides would require multiple extraction methods to screen the large number of possible pesticide residues.

QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) has been used for sample preparation methods to help monitor pesticides in fruits, vegetables, and other foods.[13−18] The big advantage of QuEChERS is that the sorbent used in these SPE methods focus on extracting the sample matrix components rather than the pesticides, hence resulting in a cleanup method. The first step of QuEChERS is to chop and homogenize the sample matrix so that a representative sample of just 10−15 g can be processed. Acetonitrile is subsequently added to the sample, and salts such as sodium chloride (and buffer salts) and magnesium sulfate are added to the acetonitrile extract and mixed vigorously and thoroughly. The salts cause the acetonitrile layer to separate from the aqueous layer, and the pesticides partition

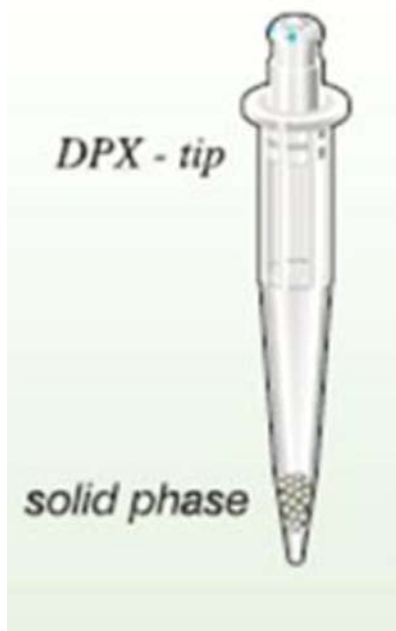

Figure 1. Schematic diagram of a DPX tip. The QuEChERS Tip in this method used PSA, $MgSO_4$, and GCB as the sorbent.

Special Issue: Florida Pesticide Residue Workshop 2012

Received: October 31, 2012
Revised: January 17, 2013
Accepted: January 18, 2013
Published: January 18, 2013

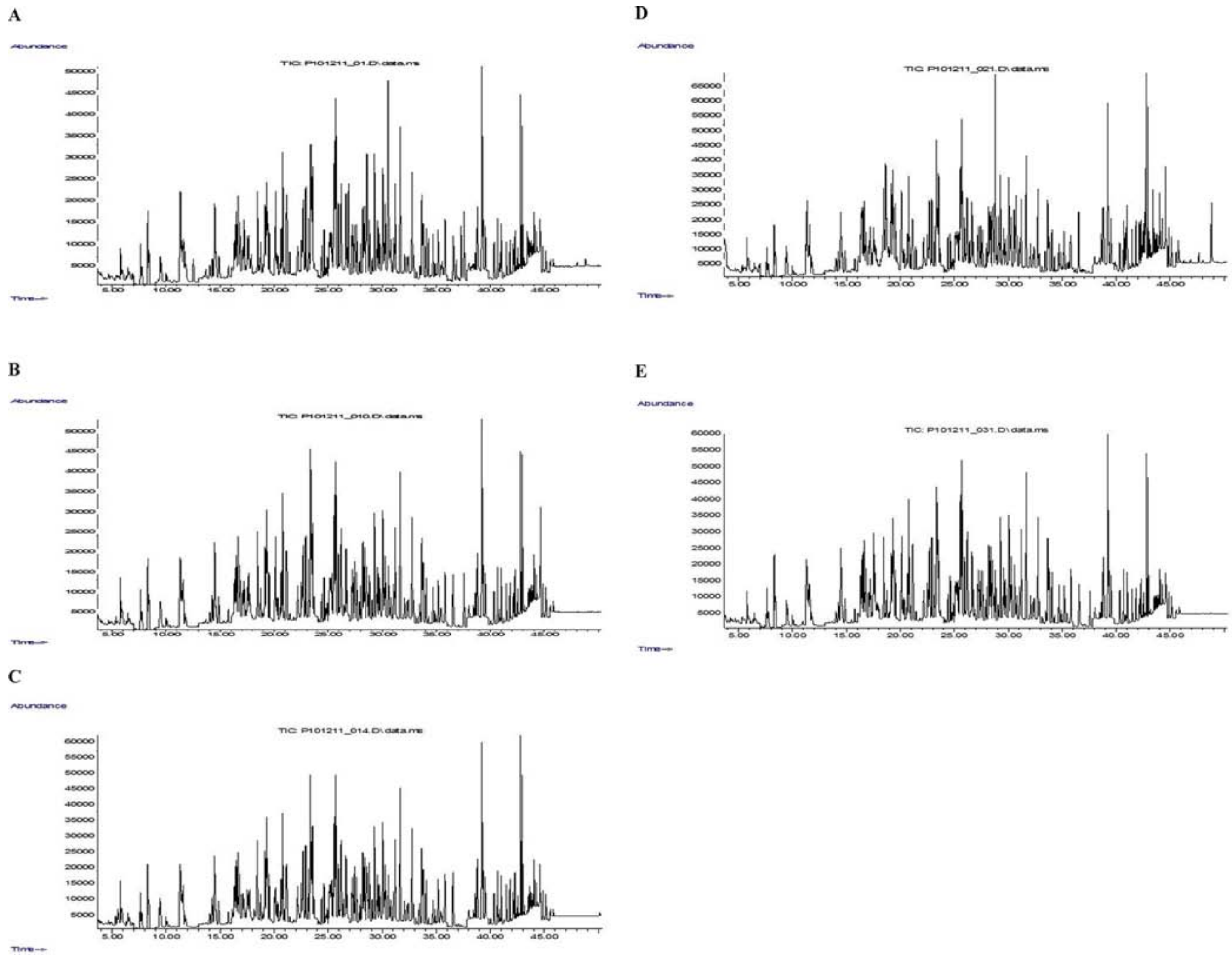

Figure 2. SIM chromatogram of pesticides spiked at 200 ppb and extracted using automated QuEChERS Tips in (A) carrot matrix, (B) tomato, (C) green beans, (D) broccoli, and (E) celery.

into the acetonitrile phase with high efficiencies. The relatively low volumes of acetonitrile used (approximately 1:1 for fruits and vegetables) eliminate the need for solvent evaporation.

However, these initial extracts are dirty and require further cleanup to remove sample matrix components.[19−22] For GC analysis, it is important to remove excess water. In addition, fatty acid components are responsible for matrix effects in GC-MS and LC-MS/MS analysis. Additional sorbent is often used to remove further sample matrix components such as pigments, but addition of other sorbents generally leads to losses of some pesticides. The most effective cleanup methods have been shown to be dispersive, but the dispersive cleanup methods require centrifugation, which may limit automation capabilities.

A more practical way to perform the dispersive SPE method is to use disposable pipet extraction (DPX) tips. These tips have a screen that contains loose sorbent material inside the pipet tip. By incorporating anhydrous magnesium sulfate ($MgSO_4$) and primary and secondary amine (PSA) for sorbent, these tips are referred to as QuEChERS Tips. The use of QuEChERS Tips has been reported previously[23,24] and found to provide similar results to dispersive tubes.

In the work presented here, an automated dispersive SPE cleanup method for QuEChERS extracts was developed using QuEChERS Tips, and the methods were combined directly with GC-MS analyses for high-throughput capabilities. The QuEChERS Tips contained PSA, $MgSO_4$, and graphitized carbon black (GCB) to efficiently clean up QuEChERS extracts prior to analysis. An automated dispersive SPE cleanup method using QuEChERS Tips is expected to facilitate routine analyses of pesticides in fruits and vegetables.

MATERIALS AND METHODS

Standards, Reagents, and Materials. Mixed standard (250) pesticides were provided by the FDA laboratory (College Park, MD, USA). The internal standard (d_{10}-parathion-diethyl) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Working solutions of standards were prepared by dissolving original stock solutions in acetonitrile. Sodium chloride (analytical reagent grade) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Anhydrous magnesium sulfate ($MgSO_4$, reagentPlus) was purchased from Sigma-Aldrich. PSA was obtained from Varian (Palo Alto, CA, USA), and GCB (to remove pigments and sterols) was obtained from Supelco (Bellefonte, P, USA). The screened pipet tips and transport adaptors (for automation) were provided by DPX Laboratories, LLC (Columbia, SC, USA). Acetonitrile and methanol were purchased from Fisher Scientific (Pittsburgh, PA, USA).

Sample Preparation. Low-fat content products, which included carrots, tomatoes, green beans, broccoli, and celery, were purchased from a local market in Columbia, SC, USA. The fruits and vegetables were chopped and ground in a blender. Thirty grams of ground carrots,

Table 1. GC-MS/SIM Program Used for Automated DPX-Q Method in GC-MS Analysis Includes Time Segment, Ions (Dwell Times), Retention Times, Target and Qualified Ions, and Pesticides Screened

group	window (min)	dwell time (ms)	scan rate (cycles/s)	t_R (min)	target and qualified ions (m/z)	pesticide
1	3.0	30	2.07	5.58	**94**, 95, 141, 110, 126	methamidophos
				5.88	**109**, 185, 79, 145, 220	dichlorvos
				6.55	**138**, 132, 134, 124, 173	allidochlor
2	7.0	45	2.59	7.70	**171**, 173, 100, 136	diclobenil
				8.37	**154**, 153, 152, 151	biphenyl
3	9.0	30	2.22	9.41	**127**, 192, 109, 164	3,4-mevinphos
				9.48	**161**, 163, 165, 99, 137	3,4′-dichloroaniline
				10.04	**211**, 213, 183, 185, 140	etridazole
4	11.0	30	1.25	11.45	**191**, 193, 206, 208, 141	chloroneb
				11.57	**170**, 169, 141, 115, 142	*o*-phenylphenol
				11.81	**250**, 248, 252, 254, 215	pentachlorobenzene
5	13.0	12	2.25	13.73	**156**, 110, 126, 141, 109	dimethoate oxon
				14.04	**203**, 215, 261, 259, 263	tecnazene
				14.28	**120**, 176, 104, 169, 196	propachlor
				14.52	**169**, 168, 167, 166	diphenylamine
				14.62	**231**, 229, 233, 158, 169	2,3,5,6-tetrachloroaniline
				14.88	**158**, 139, 126, 200, 242	ethoprop
				15.59	**185**, 145, 109, 220, 187	dichlorphos
				15.78	**276**, 316, 292, 333, 264	ethalfluralin
6	16.0	10	1.65	16.10	**127**, 193, 109, 110, 111	dicrotophos
				16.33	**306**, 264, 290, 248, 335	trifluralin
				16.46	**292**, 159, 264, 276, 332	ethalfluralin
				16.51	**322**, 97, 202, 238, 226	sulfotep-ethyl
				16.85	**181**, 183, 219, 217, 221	α-BHC
				16.67	**260**, 121, 97, 234, 75, 86	phorate
				16.651	**86**, 128, 234, 236	diallate isomer 1
				7.10	**86**, 128, 234, 236	diallate isomer 2
				17.22	**284**, 286, 282, 288, 249	hexachlorobenzene
				17.54	**280**, 265, 282, 267, 237	pentachlorophenyl methyl ester
				17.56	**206**, 178, 176, 208	dicloran
				17.65	**88**, 89, 171, 97, 115, 143	demeton-S
				17.76	**87**, 125, 93, 143, 229	dimethoate
				17.90	**202**, 174, 145, 217	ethoxiquin
7	18.0	10	2.01	18.14	**199**, 153, 243, 286, 135	schradan
				18.62	**219**, 183, 181, 217	β-BHC
				18.64	**201**, 173, 183, 144	simazine
				18.77	**181**, 219, 183, 217	lindane
				19.07	**295**, 265, 249, 237	quintozene
				19.16	**275**, 273, 277, 279, 231	pentachlorobenzonitrile
				19.21	**243**, 109, 125, 180	cyanophos
				19.18	**231**, 153, 186, 203, 288	terbufos
				19.33	**246**, 109, 137, 110, 174	fonophos
				19.46	**173**, 194, 222, 240, 255	propyzamide
				19.42	**138**, 194, 222, 236	propetamphos
				19.35	**273**, 288, 260, 217, 152	diazoxon
				19.59	**318**, 330, 55, 348	profluralin
8	19.8	15	1.38	20.10	**304**, 276, 227, 248	diazinon
				20.15	**88**, 246, 258, 125	thiometon
				20.17	**186**, 88, 142, 274	disulfoton
				20.36	**219**, 183, 181, 217	δ-BHC
				20.38	**306**, 145, 264, 326	fluchloralin

Table 1. continued

group	window (min)	dwell time (ms)	scan rate (cycles/s)	t_R (min)	target and qualified ions (m/z)	pesticide
8	19.8	15	1.39	20.56	**266**, 264, 268, 270	chlorothalonil
				20.69	**268**, 270, 145, 86	triallate
				20.82	**161**, 119, 257, 285, 313	isazophos
				20.83	**177**, 197, 199, 178	tefluthrin
				20.97	**292**, 181, 153, 125, 168	etrimfos
				20.60	**278**, 127, 151, 254, 404	tetraiodoethylene
9	20.9	10	2.15	21.18	**241**, 277, 307, 342	endosulfan ether
				21.19	**204**, 123, 288, 246	iprobenfos
				21.13	**114**, 101, 102, 156, 180	octhilinone
				21.47	**265**, 267, 263, 269	pentachloroaniline
				21.21	**318**, 261, 234, 276	tebupirimfos
				21.20	**107**, 94, 200, 170	diamidofos
				22.23	**197**, 134, 210, 199	dimethachlor
				22.18	**279**, 223, 162, 251, 281	dichlorfenthion
				22.34	**161**, 163, 57, 217, 219	propanil
10	22.0	12	1.40	22.61	**115**, 121, 125, 129, 143	prothoate
				22.76	**263**, 233, 247, 264, 200	parathion-methyl
				22.73	**286**, 288, 125, 197, 290	chlorpyrifos-methyl
				22.79	**285**, 212, 187, 198	vinclozolin
				22.93	**272**, 100, 274, 237	heptachlor
				22.97	**265**, 267, 125, 250	tolclofos-methyl
				23.23	**160**, 188, 146, 237, 269	alachlor
				23.38	**303**, 230, 338, 301	α-chlordene
				23.58	**285**, 287, 125, 167, 289	fenchlorphos (ronnel)
				23.44	**72**, 240, 73, 170	dimetilan
				23.74	**262**, 109, 247, 121, 135	fenoxon
				23.07	**127**, 195, 142, 268, 109	malaoxon
				23.62	**275**, 247, 220, 232, 149	paroxon
11	24.0	10	2.57	24.45	**296**, 246, 263, 298	pentachlorothioanisole
				24.46	**277**, 260, 109, 125, 247	fenitrothion
				24.66	**290**, 305, 276, 233	pirimphos-methyl
				24.96	**263**, 265, 293, 298	aldrin
				25.14	**230**, 338, 303, 301	γ-chlordene
				24.83	**123**, 167, 224, 226	dichlofluanid
				25.28	**230**, 338, 303, 301	β-chlordene
				25.25	**173**, 125, 158, 211	malathion
				25.39	**240**, 238, 162, 146	metolachlor
				24.89	**199**, 125, 97, 153, 171	phorate sulfone
				25.42	**199**, 97, 125, 153	phorate sulfoxide
12	25.0	10	1.49	25.75	**139**, 250, 111, 141, 252	4,4′-dichlorobenzophenone
				25.62	**278**, 125, 109, 169, 279	fenthion
				25.73	**314**, 286, 258, 260, 316	chlorpyrifos
				25.80	**291**, 263, 235, 186, 218	parathion
				26.00	**301**, 299, 303, 332	dacthal
				26.00	**225**, 212, 240, 198	cyanazine
				25.99	**262**, 125, 216, 79, 232	dicapthon
				26.67	**331**, 329, 333, 125, 316	bromophos
				26.51	**256**, 276, 291, 182, 169	crufomate
				25.62	**211**, 253, 210, 115, 193	aspon
				26.79	**266**, 218, 224, 230, 245	butralin
				25.50	**242**, 270, 298, 197, 199	chlorpyrifos oxon
				26.00	**262**, 125, 216, 109, 93	chlorthion
				26.97	**197**, 169, 141, 137, 109	demeton *S*-sulfone
				26.27	77, 141, 268, 270	fenson
				26.69	**195**, 193, 263, 265, 261	isodrin
				25.59	**301**, 115, 99, 140, 147	parathion-diethyl-*d*10 (I.S.)

Table 1. continued

group	window (min)	dwell time (ms)	scan rate (cycles/s)	t_R (min)	target and qualified ions (*m*/*z*)	pesticide
13	27.0	25	0.97	27.24	**318**, 333, 304, 290	pirimphos-ethyl
				27.94	**137**, 238, 240, 181	tolylfluanid
				28.04	**79**, 80, 149, 114	captan
				27.43	**353**, 355, 351, 357	heptachlor epoxide
				28.09	**259**, 331, 188, 186, 187	chlozolinate
				27.30	**280**, 238, 264, 281	isopropalin
				28.21	**196**, 227, 168, 140, 106	mephospholan
				27.52	**209**, 133, 132, 81, 11	metazachlor
				27.71	**153**, 199, 264, 125, 171	terbufos sulfone
14	28.0	10	2.10	28.44	**260**, 104, 76, 130	folpet
				28.29	**267**, 232, 269, 295	*β*-chlorfenvinphos
				28.29	**255**, 213, 185, 245	isofenfos
				28.36	**298**, 146, 157, 270	quinalphos
				28.74	**283**, 285, 287, 255	procymidone
				28.44	**136**, 123, 168, 107	allethrin
				28.86	**373**, 375, 377, 371	*trans*-chlordane
				29.13	**145**, 85, 125, 93	methidathion
				28.44	**274**, 246, 275, 320	phenthoate
				28.91	**127**, 193, 105, 166	crotoxyphos
15	29.0	12	1.27	29.54	**241**, 195, 237, 339	*α*-endosulfan,
				29.33	**246**, 248, 318, 316	*o*,*p*′-DDE
				29.31	**303**, 259, 242, 331, 357	bromophos-ethyl
15	19.0	12	1.27	29.77	**373**, 375, 377, 371	*cis*-chlordane
				29.63	**283**, 339, 285, 341	akton
				29.86	**331**, 329, 333, 109, 240	tetrachlorvinphos
				30.06	**409**, 407, 411, 405	*trans*-nonachlor
				30.13	**299**, 130, 148, 243, 209	ditalimfos
				30.64	**377**, 379, 125, 109, 250	jodfenphos (iodofenphos)
				30.63	**303**, 154, 288, 260, 217	fenamiphos
				30.84	**309**, 267, 311, 269, 239	prothiophos
				30.11	**176**, 160, 188, 202, 224	butachlor
				30.35	**175**, 302, 111, 127, 99	chlorfenson (ovex)
				30.23	**143**, 145, 404, 360, 157	flumetralin
16	30.9	10	1.71	31.11	**263**, 277, 380, 79, 345	dieldrin
				31.05	**339**, 208, 295, 337, 374	profenofos
				31.27	**202**, 169, 226, 258, 314	DEF (tribufos)
				31.24	**246**, 248, 318, 316	*p*,*p*′-DDE
				31.72	**235**, 237, 165, 199, 212	*o*,*p*′-DDD
				31.69	**258**, 175, 260, 302	oxadiazon
				32.35	**263**, 345, 317, 281	endrin
				32.93	**195**, 237, 241, 339	*β*-endosulfan
				33.21	**253**, 251, 139, 111	chlorobenzilate
				32.08	**215**, 183, 155, 324	azemethiphos
				32.79	**223**, 224, 167, 179, 236	ethylan
				32.45	**283**, 285, 202, 253, 204	nitrofen
				32.12	**252**, 361, 300, 280, 31	oxyfluorfen
17	33.0	10	2.57	33.51	**293**, 308, 265, 188, 156	fensulfothion
				33.71	**235**, 237, 165, 199, 212	*p*,*p*′-DDD
				33.85	**235**, 237, 165, 199, 212	*o*,*p*′-DDT
				34.13	**345**, 279, 347, 250	endrin aldehyde
				33.77	**409**, 409, 411, 405	*cis*-nonachlor
				34.10	**231**, 384, 153, 125, 233	ethion
				34.32	**269**, 325, 360, 297	chlorthiophos
				33.27	**201**, 202, 186, 265, 109	famoxon
				33.88	**310**, 125, 109, 316, 231	fenthion sulfone

Table 1. continued

group	window (min)	dwell time (ms)	scan rate (cycles/s)	t_R (min)	target and qualified ions (m/z)	pesticide
18	34.4	10	2.64	34.74	**322**, 156, 140, 125, 280	sulprofos
				34.93	**161**, 285, 313, 257, 208	triazophos
				35.23	**342**, 157, 199, 121, 125	carbophenothion
				35.50	**272**, 387, 274, 229, 422	endosulfan sulfate
				35.27	**218**, 125, 93, 109, 217	famphur
				35.44	**310**, 173, 109, 201, 218	edifenphos
				35.86	**235**, 237, 165, 199, 212	*p,p′*-DDT
				35.84	**303**, 145, 102, 173	norflurazon
19	36.0	45	1.75	36.99	**79**, 77, 80, 183	captafol
				37.60	**123**, 143, 171, 128, 338	resmethrin
				36.61	**171**, 83, 128, 172, 252	hexazinone
20	37.8	10	1.85	38.10	**317**, 345, 315, 281	endrin ketone
				38.53	**314**, 316, 187, 189, 245	iprodione
				38.64	**160**, 161, 133, 317	phosmet
				38.68	**340**, 188, 199, 77, 204	pyridaphenthion
				38.86	**341**, 339, 183, 185, 343	bromopropylate
				38.93	**157**, 169, 185, 141, 323	EPN
				39.27	**164**, 123, 165, 135, 107	tetramethrin
				39.26	**181**, 165, 166, 182	bifenthrin
				39.37	**227**, 121, 228, 152	*o,p′*-methoxychlor
				39.59	**181**, 208, 265, 125, 141	fenpropathrin
				38.11	**316**, 274, 300, 345, 258	nitralin
21	39.8	20	1.55	40.84	**160**, 132, 77, 104, 161	azinphos-methyl
				40.71	**183**, 123, 184, 124, 350	phenothrin
				40.87	**182**, 184, 367, 154, 121	phosalone
				40.96	**377**, 171, 375, 379, 155	leptophos
				40.39	**227**, 159, 229, 175, 356	tetradifon
				41.03	**272**, 237, 332, 274, 270	mirex
22	41.2	15	2.01	41.49	**181**, 197, 208, 199, 209	λ-cyhalothrin
				42.10	**132**, 160, 77, 104, 105	azinphos-ethyl
				42.15	**221**, 232, 373, 265, 328	pyrazophos
				42.19	**181**, 208, 209, 289	acrinathrin
				42.30	**208**, 357, 173, 186	dialifor
				42.32	**360**, 194, 362, 138	pyraclofos
				42.81	**183**, 165, 163, 184	*cis*-permethrin
				42.10	**160**, 132, 104, 77, 301	azinphos-methyl oxon
23	42.85	15	2.23	42.97	**183**, 165, 163, 184	*trans*-permethrin
				43.06	**362**, 226, 210, 334, 364	coumaphos
				43.60	**163**, 206, 165, 226, 199	cyfluthrin isomer 1
				43.68	**163**, 206, 165, 226, 199	cyfluthrin isomer 2
				43.72	**163**, 206, 165, 226, 199	cyfluthrin isomer 3
				43.50	**163**, 206, 165, 226, 199	cyfluthrin isomer 4
				43.83	**163**, 181, 165, 209, 208	cypermethrin isomer 1
				43.93	**163**, 181, 165, 209, 208	cypermethrin isomer 2
				44.02	**163**, 181, 165, 209, 208	cypermethrin isomer 3
				44.05	**163**, 181, 165, 209, 208	cypermethrin isomer 4
				44.10	**199**, 225, 209, 181, 451	flucythrinate isomer 1
				44.28	**199**, 225, 209, 181, 451	flucythrinate isomer 2
				44.59	**328**, 329, 189, 310, 330	fluridone
				43.18	**271**, 270, 153, 125, 97	dioxathion
24	44.7	25	3.56	44.87	**419**, 167, 181, 152, 225	fenvalerate isomer 1
				45.12	**419**, 167, 181, 152, 225	fenvalerate isomer 2
				45.10	**250**, 252, 181, 208, 502	fluvalinate isomer 1
				45.18	**250**, 252, 181, 208, 502	fluvalinate isomer 2
25	45.5	100	1.91	45.85	**253**, 181, 255, 251, 209	deltamethrin

Table 2. Recovery (Percent) and Precision (%RSD) of the Studied Pesticides in Different Matrices Spiked with 200 ppb Standard Pesticides in GC-MS Analysis

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
acrinathrin	95.7	(8.7)	105.6	(3.1)	81.4	(7.9)	77.5	(10.3)	73.5	(7.7)
akton	72.7	(11.0)	74.1	(3.6)	72.1	(7.7)	62.7	(6.7)	71.6	(2.3)
alachlor	82.9	(9.2)	79.2	(4.2)	75.5	(10.6)	66.8	(5.4)	77.2	(3.0)
aldrin	75.4	(2.0)	71.3	(3.4)	72.6	(10.4)	60.8	(6.6)	78.9	(3.1)
allethrin	85.0	(9.3)	80.8	(2.3)	78.4	(5.7)	70.6	(10.3)	90.3	(5.3)
allidochlor	75.1	(10.3)	82.4	(7.0)	79.5	(11.5)	69.9	(6.0)	93.2	(8.8)
aspon	85.4	(5.9)	77.6	(4.7)	82.3	(6.2)	72.1	(6.1)	72.4	(6.4)
azemethiphos	98.2	(4.3)	79.1	(8.6)	99.3	(4.3)	110.9	(8.0)	86.5	(6.5)
azinphos oxon	79.4	(5.7)	101.9	(6.3)	102.2	(9.5)	67.0	(9.2)	58.6	(7.7)
azinphos-ethyl	83.0	(2.3)	109.8	(9.4)	98.9	(1.7)	67.0	(8.5)	65.1	(4.1)
azinphos-methyl	88.5	(5.3)	71.7	(8.4)	71.8	(6.4)	64.5	(6.0)	68.2	(5.1)
α-BHC	82.7	(8.6)	63.4	(3.8)	60.1	(8.4)	56.4	(7.8)	70.8	(3.6)
β-BHC	78.4	(2.4)	77.1	(8.6)	75.7	(5.8)	68.1	(5.9)	77.3	(3.7)
δ-BHC	71.1	(2.7)	78.2	(4.2)	59.3	(1.1)	50.1	(4.0)	76.4	(2.0)
bifenthrin	80.2	(6.7)	74.7	(5.1)	75.1	(4.9)	63.4	(7.2)	71.9	(3.6)
biphenyl	74.3	(9.9)	68.4	(4.6)	71.9	(6.7)	61.5	(7.6)	80.2	(4.6)
bromophos	64.6	(7.6)	66.8	(5.0)	57.5	(8.7)	54.1	(5.7)	52.3	(2.2)
bromophos-ethyl	58.9	(9.4)	56.6	(3.4)	59.4	(5.2)	52.5	(9.2)	55.7	(6.0)
bromopropylate	89.1	(8.0)	88.0	(4.6)	90.1	(4.4)	72.5	(6.7)	83.9	(3.5)
butachlor	84.3	(9.2)	85.5	(3.3)	81.5	(8.0)	67.6	(5.6)	79.6	(2.7)
butralin	92.8	(5.8)	92.9	(2.1)	90.9	(4.5)	82.9	(7.1)	89.3	(3.5)
captafol	95.3	(8.8)	93.6	(9.0)	101.6	(9.5)	61.5	(4.7)	83.2	(8.6)
captan	97.2	(2.1)	94.1	(9.5)	93.2	(4.1)	87.1	(12.0)	86.6	(4.6)
carbophenothion	78.9	(7.2)	73.6	(9.5)	72.1	(10.4)	67.9	(7.8)	69.8	(4.8)
cis-chlordane	80.0	(7.2)	70.9	(4.0)	76.6	(1.0)	61.2	(5.4)	74.1	(3.7)
trans-chlordane	74.4	(1.3)	71.0	(4.2)	72.0	(1.0)	61.3	(5.4)	75.8	(2.5)
α-chlordene	76.3	(7.0)	71.1	(3.9)	70.8	(2.1)	60.8	(5.9)	72.4	(3.3)
β-chlordene	77.6	(7.6)	67.2	(3.5)	66.3	(1.5)	58.4	(5.7)	70.4	(3.0)
γ-chlordene	80.8	(8.8)	69.4	(3.5)	72.4	(9.1)	59.4	(5.3)	71.4	(1.7)
chlorfenson	72.7	(9.3)	66.5	(5.0)	67.2	(5.5)	60.2	(6.9)	68.7	(2.5)
chlorfenvinphos	92.8	(8.7)	95.1	(4.6)	81.5	(7.8)	69.2	(5.7)	77.9	(3.2)
chlorobenzilate	84.9	(6.6)	91.7	(1.2)	79.5	(6.3)	71.9	(8.7)	89.4	(1.9)
chloroneb	91.5	(4.8)	93.4	(1.6)	95.2	(11.4)	95.3	(1.1)	94.4	(6.7)
chlorothalonil	47.0	(7.6)	47.6	(7.0)	78.0	(1.6)	61.5	(9.0)	64.8	(5.9)
chlorpyrifos	63.0	(6.0)	57.8	(8.5)	56.7	(1.2)	58.0	(7.8)	59.4	(1.2)
chlorpyrifos oxon	89.2	(9.8)	89.6	(5.2)	94.8	(9.1)	98.9	(8.7)	99.9	(8.3)
chlorpyrifos-methyl	85.3	(9.4)	67.8	(4.7)	63.5	(6.5)	57.4	(6.3)	58.5	(8.4)
chlorthion	91.2	(4.4)	91.1	(10.4)	81.4	(9.4)	79.1	(5.9)	71.5	(6.4)
chlorthiophos	57.8	(1.3)	57.4	(6.0)	60.2	(7.7)	52.7	(7.3)	48.0	(7.1)
chlozolinate	73.3	(3.4)	66.7	(1.5)	58.4	(9.2)	66.7	(8.5)	63.5	(8.5)
coumaphos	46.9	(11.9)	77.2	(9.0)	72.7	(10.6)	51.6	(9.7)	35.6	(7.7)
crotoxyphos	76.7	(1.4)	67.3	(8.2)	66.1	(8.3)	57.4	(7.1)	63.7	(7.1)
crufomate	82.8	(7.4)	90.9	(8.9)	100.2	(4.3)	117.1	(4.4)	84.0	(6.2)
cyanazine	74.5	(7.5)	71.3	(3.3)	60.6	(3.2)	62.3	(9.1)	79.2	(3.5)
cyanophos	80.4	(9.6)	82.2	(3.6)	78.5	(9.4)	61.8	(6.7)	76.7	(6.7)
cyfluthrin isomer 1	96.5	(9.5)	95.1	(1.7)	87.2	(3.3)	80.2	(5.2)	70.9	(5.3)
cyfluthrin isomer 2	96.2	(3.2)	98.6	(1.3)	98.3	(6.9)	83.1	(3.9)	70.5	(9.3)
cyfluthrin isomer 3	95.2	(1.4)	97.4	(7.7)	94.5	(8.5)	88.7	(1.1)	71.6	(8.6)
cyfluthrin isomer 4	96.9	(8.8)	99.6	(8.5)	105.5	(6.4)	83.6	(7.5)	73.8	(9.8)
λ-cyhalothrin	105.4	(2.4)	99.3	(7.8)	106.0	(6.0)	85.3	(7.5)	88.4	(6.0)
cypermethrin isomer 1	92.2	(5.2)	93.9	(9.6)	87.5	(7.0)	81.1	(5.6)	75.2	(9.0)
cypermethrin isomer 2	93.3	(9.9)	99.9	(8.0)	98.2	(8.6)	79.5	(3.4)	71.0	(8.7)
cypermethrin isomer 3	100.1	(1.1)	97.9	(6.8)	99.0	(9.6)	78.5	(5.7)	70.7	(4.9)
cypermethrin isomer 4	89.4	(5.9)	94.4	(7.8)	91.5	(2.8)	77.0	(2.7)	70.5	(6.7)
dacthal	77.1	(9.9)	70.8	(3.9)	69.9	(3.2)	61.8	(6.1)	73.5	(2.6)
o,p′-DDD	79.1	(6.5)	72.0	(3.3)	75.9	(6.6)	70.2	(3.9)	75.7	(2.4)
p,p′-DDD	82.2	(5.9)	74.5	(3.5)	78.8	(5.8)	69.7	(6.1)	76.8	(3.3)
o,p′-DDE	77.0	(6.9)	69.3	(3.5)	70.8	(1.9)	60.1	(5.7)	72.6	(2.8)

Table 2. continued

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
p,*p*′-DDE	73.9	(10.8)	71.9	(3.9)	70.1	(1.6)	64.8	(6.3)	72.1	(2.9)
o,*p*′-DDT	80.8	(9.0)	83.0	(4.0)	79.2	(3.8)	57.1	(2.5)	74.9	(2.6)
p,*p*′-DDT	88.9	(4.0)	91.0	(3.1)	87.8	(9.5)	53.9	(5.3)	73.7	(3.8)
DEF (tribufos)	81.1	(8.1)	80.6	(4.1)	79.7	(5.2)	70.7	(2.1)	75.6	(2.9)
deltamethrin	61.7	(4.7)	65.8	(2.9)	55.0	(3.4)	51.4	(1.8)	50.8	(2.5)
demeton *S*-sulfone	82.9	(8.2)	70.3	(7.2)	68.2	(9.8)	17.8	(9.5)	77.6	(5.2)
demeton-S	90.8	(9.8)	96.0	(3.3)	60.5	(1.9)	47.0	(8.4)	80.7	(2.2)
dialifor	96.6	(5.0)	96.6	(9.5)	99.9	(8.6)	70.6	(8.6)	76.2	(8.2)
diallate isomer 1	75.9	(3.1)	73.3	(3.5)	73.8	(10.0)	63.4	(6.9)	76.1	(3.5)
diallate isomer 2	82.2	(2.6)	76.2	(3.1)	76.4	(3.5)	65.5	(7.1)	76.7	(2.8)
diamidofos	93.0	(1.1)	106.7	(8.4)	95.3	(5.9)	67.6	(8.5)	105.3	(3.4)
diazinon	79.3	(1.3)	76.3	(2.6)	80.2	(7.3)	67.7	(8.0)	81.9	(2.9)
diazoxon	98.2	(9.1)	115.0	(4.1)	117.8	(6.0)	89.3	(9.3)	30.3	(8.4)
dicapthon	91.3	(4.4)	91.1	(1.4)	81.4	(9.4)	79.1	(5.9)	75.1	(6.4)
dichlofluanid	91.4	(1.0)	102.0	(8.4)	102.3	(3.0)	126.6	(7.1)	115.4	(9.4)
dichlorfenthion	79.4	(8.6)	72.0	(6.7)	72.6	(8.0)	61.3	(8.1)	83.3	(3.6)
dichloroaniline	76.6	(2.2)	64.8	(9.9)	72.1	(3.2)	57.2	(7.4)	75.1	(5.3)
dichlorobenzophenone	72.6	(10.1)	63.8	(6.8)	64.8	(2.6)	61.6	(7.6)	67.1	(4.3)
dichlorphos	96.8	(1.0)	87.3	(3.1)	82.8	(1.5)	69.4	(4.9)	92.3	(5.7)
dichlorvos	82.3	(6.5)	90.1	(9.3)	80.9	(3.5)	77.1	(5.3)	84.3	(6.2)
diclobenil	75.6	(6.7)	67.3	(4.5)	69.6	(7.5)	64.4	(7.2)	77.0	(4.8)
dicloran	81.1	(5.6)	74.0	(8.6)	76.9	(6.3)	62.1	(9.9)	66.6	(5.3)
dicrotophos	100.0	(4.9)	94.2	(1.7)	108.9	(4.4)	91.2	(9.3)	83.9	(5.1)
dieldrin	92.1	(10.1)	79.7	(5.1)	77.6	(2.7)	60.7	(3.8)	92.3	(3.2)
dimethachlor	86.0	(9.7)	86.1	(3.5)	82.8	(5.5)	68.0	(7.8)	79.7	(2.7)
dimethoate	97.5	(9.5)	90.6	(1.8)	112.1	(8.5)	88.6	(6.2)	55.9	(2.8)
dimetilan	89.1	(9.9)	87.3	(5.1)	84.5	(8.5)	71.8	(5.7)	81.8	(2.0)
dioxathion	110.3	(6.7)	81.4	(1.5)	93.0	(4.2)	99.2	(10.3)	82.7	(9.6)
diphenylamine	75.5	(2.8)	73.0	(3.2)	71.8	(7.4)	59.7	(7.6)	81.9	(2.9)
disulfoton	78.0	(3.4)	74.8	(3.0)	47.5	(1.3)	40.8	(9.8)	77.9	(1.5)
ditalimfos	79.3	(7.8)	79.9	(5.0)	67.4	(7.1)	63.7	(7.0)	70.6	(2.4)
edifenphos	95.2	(6.1)	89.9	(6.3)	113.1	(1.1)	78.2	(9.8)	51.7	(6.3)
endosulfan ether	91.2	(1.9)	73.6	(8.2)	67.5	(1.2)	62.3	(8.1)	90.2	(8.8)
endosulfan sulfate	87.4	(5.9)	95.2	(1.5)	72.7	(2.7)	76.3	(7.6)	65.7	(4.3)
α-endosulfan	76.0	(9.8)	69.2	(3.9)	75.3	(7.5)	62.9	(5.8)	76.5	(3.1)
β-endosulfan	84.9	(10.5)	74.3	(6.9)	72.2	(2.9)	79.7	(7.9)	74.4	(1.7)
endrin	63.9	(1.7)	51.1	(2.9)	43.0	(1.8)	30.9	(6.8)	48.3	(8.4)
endrin aldehyde	43.4	(8.0)	68.2	(7.0)	88.5	(8.9)	64.7	(6.6)	82.3	(4.2)
endrin ketone	92.1	(4.9)	78.6	(3.6)	74.3	(8.7)	65.0	(7.6)	82.9	(3.1)
EPN	85.1	(9.2)	84.8	(10.0)	98.9	(1.4)	78.3	(8.4)	72.5	(8.7)
ethalfluralin	89.4	(7.6)	87.6	(3.6)	94.2	(4.5)	73.1	(7.8)	90.1	(3.0)
ethion	85.9	(6.4)	86.1	(4.5)	86.0	(4.7)	73.0	(6.6)	77.7	(3.8)
ethoprop	84.5	(9.9)	80.9	(3.4)	83.3	(3.0)	69.2	(7.5)	80.5	(3.6)
ethoxiquin	41.0	(0.5)	43.0	(9.4)	40.0	(9.2)	40.7	(8.8)	43.2	(10.0)
ethylan	78.8	(8.0)	76.2	(3.6)	73.2	(7.8)	66.5	(6.7)	80.6	(3.0)
etridazole	89.7	(8.0)	84.5	(2.6)	86.4	(7.2)	71.0	(4.5)	86.7	(7.5)
etrimfos	75.3	(8.2)	70.4	(7.5)	60.5	(6.0)	60.5	(1.1)	65.8	(6.4)
famoxon	70.6	(2.3)	71.4	(8.1)	70.1	(3.6)	77.4	(3.6)	78.0	(6.1)
famphur	100.5	(8.6)	102.2	(6.6)	97.2	(1.7)	67.7	(8.8)	62.3	(9.1)
fenamiphos	93.6	(5.4)	99.4	(4.1)	89.9	(9.0)	60.9	(9.7)	87.9	(6.1)
fenchlorphos	71.3	(5.7)	74.7	(1.6)	57.7	(7.8)	54.8	(6.9)	57.8	(6.3)
fenitrothion	95.1	(4.5)	96.7	(6.7)	87.0	(3.2)	77.6	(8.5)	84.6	(5.6)
fenoxon	102.7	(7.2)	116.3	(7.4)	74.7	(6.4)	74.9	(9.9)	63.7	(9.8)
fenpropathrin	77.7	(7.1)	74.6	(4.4)	78.4	(4.7)	67.6	(6.8)	71.2	(3.6)
fenson	77.8	(6.8)	70.3	(3.5)	69.5	(8.7)	62.1	(5.2)	73.8	(2.8)
fensulfothion	105.3	(9.7)	88.4	(1.0)	110.8	(2.0)	109.5	(6.1)	90.3	(5.0)
fenthion	71.3	(2.5)	66.4	(7.3)	52.1	(3.4)	47.1	(7.7)	68.8	(3.3)
fenthion sulfone	96.9	(1.7)	81.8	(8.9)	98.8	(8.8)	76.6	(7.4)	52.2	(9.7)
fenvalerate isomer 1	96.5	(3.6)	98.3	(1.2)	95.6	(7.7)	79.6	(2.8)	72.4	(7.2)

Table 2. continued

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
fenvalerate isomer 2	92.5	(3.5)	94.5	(8.7)	95.3	(7.3)	78.9	(3.8)	70.4	(6.8)
fluchloralin	56.8	(8.4)	88.2	(2.5)	92.8	(6.9)	75.6	(8.6)	89.4	(2.3)
flucythrinate isomer 1	91.4	(6.8)	99.1	(5.9)	94.6	(4.7)	82.7	(4.6)	75.4	(5.8)
flucythrinate isomer 2	93.7	(5.8)	99.8	(2.5)	91.9	(5.5)	80.3	(3.9)	72.2	(5.1)
flumetralin	85.6	(5.2)	83.6	(3.2)	84.5	(6.3)	78.1	(9.2)	80.4	(3.4)
fluridone	86.8	(9.9)	88.1	(1.9)	82.3	(3.6)	78.3	(4.4)	73.4	(5.4)
fluvalinate isomer 1	105.4	(6.0)	100.8	(3.3)	87.9	(2.8)	77.4	(7.5)	74.8	(1.8)
fluvalinate isomer 2	96.4	(8.2)	96.0	(5.1)	87.2	(3.2)	80.4	(9.4)	71.3	(1.9)
folpet	97.5	(5.6)	96.3	(1.1)	97.0	(9.4)	62.2	(8.9)	68.9	(5.5)
fonophos	77.6	(1.6)	77.5	(3.0)	77.4	(6.5)	64.7	(7.8)	77.7	(3.1)
heptachlor	84.9	(9.4)	78.6	(2.5)	80.4	(7.6)	68.4	(4.9)	83.4	(3.1)
heptachlor epoxide	75.9	(9.6)	72.6	(4.0)	74.3	(8.6)	61.9	(6.0)	78.6	(2.1)
hexachlorobenzene	40.5	(8.9)	44.8	(1.9)	51.1	(8.1)	38.9	(2.2)	36.7	(5.1)
hexazinone	91.5	(8.7)	95.1	(3.3)	90.5	(6.3)	78.7	(8.8)	85.9	(3.3)
iodofenphos	55.7	(8.0)	67.5	(6.8)	56.8	(6.7)	46.8	(6.0)	50.3	(6.7)
iprobenfos	93.8	(9.0)	88.5	(2.9)	87.4	(5.4)	71.5	(7.7)	87.0	(2.3)
iprodione	98.3	(5.5)	94.2	(5.2)	104.5	(9.2)	82.7	(4.6)	77.2	(8.1)
isazophos	79.1	(1.2)	77.4	(3.5)	79.7	(6.5)	67.0	(8.5)	76.9	(3.4)
isodrin	77.6	(6.8)	71.6	(4.4)	74.4	(9.5)	66.0	(5.7)	72.7	(3.0)
isofenfos	83.7	(4.9)	78.0	(4.3)	71.8	(8.6)	67.7	(6.4)	79.6	(1.7)
isopropalin	88.4	(6.8)	84.2	(2.1)	83.8	(5.5)	73.7	(6.6)	82.2	(2.7)
leptophos	46.2	(3.6)	53.3	(6.3)	54.0	(1.8)	41.4	(4.3)	40.2	(7.2)
lindane	75.1	(4.1)	71.0	(6.0)	74.1	(2.4)	52.2	(6.7)	69.9	(2.5)
malaoxon	80.9	(9.3)	74.1	(3.5)	71.8	(8.5)	62.1	(6.5)	82.3	(2.8)
malathion	102.9	(2.0)	112.8	(3.6)	91.7	(8.3)	80.6	(9.8)	98.7	(6.0)
metazachlor	84.3	(8.5)	91.0	(4.2)	79.9	(3.5)	69.9	(5.6)	80.6	(2.0)
methamidophos	86.8	(1.8)	91.6	(2.1)	96.4	(2.7)	93.1	(9.1)	99.3	(6.6)
methidathion	101.3	(7.2)	116.5	(6.1)	91.2	(9.3)	71.4	(7.0)	70.7	(5.7)
methoxychlor	95.6	(5.4)	95.7	(2.8)	93.8	(9.1)	67.3	(5.8)	81.5	(4.4)
metolachlor	84.3	(9.4)	80.4	(4.3)	76.1	(9.6)	88.1	(4.7)	85.6	(1.3)
mevinphos	97.9	(1.0)	90.1	(8.3)	101.7	(2.7)	59.1	(6.4)	75.2	(5.5)
mirex	79.8	(6.9)	70.7	(3.5)	72.3	(9.9)	85.5	(6.6)	73.4	(1.7)
nitralin	99.8	(3.8)	109.3	(9.0)	93.0	(2.3)	88.7	(9.0)	91.1	(2.1)
nitrofen	99.4	(5.8)	88.2	(4.2)	95.0	(9.6)	60.5	(5.8)	90.3	(2.6)
cis-nonachlor	72.6	(1.9)	72.1	(5.2)	70.6	(4.9)	62.3	(5.2)	73.8	(2.8)
trans-nonachlor	80.7	(6.6)	72.2	(3.4)	72.7	(1.4)	66.2	(5.8)	74.5	(1.8)
norflurazon	73.3	(4.3)	78.4	(9.6)	75.9	(7.2)	54.9	(1.9)	81.3	(6.7)
octhilinone	87.2	(4.7)	77.2	(6.8)	84.0	(3.4)	68.1	(7.6)	87.7	(3.5)
oxadiazon	84.2	(7.5)	73.1	(3.3)	74.2	(9.7)	64.0	(5.8)	76.0	(1.8)
oxyfluorfen	94.1	(4.9)	92.9	(7.2)	100.6	(7.7)	99.7	(6.2)	87.5	(4.3)
parathion	87.0	(3.6)	88.2	(3.3)	90.4	(6.7)	83.2	(7.2)	85.9	(4.0)
parathion-methyl	99.6	(5.5)	98.5	(2.3)	92.0	(4.1)	77.5	(4.7)	84.7	(5.2)
paroxon	101.5	(5.2)	100.9	(6.9)	108.4	(5.2)	101.0	(8.7)	82.3	(8.9)
pentachloroaniline	47.0	(9.9)	47.2	(7.9)	42.3	(9.5)	46.2	(8.5)	45.7	(5.3)
pentachlorobenzene	48.8	(1.9)	57.3	(6.5)	61.3	(5.9)	46.9	(8.4)	53.3	(3.6)
pentachlorobenzonitrile	47.1	(8.2)	47.1	(8.1)	46.1	(5.2)	39.5	(5.2)	58.6	(9.4)
pentachlorophenol-methyl	49.9	(8.2)	47.2	(2.8)	51.5	(9.6)	51.0	(9.1)	52.4	(8.7)
pentachlorothioanisole	38.6	(5.1)	45.8	(8.0)	46.5	(2.1)	39.5	(3.8)	38.2	(1.9)
cis-permethrin	71.5	(5.1)	66.1	(4.3)	74.8	(3.6)	64.1	(7.5)	67.4	(6.3)
trans-permethrin	79.2	(7.9)	72.1	(9.8)	77.7	(2.1)	66.5	(6.6)	69.8	(5.0)
phenothrin	84.8	(3.7)	80.5	(2.2)	75.6	(4.3)	70.7	(7.3)	76.0	(3.7)
phenthoate	85.0	(9.1)	83.2	(4.1)	82.2	(9.6)	67.3	(5.4)	72.0	(5.9)
o-phenylphenol	79.3	(9.2)	76.8	(3.2)	78.3	(4.6)	67.8	(5.2)	77.9	(3.4)
phorate	86.7	(6.3)	100.1	(7.9)	109.6	(7.9)	116.3	(1.6)	103.9	(9.0)
phorate sulfone	96.7	(8.9)	90.3	(4.4)	81.6	(9.1)	69.7	(7.5)	78.8	(4.6)
phorate sulfoxide	90.3	(9.3)	85.0	(5.9)	76.2	(4.7)	67.4	(6.6)	81.4	(4.2)
phosalone	80.3	(1.1)	110.3	(6.5)	89.9	(7.4)	68.7	(8.8)	56.7	(8.8)
phosmet	99.5	(4.7)	95.5	(5.8)	103.1	(6.8)	93.3	(7.9)	81.1	(8.8)
pirimphos-ethyl	73.2	(1.4)	64.9	(8.7)	67.8	(3.5)	65.5	(7.5)	71.8	(5.1)

dx.doi.org/10.1021/jf304648h | *J. Agric. Food Chem.* 2013, 61, 2299−2314

Table 2. continued

pesticide	carrot		tomato		bean		brocooli		celery	
	% recovery (%RSD)									
pirimphos-methyl	74.3	(9.4)	69.9	(6.6)	73.2	(2.3)	64.6	(6.4)	71.3	(3.9)
procymidone	76.2	(9.3)	70.7	(4.4)	69.7	(2.2)	60.8	(6.3)	74.6	(2.2)
profenofos	89.7	(8.6)	96.8	(7.4)	92.2	(5.8)	70.9	(5.6)	57.3	(6.8)
profluralin	87.9	(7.4)	83.8	(2.5)	91.1	(8.1)	74.2	(8.2)	86.6	(3.2)
propachlor	83.3	(7.9)	92.3	(5.5)	86.3	(2.9)	66.1	(7.0)	79.3	(3.7)
propetamphos	82.9	(5.2)	80.8	(3.0)	81.2	(6.5)	65.7	(7.8)	78.8	(2.6)
propyzamide	78.6	(4.5)	71.1	(3.0)	80.2	(6.6)	63.0	(7.6)	71.1	(3.5)
prothiophos	61.8	(3.4)	63.5	(4.4)	59.2	(9.9)	56.1	(6.8)	57.7	(9.0)
prothoate	91.2	(2.0)	88.6	(3.9)	91.8	(6.4)	92.0	(8.6)	95.3	(2.5)
pyraclofos	96.4	(6.9)	95.9	(5.4)	107.9	(5.0)	84.6	(8.9)	88.2	(7.7)
pyrazophos	40.2	(9.8)	70.4	(8.0)	78.5	(7.6)	53.5	(1.8)	45.6	(7.8)
pyridaphenthion	106.3	(6.2)	109.8	(3.5)	106.8	(4.2)	75.6	(8.6)	74.2	(7.3)
quinalphos	87.3	(3.2)	68.1	(6.8)	60.1	(1.3)	67.7	(7.6)	97.5	(4.6)
quintozene	55.3	(3.0)	65.1	(3.1)	61.0	(4.4)	57.4	(2.2)	51.5	(9.5)
resmethrin	87.5	(9.3)	82.8	(2.2)	90.1	(2.3)	78.6	(2.5)	63.7	(9.8)
simazine	44.2	(2.6)	47.1	(9.2)	55.6	(7.8)	54.1	(4.2)	50.5	(8.9)
sulfotep-ethyl	90.1	(7.9)	80.0	(5.1)	83.3	(6.6)	71.0	(7.3)	74.9	(7.0)
sulprofos	83.1	(4.0)	79.2	(6.9)	57.7	(7.0)	49.6	(9.3)	69.6	(5.3)
tebupirimfos	76.8	(2.6)	74.6	(3.3)	77.7	(7.3)	63.2	(7.6)	76.2	(3.3)
tecnazene	71.0	(3.6)	61.4	(1.5)	69.9	(2.5)	60.2	(6.3)	73.4	(4.3)
tefluthrin	73.9	(1.7)	73.1	(3.6)	76.2	(7.8)	62.5	(7.5)	76.9	(3.3)
terbufos	87.2	(9.4)	84.2	(3.6)	89.5	(7.3)	71.7	(7.7)	74.0	(4.0)
terbufos sulfone	82.7	(9.2)	83.8	(3.7)	78.8	(8.6)	68.5	(5.7)	76.7	(2.8)
tetrachloroaniline	56.6	(1.1)	56.3	(5.2)	49.5	(4.7)	49.9	(8.2)	54.0	(7.3)
tetrachlorvinphos	71.3	(9.8)	82.5	(5.4)	72.4	(6.4)	92.6	(5.3)	73.8	(9.3)
tetradifon	81.8	(7.0)	67.9	(6.9)	70.5	(4.0)	59.5	(7.2)	70.6	(6.1)
tetraiodoethylene	67.8	(10.0)	73.6	(4.4)	52.4	(5.4)	46.1	(9.9)	60.7	(4.0)
tetramethrin	93.6	(6.6)	93.6	(3.7)	88.2	(5.3)	70.2	(7.2)	80.8	(2.9)
thiometon	79.4	(1.2)	76.3	(2.7)	44.8	(3.5)	44.1	(7.8)	73.9	(1.0)
tolclofos-methyl	71.6	(10.0)	64.6	(7.4)	63.7	(2.2)	58.3	(6.2)	66.9	(3.8)
tolylfluanid	104.0	(11.0)	108.4	(9.1)	107.6	(4.7)	94.9	(5.6)	115.2	(9.6)
triallate	74.4	(2.7)	73.1	(4.0)	75.1	(7.2)	62.7	(9.8)	76.7	(2.9)
triazophos	98.4	(3.7)	103.5	(9.7)	106.8	(9.5)	79.0	(6.9)	70.2	(5.9)
trifluralin	88.1	(7.4)	87.8	(2.8)	91.2	(3.9)	75.9	(8.2)	85.5	(4.3)
vinclozolin	91.1	(9.8)	76.3	(4.1)	76.7	(7.2)	62.8	(6.7)	79.4	(2.1)

oranges, green beans, broccoli, and celery were each weighed into separate 50 mL centrifuge tubes, and 30 mL of acetonitrile was added to each tube. The resulting solutions were shaken for 1 min followed by the addition of sodium chloride (3.0 g) and anhydrous magnesium sulfate (12.0 g). The centrifuge tubes were shaken vigorously for 1−2 min to prevent salt agglomerates before centrifugation at 3000 rpm for 10 min. The supernatants were used for further automated QuEChERS Tip cleanup for GC-MS analysis.

Spiking Procedure. The blank extract of the sample matrix (500 μL) was placed into a small shell vial and then spiked with the pesticide standard stock solution. The matrix-matched standard was used for recovery studies, in which the pesticide standard stock solution was added after the automated QuEChERS Tip cleanup procedure.

GC-MS System and Parameters. Analysis of pesticides was performed on a model 6890 gas chromatograph with a model 5975 mass selective detector (Agilent Technologies, Little Falls, DE, USA) equipped with a Gerstel Dual rail MPS-2 Prepstation with DPX option (Linthicum, MD, USA). The Rtx-5 column (5% diphenyl/95% dimethyl polysiloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness, Restek Corp., Bellefonte, PA, USA) was used for the separation of pesticides. Constant flow at 1.0 mL/min of helium carrier gas was used. The inlet temperature was set at 250 °C. The total GC analysis time was 50 min. The temperature program consisted of a ramp from 105 °C (2 min hold) to 130 °C at a rate of 15 °C/min, increased to 240 °C at 3 °C/min, followed by the final ramp to 300 °C at 20 °C/min, and then held at 300 °C for 7 min. Injections of 2 μL were made in splitless mode using the MPS-2 system.

For automated DPX extractions, the dual rail MPS-2 used a 10 μL syringe (left side) for GC injections and a 2.5 mL syringe (right side) for automated DPX extractions. The automated extractions and subsequent GC-MS injections and analysis were controlled using Gerstel Maestro software, which is integrated with the Agilent Chemstation software (for GC-MS control).

The mass spectrometer (MS) was operated in electron impact (EI) mode at 70 eV. The MS source temperature was 230 °C. The MS transfer line and quadrupole temperature were set at 280 and 150 °C, respectively. Detection was accomplished using selected ion monitoring (SIM) using one target ion and three to four qualifier ions as listed in Table 1.

Automated QuEChERS Tip Cleanup Method. The QuEChERS Tips (Figure 1) contained 75 mg of $MgSO_4$, 25 mg of PSA, and 12.5 mg of GCB to extract 500 μL of the acetonitrile sample solution. The tips were fitted with transport adaptors to be used with the automated sampler. The solution was slowly aspirated into the QuEChERS Tips and then dispensed after a few seconds. This procedure was repeated three times with the final elution into a clean GC vial (which was capped with a thick septum slit cap). The QuEChERS Tip was further eluted from the top with an additional 250 μL of acetonitrile to ensure the pesticides were efficiently removed from the sorbent. This resulted in a final volume of approximately 500 μL of final extract. The samples were injected into the GC-MS for analysis.

Table 3. Recovery (Percent) and Precision (%RSD) of the Studied Pesticides in Different Matrices Spiked with 1000 ppb Standard Pesticides in GC-MS Analysis

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
acrinathrin	99.3	(4.1)	96.1	(6.7)	92.0	(9.5)	98.4	(3.9)	95.2	(4.3)
akton	81.3	(2.8)	89.6	(5.9)	94.4	(3.5)	88.7	(7.9)	99.4	(2.0)
alachlor	85.9	(4.4)	93.9	(1.1)	93.1	(5.6)	92.2	(7.0)	98.1	(3.8)
aldrin	78.0	(3.5)	86.4	(2.8)	94.1	(3.4)	89.3	(7.9)	99.7	(2.5)
allethrin	87.8	(4.3)	96.6	(1.9)	97.0	(5.7)	93.3	(9.6)	95.9	(0.4)
allidochlor	92.9	(4.5)	96.9	(10.6)	99.4	(4.3)	99.6	(2.4)	96.7	(8.8)
aspon	94.5	(1.7)	95.3	(3.7)	95.3	(4.6)	93.4	(7.7)	98.2	(1.5)
azemethiphos	99.0	(10.7)	99.0	(5.3)	96.6	(1.3)	98.7	(5.1)	94.1	(3.7)
azinphos oxon	100.00	(8.7)	94.7	(4.9)	98.8	(4.2)	97.1	(4.5)	97.6	(1.0)
azinphos-ethyl	98.1	(2.2)	98.9	(4.5)	99.6	(4.9)	96.7	(4.1)	99.7	(2.1)
azinphos-methyl	94.6	(4.5)	96.9	(5.4)	93.0	(5.3)	90.2	(6.7)	98.1	(3.2)
α-BHC	78.4	(3.0)	85.7	(1.0)	87.4	(3.8)	84.9	(5.8)	99.7	(0.3)
β-BHC	78.0	(2.4)	90.6	(1.5)	97.2	(4.7)	97.2	(7.2)	97.1	(2.6)
δ-BHC	79.9	(7.4)	84.9	(1.5)	98.4	(9.6)	93.1	(4.3)	96.8	(1.4)
bifenthrin	81.4	(2.7)	91.3	(0.8)	93.3	(2.7)	87.5	(5.6)	96.5	(2.7)
biphenyl	80.3	(3.8)	87.9	(1.1)	94.6	(3.1)	90.3	(7.1)	97.3	(1.7)
bromophos	78.6	(6.1)	91.4	(2.2)	78.3	(7.0)	84.4	(7.6)	96.4	(2.7)
bromophos-ethyl	75.8	(3.2)	83.7	(6.7)	86.7	(2.9)	82.6	(8.2)	91.6	(2.6)
bromopropylate	94.5	(4.1)	98.5	(1.4)	96.6	(3.7)	90.4	(9.7)	97.2	(2.4)
butachlor	85.8	(6.6)	96.4	(1.9)	95.3	(5.7)	90.9	(8.0)	94.5	(1.2)
butralin	98.5	(4.7)	95.8	(4.3)	98.2	(10.4)	94.9	(7.7)	94.9	(1.5)
captafol	99.5	(8.3)	94.9	(3.4)	99.1	(7.6)	96.0	(7.7)	96.2	(1.5)
captan	96.4	(8.6)	94.4	(8.9)	90.6	(5.9)	98.0	(2.9)	90.3	(5.7)
carbophenothion	87.8	(4.4)	96.7	(1.2)	97.7	(5.7)	92.2	(9.3)	98.2	(2.2)
cis-chlordane	78.0	(3.3)	86.4	(0.3)	93.9	(3.5)	88.6	(7.4)	98.8	(0.6)
trans-chlordane	77.2	(3.2)	87.1	(0.4)	93.8	(3.6)	88.4	(8.4)	95.6	(0.7)
α-chlordene	78.9	(1.5)	87.5	(0.6)	93.0	(3.5)	88.1	(7.4)	98.5	(1.6)
β-chlordene	77.9	(6.8)	86.8	(0.4)	93.3	(3.6)	90.0	(6.9)	95.0	(0.4)
γ-chlordene	77.5	(4.1)	85.7	(1.1)	93.5	(4.2)	88.8	(7.9)	99.0	(0.3)
chlorfenson	79.7	(3.0)	89.4	(0.8)	92.3	(3.8)	89.1	(8.8)	96.2	(2.6)
chlorfenvinphos	87.9	(7.6)	89.3	(3.3)	94.0	(7.7)	91.6	(8.4)	95.2	(0.5)
chlorobenzilate	99.6	(2.5)	87.2	(4.5)	96.1	(2.6)	98.7	(3.6)	93.3	(7.3)
chloroneb	85.8	(8.5)	93.7	(1.1)	94.4	(2.8)	40.7	(7.1)	98.9	(2.6)
chlorothalonil	52.1	(10.5)	88.9	(9.0)	92.4	(4.4)	93.2	(4.4)	93.9	(9.3)
chlorpyrifos	93.3	(8.8)	78.1	(5.4)	96.9	(7.2)	98.6	(5.8)	91.9	(7.5)
chlorpyrifos oxon	81.9	(3.5)	90.3	(1.2)	90.6	(4.9)	77.3	(2.4)	98.3	(0.6)
chlorpyrifos-methyl	84.9	(6.8)	96.8	(3.0)	90.3	(8.4)	88.6	(7.3)	97.2	(0.3)
chlorthion	96.4	(3.7)	98.7	(6.1)	94.8	(4.6)	96.9	(7.6)	99.1	(3.1)
chlorthiophos	74.0	(2.9)	81.6	(0.0)	84.8	(3.3)	82.5	(9.4)	87.4	(3.3)
chlozolinate	68.3	(6.5)	77.0	(10.3)	72.6	(9.5)	95.6	(5.7)	79.8	(1.8)
coumaphos	91.5	(1.9)	89.7	(6.9)	85.1	(7.1)	79.7	(4.7)	81.5	(3.6)
crotoxyphos	83.2	(2.2)	90.4	(0.9)	90.0	(2.5)	89.1	(8.3)	94.7	(5.1)
crufomate	97.6	(2.6)	91.8	(8.2)	96.9	(5.9)	97.0	(9.3)	87.8	(6.2)
cyanazine	78.5	(2.6)	84.3	(1.1)	92.7	(6.3)	93.4	(2.0)	93.9	(2.7)
cyanophos	80.5	(4.1)	99.1	(1.8)	94.3	(8.6)	91.5	(6.5)	98.8	(0.8)
cyfluthrin isomer 1	99.8	(4.5)	98.3	(3.5)	96.5	(9.6)	98.3	(7.5)	99.5	(1.3)
cyfluthrin isomer 2	95.0	(9.3)	99.3	(3.0)	99.6	(7.7)	94.8	(6.9)	95.9	(3.5)
cyfluthrin isomer 3	94.6	(4.8)	97.0	(9.8)	94.3	(1.7)	97.9	(7.6)	87.8	(1.3)
cyfluthrin isomer 4	100.00	(8.9)	100.00	(4.3)	98.5	(8.2)	94.1	(6.3)	99.2	(2.4)
λ-cyhalothrin	96.5	(5.0)	83.9	(2.6)	99.5	(8.0)	99.1	(5.8)	98.3	(2.3)
cypermethrin isomer 1	99.3	(10.0)	94.2	(3.9)	94.6	(3.8)	98.2	(6.5)	98.0	(2.0)
cypermethrin isomer 2	97.5	(3.2)	98.2	(6.3)	95.1	(3.1)	97.0	(6.2)	92.9	(3.7)
cypermethrin isomer 3	99.0	(9.0)	90.1	(8.7)	94.7	(9.2)	99.8	(3.6)	89.1	(7.0)
cypermethrin isomer 4	97.9	(3.1)	99.3	(7.6)	92.2	(9.0)	99.6	(7.0)	99.8	(0.9)
dacthal	78.4	(2.2)	86.4	(1.8)	93.7	(3.6)	89.7	(9.1)	99.2	(0.4)
o,p′-DDD	80.2	(3.4)	87.3	(0.8)	94.8	(2.4)	88.8	(8.3)	95.6	(2.4)
p,p′-DDD	81.6	(2.6)	87.5	(1.3)	95.7	(3.3)	91.9	(4.9)	96.5	(1.8)
o,p′-DDE	77.5	(3.3)	85.1	(2.3)	92.6	(3.7)	87.9	(7.5)	96.8	(1.3)

Table 3. continued

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
p,p′-DDE	78.2	(2.7)	85.9	(0.4)	92.5	(4.1)	88.2	(7.4)	95.4	(0.7)
o,p′-DDT	85.2	(6.9)	99.8	(1.2)	92.8	(6.9)	92.1	(7.2)	98.9	(2.7)
p,p′-DDT	85.9	(9.7)	95.4	(3.2)	93.4	(8.5)	94.9	(7.5)	98.5	(2.7)
DEF (tribufos)	88.8	(5.9)	97.8	(1.3)	97.5	(5.2)	93.5	(9.0)	94.2	(2.5)
deltamethrin	96.4	(4.7)	99.0	(6.2)	97.2	(6.1)	95.5	(7.6)	97.7	(5.1)
demeton *S*-sulfone	81.1	(2.4)	91.1	(0.8)	96.9	(5.4)	89.4	(7.3)	99.0	(2.1)
demeton-S	88.0	(4.5)	99.9	(3.6)	96.6	(8.0)	92.5	(8.1)	98.7	(1.3)
dialifor	98.6	(4.7)	99.1	(3.8)	96.4	(4.7)	99.0	(4.9)	97.7	(2.3)
diallate isomer 1	83.3	(2.8)	89.9	(0.6)	95.1	(3.9)	91.4	(7.4)	98.6	(0.5)
diallate isomer 2	84.9	(2.9)	91.2	(0.4)	95.9	(4.0)	92.5	(6.5)	96.3	(0.6)
diamidofos	88.3	(6.9)	98.3	(2.1)	98.0	(3.4)	96.2	(2.7)	95.6	(1.1)
diazinon	91.5	(3.4)	95.5	(1.9)	98.3	(5.1)	93.3	(6.3)	99.9	(0.3)
diazoxon	94.3	(10.5)	84.4	(1.9)	96.7	(4.0)	92.3	(6.6)	92.2	(2.1)
dicapthon	96.4	(3.7)	85.9	(6.1)	94.8	(4.6)	96.7	(1.7)	97.1	(3.1)
dichlofluanid	98.7	(4.0)	84.6	(5.4)	99.4	(8.5)	98.8	(5.2)	97.3	(9.2)
dichlorfenthion	78.2	(4.8)	85.3	(1.3)	93.1	(3.2)	88.4	(8.3)	98.9	(1.6)
dichloroaniline	83.4	(5.0)	98.3	(1.5)	93.5	(9.0)	85.9	(8.0)	98.0	(1.3)
dichlorobenzophenone	83.6	(3.4)	90.2	(0.9)	91.6	(4.8)	88.8	(7.6)	98.1	(0.4)
dichlorphos	99.7	(7.5)	85.6	(2.5)	99.3	(10.0)	92.2	(6.2)	98.7	(1.2)
dichlorvos	95.4	(1.3)	91.5	(5.1)	93.0	(5.8)	97.9	(0.8)	81.5	(8.8)
diclobenil	79.0	(3.6)	87.3	(0.8)	93.6	(2.9)	88.8	(6.9)	99.1	(0.9)
dicloran	90.0	(5.9)	83.2	(2.7)	90.5	(8.9)	92.4	(7.5)	94.8	(1.7)
dicrotophos	95.6	(7.5)	83.5	(5.2)	91.7	(7.5)	92.5	(7.9)	95.7	(4.4)
dieldrin	76.9	(3.3)	85.1	(0.4)	95.2	(4.1)	89.8	(7.3)	96.4	(1.9)
dimethachlor	89.2	(7.5)	98.5	(2.2)	94.3	(7.8)	94.0	(7.7)	98.2	(0.4)
dimethoate	99.6	(2.3)	83.4	(1.4)	97.2	(10.0)	95.3	(6.5)	97.6	(1.7)
dimetilan	97.5	(6.9)	99.8	(2.3)	93.6	(6.2)	91.6	(7.7)	99.1	(1.8)
dioxathion	93.2	(9.1)	97.8	(10.6)	96.4	(7.3)	98.9	(5.0)	93.0	(4.7)
diphenylamine	85.3	(3.5)	94.4	(1.3)	94.4	(5.6)	90.0	(6.2)	97.7	(0.2)
disulfoton	87.0	(4.1)	92.4	(3.3)	96.0	(4.7)	90.7	(8.4)	96.1	(2.4)
ditalimfos	82.9	(7.7)	98.1	(3.0)	97.4	(7.5)	93.0	(8.9)	99.5	(0.9)
edifenphos	98.2	(8.2)	80.8	(9.1)	96.6	(0.6)	92.9	(9.0)	96.9	(8.8)
endosulfan ether	75.4	(4.3)	81.3	(1.2)	93.4	(6.7)	88.9	(9.6)	99.3	(3.0)
endosulfan sulfate	79.1	(4.6)	99.0	(3.0)	97.7	(8.4)	90.8	(4.6)	98.3	(3.2)
α-endosulfan	77.0	(3.5)	86.3	(0.8)	94.0	(4.8)	88.3	(6.6)	99.0	(1.4)
β-endosulfan	79.7	(3.3)	91.2	(1.2)	95.0	(4.0)	92.5	(9.4)	96.8	(2.5)
endrin	71.7	(2.8)	96.8	(5.4)	95.6	(6.3)	93.2	(7.6)	97.1	(1.7)
endrin aldehyde	34.3	(2.8)	44.8	(7.8)	55.4	(2.1)	47.1	(6.8)	52.0	(6.7)
endrin ketone	97.2	(3.9)	92.1	(0.2)	99.8	(9.5)	97.9	(2.9)	99.6	(0.9)
EPN	98.4	(4.3)	99.1	(2.6)	98.5	(1.6)	96.1	(7.1)	98.1	(2.9)
ethalfluralin	95.6	(2.8)	74.9	(2.7)	99.7	(5.3)	99.9	(7.5)	94.2	(1.9)
ethion	89.2	(4.8)	98.4	(1.6)	96.3	(5.3)	92.6	(8.6)	95.0	(1.7)
ethoprop	92.8	(5.6)	95.3	(2.1)	95.1	(9.6)	95.2	(6.1)	98.1	(0.6)
ethoxiquin	88.5	(6.8)	92.5	(2.6)	71.7	(7.9)	51.9	(4.9)	51.8	(0.5)
ethylan	80.7	(3.7)	89.9	(0.8)	93.4	(3.2)	88.3	(8.5)	96.4	(2.3)
etridazole	98.8	(4.1)	91.3	(5.8)	97.5	(7.3)	86.3	(9.2)	98.5	(1.1)
etrimfos	93.5	(9.4)	75.2	(2.2)	83.1	(7.4)	96.1	(9.8)	92.5	(4.8)
famoxon	82.7	(4.1)	86.8	(4.3)	96.8	(0.8)	87.7	(8.5)	93.6	(2.2)
famphur	85.9	(2.9)	98.8	(5.5)	98.6	(5.9)	94.0	(9.4)	99.7	(3.8)
fenamiphos	98.6	(2.6)	94.7	(4.0)	96.6	(1.8)	96.1	(9.7)	99.2	(1.3)
fenchlorphos	80.7	(4.7)	91.4	(1.7)	89.1	(6.3)	87.1	(6.8)	99.5	(0.6)
fenitrothion	98.7	(4.0)	86.2	(3.9)	93.5	(8.5)	85.0	(8.4)	97.0	(1.6)
fenoxon	100.0	(1.7)	84.1	(8.0)	97.5	(1.6)	94.7	(8.1)	93.4	(5.0)
fenpropathrin	86.2	(2.6)	96.6	(0.9)	96.0	(4.3)	91.6	(5.0)	98.2	(2.7)
fenson	81.0	(3.4)	89.3	(1.0)	91.7	(3.7)	89.1	(8.4)	98.9	(0.9)
fensulfothion	93.7	(5.8)	83.3	(5.1)	96.5	(4.7)	95.1	(4.0)	96.4	(2.1)
fenthion	79.4	(4.1)	93.0	(3.6)	96.4	(2.7)	89.2	(9.0)	97.5	(3.1)
fenthion sulfone	89.2	(7.0)	91.5	(6.9)	95.4	(5.4)	97.2	(9.6)	96.8	(5.3)
fenvalerate isomer 1	96.5	(1.7)	98.1	(3.3)	96.0	(3.9)	96.7	(6.4)	99.9	(3.3)

Table 3. continued

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
fenvalerate isomer 2	98.5	(2.4)	94.3	(3.3)	95.4	(2.7)	95.2	(6.3)	96.2	(3.8)
fluchloralin	94.1	(1.4)	91.6	(2.4)	96.8	(4.8)	95.9	(7.3)	94.5	(2.4)
flucythrinate isomer 1	96.2	(3.2)	93.4	(3.5)	98.2	(9.2)	98.2	(4.6)	98.3	(3.3)
flucythrinate isomer 2	95.4	(3.3)	97.1	(4.4)	95.8	(3.3)	98.8	(7.4)	97.3	(4.3)
flumetralin	98.7	(1.5)	98.9	(2.0)	96.8	(10.8)	92.3	(9.1)	95.8	(1.4)
fluridone	93.1	(2.9)	98.8	(6.8)	97.4	(3.1)	93.4	(6.1)	84.5	(2.2)
fluvalinate isomer 1	99.7	(7.4)	93.2	(3.3)	95.6	(7.6)	98.5	(9.8)	97.0	(4.2)
fluvalinate isomer 2	97.7	(4.9)	98.7	(9.6)	94.6	(8.4)	99.5	(9.8)	97.6	(5.6)
folpet	98.8	(5.8)	86.0	(9.1)	90.5	(8.3)	95.5	(1.4)	97.7	(3.8)
fonophos	89.4	(3.4)	95.9	(1.9)	95.1	(5.7)	92.4	(6.7)	95.7	(0.2)
heptachlor	95.0	(6.3)	80.2	(3.3)	98.2	(4.4)	95.3	(7.2)	99.2	(1.7)
heptachlor epoxide	79.2	(3.5)	87.3	(0.8)	94.2	(3.9)	88.7	(7.2)	97.9	(0.3)
hexachlorobenzene	47.3	(4.6)	54.9	(0.6)	58.0	(2.6)	57.2	(7.9)	60.6	(6.5)
hexazinone	86.4	(7.0)	96.6	(1.9)	94.6	(5.4)	90.6	(5.4)	94.6	(2.6)
iodofenphos	73.4	(9.9)	91.6	(1.7)	84.5	(7.9)	85.4	(8.3)	93.7	(0.3)
iprobenfos	93.3	(6.9)	96.5	(2.5)	96.3	(8.3)	93.8	(7.3)	97.4	(2.1)
iprodione	99.5	(5.3)	95.3	(6.3)	97.9	(3.2)	97.1	(9.3)	96.1	(9.3)
isazophos	90.4	(3.6)	94.1	(0.9)	95.4	(5.5)	91.5	(6.8)	99.8	(0.6)
isodrin	84.5	(5.6)	99.0	(6.5)	94.7	(6.2)	92.7	(7.4)	99.8	(0.9)
isofenfos	85.4	(2.6)	92.9	(1.6)	95.4	(3.7)	91.1	(9.0)	98.6	(1.2)
isopropalin	95.8	(5.3)	98.9	(0.3)	96.7	(6.0)	91.0	(7.9)	99.9	(0.5)
leptophos	70.9	(3.9)	78.8	(1.6)	72.6	(7.4)	72.7	(5.6)	81.3	(5.1)
lindane	77.9	(2.3)	86.4	(1.1)	92.8	(4.2)	87.7	(5.2)	98.0	(0.8)
malaoxon	82.0	(3.0)	88.6	(0.5)	94.2	(4.2)	90.8	(7.6)	99.8	(0.1)
malathion	95.2	(4.3)	96.9	(4.1)	96.4	(1.2)	92.1	(7.1)	99.5	(1.9)
metazachlor	89.3	(7.7)	99.7	(2.2)	96.9	(5.8)	97.5	(4.6)	98.8	(1.1)
methamidophos	90.1	(4.4)	96.1	(6.9)	93.4	(8.8)	97.1	(8.8)	80.4	(5.9)
methidathion	97.3	(2.3)	93.2	(4.8)	97.3	(2.3)	97.9	(7.9)	97.7	(0.5)
methoxychlor	96.2	(8.6)	82.9	(2.7)	92.5	(6.7)	92.6	(6.2)	99.9	(2.9)
metolachlor	85.3	(3.2)	95.1	(1.9)	97.0	(4.8)	92.1	(8.9)	98.7	(0.7)
mevinphos	79.5	(11.7)	97.7	(10.6)	96.5	(2.6)	97.7	(5.8)	82.6	(5.2)
mirex	74.9	(3.1)	86.2	(0.5)	90.9	(3.3)	87.2	(6.0)	96.6	(3.2)
nitralin	98.1	(10.6)	98.7	(2.1)	93.7	(4.8)	95.9	(6.8)	94.6	(2.5)
nitrofen	97.3	(8.6)	83.6	(2.3)	97.1	(2.8)	97.7	(5.0)	97.1	(1.4)
cis-nonachlor	79.3	(2.8)	88.2	(1.0)	94.2	(3.8)	89.9	(8.2)	98.2	(0.4)
trans-nonachlor	77.1	(2.5)	86.8	(0.5)	94.5	(3.0)	88.9	(8.4)	99.5	(2.1)
norflurazon	87.8	(9.4)	96.8	(2.6)	88.6	(7.6)	88.7	(8.3)	96.1	(1.8)
octhilinone	91.3	(6.1)	99.5	(2.6)	92.8	(11.4)	94.6	(9.2)	95.7	(1.9)
oxadiazon	80.3	(3.4)	88.7	(1.6)	94.8	(3.0)	90.8	(8.8)	94.6	(1.9)
oxyfluorfen	99.1	(6.5)	95.7	(1.9)	96.6	(9.6)	96.1	(4.9)	95.4	(1.5)
parathion	90.9	(9.5)	93.7	(1.6)	96.2	(5.8)	98.8	(7.3)	99.0	(1.5)
parathion-methyl	97.9	(2.8)	86.5	(4.6)	97.9	(6.1)	92.2	(7.8)	96.6	(0.3)
paroxon	84.5	(3.8)	85.9	(11.4)	98.0	(3.8)	97.9	(9.8)	93.2	(4.6)
pentachloroaniline	60.3	(2.9)	68.1	(0.9)	70.5	(0.9)	69.3	(7.2)	72.4	(3.2)
pentachlorobenzene	64.8	(1.7)	73.8	(0.8)	80.3	(1.0)	77.1	(8.2)	87.3	(4.0)
pentachlorobenzonitrile	54.0	(4.3)	61.5	(0.9)	65.6	(1.3)	64.0	(7.9)	64.9	(4.5)
pentachlorophenol-methyl	69.1	(1.6)	76.6	(0.3)	82.9	(2.1)	79.7	(7.7)	87.5	(2.3)
pentachlorothioanisole	45.3	(5.9)	52.0	(1.3)	54.8	(2.4)	54.5	(7.7)	53.8	(5.7)
cis-permethrin	82.7	(3.8)	92.4	(1.0)	91.3	(3.0)	86.9	(5.4)	92.9	(2.5)
trans-permethrin	82.9	(4.9)	93.2	(1.5)	91.4	(3.1)	87.6	(5.4)	94.8	(3.0)
phenothrin	87.1	(3.6)	96.2	(1.2)	95.8	(4.5)	91.0	(5.4)	97.4	(1.7)
phenthoate	96.0	(5.3)	96.4	(2.2)	93.9	(5.7)	94.2	(7.1)	95.9	(1.3)
o-phenylphenol	91.1	(3.4)	99.7	(0.7)	93.8	(7.5)	91.7	(6.3)	97.2	(0.5)
phorate	99.9	(2.0)	87.8	(9.7)	96.5	(5.1)	98.2	(7.3)	79.0	(4.1)
phorate sulfone	86.8	(10.5)	93.0	(2.9)	97.2	(6.4)	96.2	(7.3)	99.0	(2.1)
phorate sulfoxide	93.0	(4.2)	83.0	(1.5)	99.6	(8.2)	96.7	(7.2)	96.2	(0.8)
phosalone	99.2	(0.9)	98.7	(5.2)	99.4	(3.4)	98.4	(4.5)	98.7	(2.3)
phosmet	97.8	(6.3)	94.0	(5.0)	99.3	(4.4)	98.3	(5.2)	99.3	(8.4)
pirimphos-ethyl	84.5	(3.1)	92.3	(1.2)	94.4	(4.7)	91.1	(7.8)	95.0	(0.6)

dx.doi.org/10.1021/jf304648h | *J. Agric. Food Chem.* 2013, 61, 2299−2314

Table 3. continued

pesticide	% recovery (%RSD)									
	carrot		tomato		bean		brocooli		celery	
pirimphos-methyl	87.2	(3.9)	94.5	(1.3)	94.6	(5.4)	91.9	(7.1)	96.2	(0.5)
procymidone	78.9	(3.3)	88.5	(0.3)	94.8	(2.9)	90.5	(8.7)	97.3	(0.6)
profenofos	99.5	(6.7)	97.1	(9.0)	99.1	(0.7)	97.0	(8.3)	95.7	(2.8)
profluralin	95.0	(8.1)	89.3	(1.8)	97.1	(10.6)	94.6	(7.4)	98.9	(1.7)
propachlor	95.8	(11.0)	99.7	(3.8)	96.6	(9.7)	96.2	(6.0)	99.2	(1.3)
propetamphos	93.1	(5.1)	98.1	(1.6)	95.3	(7.2)	93.4	(7.1)	96.6	(0.4)
propyzamide	91.7	(1.9)	97.0	(1.8)	94.0	(6.4)	91.2	(8.4)	98.6	(0.4)
prothiophos	80.3	(2.5)	89.1	(1.1)	92.2	(3.3)	88.9	(8.2)	96.2	(0.9)
prothoate	97.3	(5.6)	97.2	(1.0)	99.4	(4.2)	95.3	(8.1)	99.4	(1.4)
pyraclofos	99.9	(1.0)	99.3	(11.1)	91.8	(3.9)	96.2	(4.3)	89.6	(7.1)
pyrazophos	88.1	(1.1)	99.4	(2.4)	81.6	(4.7)	77.8	(5.9)	81.8	(4.5)
pyridaphenthion	98.3	(2.7)	90.1	(5.2)	94.6	(2.0)	99.6	(4.6)	97.2	(2.5)
quinalphos	89.0	(9.9)	97.1	(0.7)	91.3	(2.9)	94.2	(7.7)	96.9	(0.5)
quintozene	82.2	(6.2)	88.6	(1.5)	87.9	(8.6)	84.5	(6.2)	86.3	(0.3)
resmethrin	89.1	(3.3)	98.9	(0.5)	68.6	(8.7)	54.9	(3.7)	54.0	(3.6)
simazine	63.3	(7.1)	73.8	(6.9)	80.8	(8.7)	54.8	(1.1)	81.6	(4.9)
sulfotep-ethyl	99.6	(5.2)	95.2	(2.6)	97.8	(8.3)	96.2	(6.6)	98.1	(0.4)
sulprofos	84.8	(3.2)	94.6	(0.7)	95.4	(4.7)	90.6	(9.0)	98.6	(2.2)
tebupirimfos	87.8	(2.6)	93.6	(1.2)	96.1	(5.0)	92.0	(7.0)	99.3	(0.4)
tecnazene	91.6	(7.0)	88.7	(1.6)	92.9	(9.3)	88.2	(7.7)	93.1	(0.5)
tefluthrin	83.0	(3.0)	88.4	(0.4)	94.1	(4.3)	89.5	(6.7)	98.6	(0.4)
terbufos	98.9	(4.2)	99.9	(1.2)	99.5	(7.3)	95.6	(7.0)	99.6	(0.2)
terbufos sulfone	89.2	(5.6)	99.1	(1.1)	96.9	(5.0)	93.9	(8.5)	99.7	(1.2)
tetrachloroaniline	73.9	(2.3)	82.7	(0.3)	87.4	(2.6)	83.4	(6.8)	90.6	(1.6)
tetrachlorvinphos	97.8	(5.5)	95.1	(6.1)	97.3	(1.4)	96.5	(7.3)	98.0	(9.0)
tetradifon	75.2	(3.7)	87.7	(1.6)	91.1	(2.8)	87.0	(5.4)	95.0	(4.0)
tetraiodoethylene	79.0	(2.2)	97.4	(8.2)	92.6	(6.2)	97.9	(1.9)	87.3	(4.5)
tetramethrin	87.9	(7.1)	85.8	(4.0)	93.8	(6.9)	91.4	(6.5)	97.7	(2.6)
thiometon	88.9	(3.5)	93.5	(0.9)	92.1	(5.7)	88.4	(8.0)	96.5	(0.2)
tolclofos-methyl	82.6	(3.2)	90.5	(1.2)	93.0	(4.6)	89.7	(7.5)	97.6	(0.2)
tolylfluanid	93.6	(5.5)	91.9	(7.3)	97.9	(8.7)	91.3	(9.3)	98.3	(9.6)
triallate	82.4	(3.0)	89.1	(1.2)	94.4	(4.0)	90.2	(6.6)	96.4	(0.3)
triazophos	97.6	(10.1)	93.2	(4.7)	99.8	(8.7)	97.9	(9.6)	96.9	(2.4)
trifluralin	99.7	(6.6)	88.7	(2.2)	99.6	(1.4)	94.9	(6.8)	96.7	(1.3)
vinclozolin	84.2	(4.3)	89.5	(1.2)	95.3	(3.8)	91.0	(7.1)	93.3	(0.6)

Validation Study. Recovery studies of automated QuEChERS Tips were conducted using five different matrices of carrots, tomatoes, green beans, broccoli, and celery. The solution of each matrix was spiked at a low concentration (200 ppb) and high concentration (1000 ppb) of the standard pesticide mix. To eliminate matrix interferences, a matrix-matched sample was obtained method. The calculation of the recovery in this study was based on peak area ratios of analytes to internal/external standard. Recoveries were calculated by using the following equation:

$$\% \text{ recovery} = \frac{\frac{\text{peak area of pesticide in sample}}{\text{peak area of internal standard in sample}} \times 100}{\frac{\text{peak area of pesticide in matrix-matched sample}}{\text{peak area of external standard in matrix-matched sample}}} \quad (1)$$

RESULTS AND DISCUSSION

The QuEChERS Tip cleanup method was performed to remove the sample matrix in the extract prior to chromatographic analysis. The removal of water ($MgSO_4$) and fatty acids (PSA) is necessary to ensure reproducible peak intensities for quantitative analysis. GCB is used to remove pigments, particularly chlorophyll and carotenoids, with its strong affinity toward planar molecules. High levels of chlorophyll can contaminate the GC inlet liner and cause greatly reduced peak intensities and irreproducible results. Five different matrices (carrots, tomatoes, green beans, broccoli, and celery) were used to determine effects of matrices on recoveries and linearity. Examples of SIM chromatograms of pesticides spiked at 200 ppb and extracted by the automated QuEChERS Tip method in all five matrices are shown in Figure 2. All 250 pesticides were separated and analyzed in 46 min, and the retention time of each pesticide is shown in Table 1. The GC-MS method provided good separation and high sensitivity for these pesticides.

Recoveries of Pesticides. To study the accuracy and the precision of automated QuEChERS Tip cleanup method using GC-MS analysis, five different sample matrices were spiked with standard pesticides at a low level (200 μg/mL) and a high level (1000 μg/mL). The results of the average recoveries and %RSDs of pesticides spiked at the low level are shown in Table 2. The recoveries ranged from 71 to 110% with RSDs of <12% in carrot matrix, from 70 to 117% with RSDs of <11% for tomato matrix, from 72 to 113% with RSDs of <12% in green bean matrix, from 70 to 117% with RSDs of <12% for broccoli matrix, and from 71 to 115% with RSDs of <10% for celery matrix. Low recovery of 15 pesticides in the range of 48−68% was observed, and these losses are most likely due to the absorption to GCB.

Recoveries at a high level (1000 μg/mL) were also studied, and results are shown in Table 3. The recoveries achieved ranged from 71 to 100% with RSDs of <11% in carrot matrix, from 74 to 100% with RSDs of <11% for tomato matrix, from 72 to 100% with RSDs of <12% in green bean matrix, from 73 to 100% with RSDs of <10% for broccoli matrix, and from 73 to 100% with RSDs of <10% for celery matrix. Only four pesticides (endrin aldehyde, hexaxhlorobenzene, pentachlorobenzonitrile, and pentachlorothioanisole) showed <65% recovery.

Automated QuEChERS Tips provide a straightforward method for cleanup of pesticide extracts from fruits and vegetables. The cleanup procedure after initial solvent extraction is focused on removing fatty acid and pigments rather than extracting and isolating the pesticides. The method is comprehensive and provides high recoveries for most pesticides. However, lower recoveries (<70%) for particular pesticides were obtained in green bean and broccoli matrices, for example, 64% recovery of methomyl and 62% recovery of demeton-S in green bean matrices, possibly due to absorption by GCB. According to the European Quality Control Guidelines for pesticide residue analysis in food and feed,[25] a quantitative analytical method should be demonstrated at initial and extended validation as being capable of providing mean recovery values at each spiking level and for at least one representative commodity from each relevant group within the range 70−120%, with <20% of reproducibility (RSD) for all compounds analyzed using the certain method. For analysis of multiresidue methods, recoveries outside this range may be accepted. Thus, the reasonably high recovery and reproducibility of multiresidue pesticides using automated QuEChERS Tips and GC-MS are within acceptable ranges for analysis of multiresidue pesticides in food and feed.

This automated QuEChERS Tip cleanup method for pesticide analysis in fruits and vegetables is simple, fast, and sensitive and uses low volumes of solvent. It is also nontedious due to the use of automation. This automated method proves to be very reproducible and efficient for analysis of mutiresidue pesticides in different kinds of matrices.

AUTHOR INFORMATION

Corresponding Author

*Phone: 1 (803) 622-9570. E-mail: brewer@sc.edu. Fax: 1 (803) 777-9521.

Notes

The authors declare the following competing financial interest(s): W. Brewer is part owner of DPX Labs, the company that manufactures and sells DPX products. This paper focuses on the use of QuEChERS Tips, which are sold by DPX Labs.

ACKNOWLEDGMENTS

We acknowledge the Food and Drug Administration (FDA) for providing pesticide standards and DPX Laboratories for providing DPX supplies. We are also indebted to Gerstel for use of the multipurpose autosampler.

ABBREVIATIONS USED

QuEChERS, Quick, Easy, Cheap, Effective, Rugged, and Safe; DPX, disposable pipet extraction; GCB, graphitized carbon black; OC, organochlorine; PSA, primary−secondary amine; RSD, relative standard deviations; SDVB, styrene-divinylbenzene; SPE, solid phase extraction; dSPE, dispersive solid-phase extraction

REFERENCES

(1) U.S. FDA. Databases on toxicology, hazardous chemicals, environmental health, and toxic releases. U.S. National Library of Medicine; http://toxnet.nlm.nih (accessed June 2, 2011)

(2) EPA. Databases on toxicology, hazardous chemicals, environmental health, and toxic releases. U.S. National Library of Medicine; http://toxnet.nlm.nih (accessed June 2, 2011).

(3) Wang, X.; Zhao, X.; Liu, X.; Li, Y.; Fu, L.; Hu, J.; Huang, C. Homogeneous liquid-liquid extraction combined with gas chromatography-electron capture detector for the determination of three pesticide residues in soils. *Anal. Chim. Acta* **2008**, *620*, 162−169.

(4) Pirard, C.; Widart, J.; Nguyen, B. K.; Deleuze, C.; Heudt, L.; Haubruge, E.; Pauw, E.; Focant, J. F. Development and validation of a multi-residue method for pesticide determination in honey using on-column liquid-liquid extraction and liquid chromatography-tandem mass spectrometry. *J. Chromatogr., A* **2007**, *1152*, 116−123.

(5) Lee, J. M.; Park, J. W.; Jang, G. C.; Hwang, K. J. Comparative study of pesticide multi-residue extraction in tobacco for gas chromatography-triple quadrupole mass spectrometry. *J. Chromatogr., A* **2008**, *1187*, 25−33.

(6) Wu, J.; Lu, J.; Wilson, C.; Lin, Y.; Lu, H. Effective liquid-liquid extraction method for analysis of pyrethroid and phenylpyrazole pesticides in emulsion-prone surface water samples. *J. Chromatogr., A* **2010**, *1217*, 6327−6333.

(7) Zrostlikova, J.; Hajslova, J.; Kovalczuk, T.; Stepan, R.; Poustka, J. Determination of seventeen polar/thermolabile pesticides in apples and apricots by liquid chromatography/mass spectrometry. *J. AOAC Int.* **2003**, *86*, 612−622.

(8) Fenoll, J.; Hellín, P.; Martínez, C. M.; Flores, P. Multiresidue analysis of pesticides in vegetables and citrus fruits by LC-MS-MS. *Chromatographia* **2010**, *72*, 857−866.

(9) Guan, S.-X.; Yu, Z.-G.; Yu, H.-N.; Song, C.-H.; Song, Z.-Q.; Qin, Z. Multi-walled carbon nanotubes as matrix solid-phase dispersion extraction adsorbent for simultaneous analysis of residues of nine organophosphorus pesticides in fruit and vegetables by rapid resolution LC-MS-MS. *Chromatographia* **2011**, *73*, 33−41.

(10) Ferrer, C.; Martínez-Bueno, M. J.; Lozano, A.; Fernández-Alba, A. R. Pesticide residue analysis of fruit juices by LC-MS/MS direct injection. One year pilot survey. *Talanta* **2011**, *83*, 1552−1561.

(11) Singer, H.; Jaus, S.; Hanke, I.; Lück, A.; Hollender, J.; Alder, A. C. Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behavior in wastewater and surface water. *Environ. Pollut.* **2010**, *158*, 3054−3064.

(12) García-Chao, M.; Agruña, M. J.; Flores Calvete, G.; Sakkas, V.; Llompart, M.; Dagnac, T. Validation of an off line solid phase extraction liquid chromatography-tandem mass spectrometry method for the determination of systemic insecticide residues in honey and pollen samples collected in apiaries from NW Spain. *Anal. Chim. Acta* **2010**, *672*, 107−113.

(13) Kmella, B.; Abranko, L.; Fodora, P.; Lehotay, S. J. Routine approach to qualitatively screening 300 pesticides and quantification of those frequently detected in fruit and vegetables using liquid chromatography tandem mass spectrometry (LC-MS/MS). *Food Addit. Contam* **2010**, *27*, 1415−1430.

(14) Lehotay, S. J. Quick, easy, cheap, effective, rugged, and safe (QuEChERS) approach for the determination of pesticide residues. In *Pesticide Protocols: Methods in Biotechnology 19*; Martínez Vidal, J. L., Garrido Frenich, A., Eds.; Humana Press: Totowa, NJ, 2005; pp 239−261.

(15) Lehotay, S.; Mastovská, K.; Yun, S. Evaluation of two fast and easy methods for pesticide residue analysis in fatty food matrixes. *J. AOAC Int.* **2005**, *88*, 630−638.

(16) Parejaa, L.; Cesio, V.; Heinzen, H.; Fernández-Alba, A. Evaluation of various QuEChERS based methods for the analysis of herbicides and other commonly used pesticides in polished rice by LC−MS/MS. *Talanta* **2011**, *83*, 1613−1622.

(17) Wong, J.; Hao, C.; Zhang, K.; Yang, P.; Banerjee, K.; Hayward, D.; Takhar, I.; Scheiber, A.; Tech, K.; Sack, C.; Smoker, M.; Chen, X.; Utture, S. C.; Oulkar, D. Development and interlaboratory validation of

a QuEChERS-based liquid chromatography-tandem mass spectrometry method for multiresidue pesticide analysis. *J. Agric. Food Chem.* **2010**, *58*, 5897−5903.

(18) Lehotay, S. J.; Son, K A.; Kwon, H.; Koesukwiwata, U.; Fu, W.; Mastovska, K.; Hoh, E.; Leepipatpiboon, N. Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. *J. Chromatogr., A* **2010**, *1217*, 2548−2560.

(19) Riedel, M.; Speer, K.; Stuke, S.; Schmeer, K. Simultaneous analysis of 70 pesticides using HPLC/MS/MS: a comparison of the multiresidue method of Klein and Alder and the QuEChERS method. *J. AOAC Int.* **2010**, *93*, 1972−1986.

(20) Lehotay, S. Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: a collaborative study. *J. AOAC Int.* **2007**, *90*, 485−520.

(21) Liua, G.; Rong, L.; Guo, B.; Zhang, M.; Li, S.; Wu, Q.; Chen, J.; Chen, B.; Yao, S. Development of an improved method to extract pesticide residues in foods using acetonitrile with magnesium sulfate and chloroform. *J. Chromatogr., A* **2011**, *1218*, 1429−1436.

(22) Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in produce. *J. AOAC Int.* **2003**, *86*, 412−431.

(23) Koesukwiwat, U.; Lehotay, S. J.; Miao, S.; Leepipatpiboon, N. High throughput analysis of 150 pesticides in fruits and vegetables using QuEChERS and low-pressure gas chromatography−time-of-flight mass spectrometry. *J. Chromatogr., A* **2010**, *1217* (43), 6692.

(24) Podhorniak, L. Tubes or Tips? Presented at the Florida Pesticide Residue Workshop, St. Pete Beach, FL, July 2010.

(25) European Commission. Method validation and quality control procedures for pesticide residues analysis in food and feed, Document No. SANCO/10684/2009, Brussels, Jan 1, 2010; http://ec.europa.eu/food/plant/protection/resources/qualcontrol_en.pdf (accessed June 22, 2011).