SPECIAL GUEST EDITOR SECTION

Multiresidue Method for the Determination of Residues of 251 Pesticides in Fruits and Vegetables by Gas Chromatography/ Mass Spectrometry and Liquid Chromatography with Fluorescence Detection

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A method is described for the determination of 251 pesticide and degradation product residues in fruit and vegetable samples. Extraction of the sample with acetonitrile is followed by a salting-out step. Co-extractives are removed by passing a portion of the acetonitrile extract through an octadecyl (C_{18}) solid-phase extraction cleanup cartridge and then, in a second cleanup, through a carbon cartridge coupled to an amino propyl cartridge. Determination is by gas chromatography with mass-selective detection in the selected-ion monitoring mode, and by liquid chromatography with post-column reaction and fluorescence detection for *N*-methyl carbamates. The method has been used for analysis of various fruits and vegetables, such as apple, banana, cabbage, carrot, cucumber, lettuce, orange, pear, pepper, and pineapple. Limits of detection range between 0.02 and 1.0 mg/kg for most compounds. Over 80% of the compounds have a limit of detection of ≤0.04 mg/kg.

Regulatory agencies involved in the monitoring of pesticide residues in foods require fast and efficient multiresidue methods with a broad scope of application in order to maximize the coverage of their monitoring activities. This method was developed in support of the Agriculture and Agri-Food Canada (now Canadian Food Inspection Agency) pesticide residue monitoring program. The results of this program have been published elsewhere (1).

This paper describes a much improved version of a previously published method (2). The cleanup has been modified, a new internal standard has been added, and the scope of the method has been increased to cover a larger number of pesticides. This multiresidue method is suitable for the determination of 239 pesticides and degradation products in fruits and vegetables by gas chromatography/mass-selective detection (GC/MSD), and 12 *N*-methyl carbamate insecticides by liquid chromatography (LC) with fluorescence detection, for a total of 251 compounds.

The method uses acetonitrile for extraction, which is followed by a salting-out step (3). In this particular method, salting out results in phase separation. A first cleanup is performed by passing a portion of the acetonitrile phase through an octadecyl (C_{18}) (4) solid-phase extraction (SPE) tube for removal of nonpolar co-extractives. An aliquot of the extract is concentrated for the second cleanup on a carbon SPE tube coupled to an amino propyl cartridge with acetonitrile–toluene (3 + 1, v/v) as the elution solvent (2, 5). The sensitivity of the method is appropriate for monitoring pesticide residues in foods. The method is ideal for analysis of the large number of samples received in a regulatory laboratory.

METHOD

Reagents

(**a**) *Solvents*.—Acetonitrile, acetone, toluene, and methanol; all Ultra-Resi Analyzed (J.T. Baker, Phillipsburg, NJ).

(**b**) *Purified water*.—Prepared by using Milli-Q water purification system (Millipore, Beford, MA).

(**c**) *Hydrochloric acid*.—Reagent grade, 36.5–38.0% (J.T. Baker).

(**d**) *pH 3 water*.—Water adjusted to pH 3.0 with a solution of 1 part concentrated hydrochloric acid mixed with 4 parts water.

(**e**) *Sodium chloride*.—Analar reagent (BDH Chemicals, Dorset, UK).

(**f**) *Sodium sulfate*.—Anhydrous, granular (Baker-Analyzed reagent).

(**g**) *Octadecyl (C_{18}) SPE tubes*.—Bond Elut, 6 mL, 1 g (Varian, Palo Alto, CA).

(**h**) *Carbon SPE tubes*.—Envi-Carb, 3 mL, 500 mg (Supelco, Inc., Bellefonte, PA).

(**i**) *Amino propyl SPE tubes*.—360 mg classic Sep-Pak cartridges (Millipore, Waters Chromatography, Milford, MA).

(**j**) *Nitrogen*.—Prepurified grade (Liquid Carbonic Inc., Chicago, IL).

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(**k**) *Helium*.—Ultrapure grade (Liquid Carbonic Inc.).

(**l**) *Stock standard solutions*.—Standards are obtained from commercial sources or from the pesticide manufacturers. Individual stock standards are prepared in acetone for most compounds and in methanol for carbamates. Concentrations range from 400 to 4000 ng/μL, according to solubility.

(**m**) *Intermediate solutions*.—Mixed-compounds intermediate solutions are prepared from the stock solutions at concentrations ranging from 50 to 200 ng/μL.

(**n**) *Spiking solutions*.—Intermediate solutions are combined to yield 2 spiking solutions, each containing approximately 120 pesticides at concentrations of 10–50 ng/μL, according to their respective sensitivities. Carbamates are included in separate spiking solutions.

(**o**) *Internal standard*.—Aldrin solution prepared at 50 ng/μL in acetone.

(**p**) *Internal standard (carbamate)*.—Isoprocarb solution prepared at 40 ng/μL in methanol.

Apparatus

(**a**) *Gas chromatograph*.—Hewlett-Packard 5890 Series II (Hewlett-Packard, Wilmington, DE).

(**b**) *Autosampler*.—Hewlett-Packard 7673A.

(**c**) *Injector*.—Split-splitless, with electronic pressure control.

(**d**) *Mass-selective detector*.—Hewlett-Packard 5972A.

(**e**) *Workstation*.—DOS Chemstation G1034C, version C.01.05 (Vectra 486 with 330 megabytes hard drive, 16 megabytes RAM).

(**f**) *Analytical column*.—DB-1701, 30 m × 0.25 mm id, 0.15 μm film thickness (J&W Scientific, Folsom, CA).

(**g**) *Retention gap*.—A 30 cm length of column of same type as analytical column.

(**h**) *Food Processor*.—Robot Coupe Model R300 (Robot Coupe USA Inc., Jackson, MS).

(**i**) *Analytical balance*.—Mettler AE 163.

(**j**) *Homogenizer*.—Omni-Mixer Model 17105 (Omni International, Gainesville, VA).

(**k**) *Centrifuge*.—Dynac, Cat. No. 0101 (Becton, Dickinson, & Co., Parsippany, NJ).

(**l**) *Nitrogen evaporator*.—Meyer N-Evap Model 111 (Organomation Associates Inc., Berlin, MA), with water bath set at 35°C.

(**m**) *Rotary evaporator*.—Model R110 (Brinkmann Instruments Inc., Westbury, NY) equipped with Model 7049-00 Cole Parmer aspirator pump (Cole Parmer, Niles, IL) and refrigerated circulating bath (Neslab Instruments Inc., Portsmouth, NH) to maintain the temperature of the antifreeze, ethylene glycol–water (1 + 1), in condensing coil at −15°C. Water bath set at 35°C.

Extraction

Prepare edible portion of sample as described in Section 4 of *Analytical Methods for Pesticide Residues in Food* (6). To spike quality control sample at 0.2 mg/kg, add 1.0 mL spiking solution (10 ng/μL for most compounds) to 50 g known blank, and let stand for 15 min before extraction. Homogenize 50 g chopped sample with 100 mL acetonitrile, using Omni-Mixer at half speed for 5 min. Add 10 g sodium chloride, and homogenize for another 5 min.

Cleanup

Precondition C_{18} SPE tube with acetonitrile. Further condition tube by loading ca 2 mL acetonitrile extract (top layer) into C_{18} tube, elute, and discard. Load ca 15 mL acetonitrile layer onto C_{18} cartridge, and elute by gravity into 15 mL centrifuge tube. Stop collecting eluate when volume in collection tube reaches 13 mL. Add sodium sulfate to bring liquid to 15 mL. Cap tube and shake well. Centrifuge at high speed for 5 min. Transfer 10 mL aliquot (equivalent to 5 g sample) to second 15 mL centrifuge tube. Evaporate extract to 0.5 mL under nitrogen. Attach amino propyl cartridge to bottom of carbon SPE tube, and precondition tubes with acetonitrile–toluene (3 + 1). Quantitatively transfer extract to carbon cartridge by rinsing with acetonitrile–toluene (3 + 1), and elute with 20 mL acetonitrile–toluene (3 + 1). Evaporate eluate to low volume with rotary evaporator. Add two 10 mL portions of acetone, and evaporate to low volume with rotary evaporator after each addition to make solvent exchange to acetone. Quantitatively transfer extract to 15 mL graduated centrifuge tube, and evaporate to <2.5 mL under nitrogen. Add 50 μL internal standard (1.0 ng/μL, final concentration of aldrin), and dilute extract to 2.5 mL with acetone. Transfer 0.5 mL to vial for GC/MSD analysis. The concentration of the sample represented by the extract is 2 g/mL. Prepare standards in blank matrix of commodity being analyzed by adding 10 μL internal standard (aldrin, 50 ng/μL) and 20 μL spiking solution (10 ng/μL for most compounds) to 500 μL blank extract, to produce a final concentration of 1.0 ng/μL for aldrin and 0.4 ng/μL for most compounds. The remaining 2 mL extract is used for carbamate analysis after solvent exchange to 0.8 mL pH 3 water and addition of 20 μL carbamate internal standard (1.0 ng/μL, final concentration of isoprocarb).

Determination

Sample extracts are injected into the GC/MSD system under the following conditions: splitless injection mode; injection volume, 2 μL; injector temperature, 250°C; detector temperature, 285°C; and carrier gas, helium. The gas chromatograph is operated in constant flow mode (electronic pressure control) at 0.9 mL/min. GC temperature program: hold 2.0 min at 70°C, 70° to 130°C at 25°C/min, 130° to 220°C at 2°C/min, 220° to 280°C at 10°C/min, hold 6.6 min at 280°C. A 30 cm length of column of the same type as the analytical column is used as a retention gap.

Two injections are required to analyze for all pesticides. Compounds are identified according to their retention times and ion ratios. Table 1 lists the compounds along with their

Table 1. Retention times (Rt), ions monitored,[a] and ratios (sorted by retention time) for compounds determined by the multiresidue method

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Dichlorvos-naled	FV-1	7.24	185	109	220		4.61	0.19	
EPTC	FV-1	7.89	189	132			1.40		
Bendiocarb degr.[c]	FV-2	7.99	166	151	126		1.86	1.82	
Allidochlor	FV-2	8.28	138	132	173		1.12	0.14	
Methamidophos	FV-2	8.88	141	94	95		2.31	1.60	
Butylate	FV-1	9.06	217	174			5.20		
Promecarb degr.	FV-1	9.09	135	150			0.35		
Chlorthiamid degr.	FV-2	9.36	171	173	136		0.64	0.18	
Dichlobenil	FV-1	9.37	171	173			0.62		
Dichlormid	FV-1	9.51	168	166			1.53		
Vernolate	FV-2	9.59	86	128			1.14		
Pebulate	FV-2	9.97	128	161	203		0.12	0.06	
Aminocarb degr.	FV-1	10.06	150	151	136		1.27	0.79	
Etridiazole	FV-2	10.12	211	183			0.97		
Chlormephos	FV-1	10.46	234	121			3.19		
Nitrapyrin	FV-2	10.85	194	196	198		0.97	0.31	
Mexacarbate degr.	FV-2	11.18	165	150	134		0.81	0.34	
Bufencarb degr.	FV-1	11.24	121	122	107		0.37	0.22	
cis-Mevinphos	FV-1	11.82	127	192	164	109	0.20	0.06	0.23
Propham	FV-2	11.85	179	137			1.28		
trans-Mevinphos	FV-1	12.17	127	192	164	109	0.22	0.06	0.23
Chloroneb	FV-2	12.43	191	193	206		0.64	0.53	
o-Phenylphenol	FV-2	13.57	170	169	141	115	0.66	0.29	0.21
Tecnazene	FV-1	14.96	261	215			1.54		
Cycloate	FV-2	15.09	154	83	215		2.26	0.07	
Captafol degr.	FV-2	15.56	151	79	80		1.31	0.73	
Captan degr.	FV-1	15.60	151	79	80		1.26	0.71	
Heptenophos	FV-2	15.89	124	215	250		0.09	0.07	
Acephate	FV-1	15.89	136	94			0.54		
Demeton-*S*	FV-1	16.04	171	88	143		6.27	0.55	
Hexachlorobenzene	FV-1	16.51	284	286	282		0.77	0.56	
Ethoprophos	FV-2	16.98	158	242	139		0.08	0.47	
Diphenylamine	FV-1	17.09	169	167	168		0.34	0.63	
Di-allate 1	FV-1	17.46	234	236			0.36		
Chlordimeform	FV-2	17.67	196	181			0.75		
Propachlor	FV-1	17.68	120	176	211		0.23	0.05	
Demeton-*S*-methyl	FV-2	18.08	88	109	142		0.26	0.17	
Di-allate 2	FV-1	18.48	234	236			0.36		
Ethalfluralin	FV-1	18.61	276	316			0.50		
Phorate	FV-1	18.86	260	231			0.73		
Trifluralin	FV-1	19.27	306	264			1.18		
Sulfallate	FV-2	19.31	188	116	148		0.09	0.06	

Table 1. (*continued*)

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Chlorpropham	FV-2	19.39	213	127			3.21		
Benfluralin	FV-1	19.45	292	264			0.23		
Sulfotep	FV-1	19.54	322	202			1.15		
alpha-BHC	FV-1	19.83	219	183			1.16		
Bendiocarb	FV-2	20.74	151	166	223		0.41	0.08	
Quintozene	FV-1	20.82	295	237			1.79		
Promecarb degr.	FV-1	20.93	135	150			0.62		
Omethoate	FV-1	21.15	156	110			1.10		
Terbufos	FV-2	21.71	231	153			0.38		
Demeton-*O*	FV-1	21.74	88	114	170		0.15	0.12	
Desethylatrazine	FV-1	21.86	172	174			0.31		
Clomazone	FV-2	21.92	204	125			2.14		
Prometon	FV-2	22.01	225	210	168		1.44	1.17	
Tri-allate	FV-1	22.32	268	270			0.67		
Fonofos	FV-1	22.40	246	109			4.50		
Diazinon	FV-1	22.67	304	179			3.58		
Terbumeton	FV-2	22.77	210	169	225		0.94	0.25	
Dicrotophos	FV-1	22.77	127	193			0.07		
Lindane	FV-2	22.98	219	183			1.28		
Dioxathion	FV-1	23.18	125	153	270		0.29	0.35	
Disulfoton	FV-2	23.60	142	274			0.29		
Profluralin	FV-1	23.68	318	330			0.30		
Dicloran	FV-2	23.78	206	176			1.37		
Propazine	FV-1	24.04	229	214			1.85		
Atrazine	FV-2	24.12	215	200			1.88		
Etrimfos	FV-2	24.14	292	277			0.44		
Simazine	FV-1	24.21	201	186			0.70		
Heptachlor	FV-1	24.50	272	274			0.79		
Chlorbufam	FV-1	24.59	223	164			1.00		
Schradan	FV-2	24.59	199	135			1.74		
Aminocarb	FV-1	24.65	151	208	150		0.12	0.73	
Terbuthylazine	FV-1	24.78	214	173			0.55		
Monolinuron	FV-2	24.80	214	126			1.43		
Secbumeton	FV-2	25.33	196	210	225		0.20	0.14	
Dichlofenthion	FV-1	25.82	279	223			1.36		
Cyanophos	FV-1	26.09	243	125			1.34		
Isazofos	FV-2	26.10	161	257	313		0.28	0.04	
Mexacarbate	FV-2	26.28	165	222	150		0.21	0.86	
Propyzamide	FV-1	26.45	173	175			0.63		
Aldrin[d]	FV-1	26.48	263	265			0.66		
Pirimicarb	FV-2	26.50	166	238			0.16		
Dimethoate	FV-1	26.60	87	229	143		0.04	0.09	
Monocrotophos	FV-2	26.68	127	192	109		0.09	0.11	

Table 1. (*continued*)

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Chlorpyrifos-methyl	FV-1	26.93	286	288			0.65		
Fluchloralin	FV-2	27.56	306	326	264		0.82	0.83	
Fenchlorphos	FV-1	27.75	285	287			0.68		
Desmetryn	FV-1	27.91	198	213			1.49		
Dinitramine	FV-2	28.00	305	307	261		0.37	0.41	
Dimethachlor	FV-2	28.23	210	134	197		8.78	3.13	
Chlorothalonil	FV-1	28.75	266	264			0.78		
Alachlor	FV-1	28.80	188	160			1.27		
Prometryn	FV-1	29.22	241	226			0.68		
Metobromuron	FV-2	29.23	258	61			16.26		
Cyprazine	FV-2	29.33	212	227	229		0.89	0.12	
Ametryn	FV-2	29.34	227	212			1.12		
Simetryn	FV-1	29.45	170	155			0.93		
Pirimiphos-methyl	FV-1	29.53	290	305			0.52		
Vinclozolin	FV-1	29.55	285	287			0.62		
Thiobencarb	FV-2	29.79	100	257	125		0.09	0.25	
Metribuzin	FV-2	29.82	198	199			0.29		
beta-BHC	FV-1	29.90	219	183			1.17		
Terbutryn	FV-1	30.21	226	241			0.51		
Metalaxyl	FV-2	30.37	206	249			0.46		
Panathion-methyl	FV-2	30.42	263	125			2.15		
Chlorpyrifos	FV-1	30.61	314	199			3.18		
Aspon	FV-1	30.97	211	253			0.27		
Dicofol	FV-1	31.14	250	139			5.88		
Oxychlordane	FV-2	31.21	115	185	149		0.62	0.51	
Malaoxon	FV-1	31.25	268	195			1.85		
Chlorthal-dimethyl	FV-2	31.26	301	299			0.81		
Phosphamidon	FV-1	31.31	264	193			0.28		
delta-HCH	FV-2	31.35	183	219	217		0.86	0.68	
Metolachlor	FV-1	31.63	238	162			2.14		
Terbacil	FV-2	31.91	160	161	216		1.33	0.02	
Fenthion	FV-1	32.01	278	169			0.33		
Bromophos	FV-1	32.15	331	329			0.77		
Dichlofluanid	FV-1	32.39	226	123			5.26		
Fenitrothion	FV-1	32.46	277	260			0.59		
Pirimiphos-ethyl	FV-2	32.67	333	304			1.26		
Malathion	FV-1	32.68	158	125			2.23		
Paraoxon	FV-1	32.71	275	109			11.06		
Heptachlor epoxide	FV-2	32.76	237	183	217		2.02	1.21	
Nitrothal-isopropyl	FV-2	33.21	236	212			0.75		
Butralin	FV-2	33.42	266	250			0.14		
Ethofumesate	FV-1	33.48	161	286	207		0.25	1.04	
Triadimefon	FV-1	33.99	208	210			0.30		

Table 1. (*continued*)

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Parathion	FV-2	34.05	291	139			1.20		
Isopropalin	FV-1	34.15	280	238			0.60		
Pendimethalin	FV-2	34.34	252	281			0.08		
Fenson	FV-2	34.36	268	141			4.41		
Linuron	FV-2	34.40	248	160	250		1.44	0.62	
alpha-Endosulfan	FV-1	34.42	277	339	243		0.57	1.37	
Chlorthiamid	FV-2	34.45	205	170			2.36		
Chlorbenside	FV-1	34.54	125	268			0.07		
Allethrin	FV-2	34.82	123	136			0.28		
Chlorfenvinphos	FV-1	34.97	323	267			2.51		
trans-Chlordane	FV-1	35.22	373	375			0.93		
Bromophos-ethyl	FV-1	35.35	359	303			1.31		
Chlorthion	FV-2	35.56	297	125			4.38		
Quinalphos	FV-1	35.59	146	298			0.09		
Propanil	FV-2	35.69	161	163			0.66		
Diphenamid	FV-2	35.71	167	239			0.16		
Crufomate	FV-2	35.79	256	182			0.83		
cis-Chlordane	FV-1	35.91	373	375			0.93		
Isofenphos	FV-1	35.92	213	255			0.29		
Metazachlor	FV-2	36.11	209	133			1.82		
Phenthoate	FV-2	36.19	246	274			3.83		
Chlorfenvinphos	FV-1	36.26	323	267			2.51		
Penconazole	FV-1	36.33	248	159			1.85		
Tolylfluanid	FV-1	36.61	238	137			3.56		
p,p′-DDE	FV-1	37.06	318	246			1.75		
Folpet	FV-2	37.21	260	262			0.69		
Prothiofos	FV-2	37.50	309	267			1.34		
Dieldrin	FV-1	37.55	277	263			1.47		
Butachlor	FV-1	37.75	176	160			0.84		
Chlorflurecol-methyl	FV-2	37.77	215	217	152		0.32	0.44	
Captan	FV-1	38.05	149	79			6.28		
Iodofenphos	FV-1	38.08	377	379			0.44		
Tribufos	FV-2	38.16	169	202			0.50		
Chlozolinate	FV-2	38.23	259	331			0.43		
Crotoxyphos	FV-2	38.56	193	127			3.65		
Methidathion	FV-1	38.70	145	85			0.75		
Tetrachlorvinphos	FV-1	38.83	329	331			0.95		
Chlorbromuron	FV-2	38.84	61	294			0.06		
Procymidone	FV-1	38.85	283	285			0.69		
Flumetralin	FV-2	38.98	143	157			0.14		
Endrin	FV-1	39.09	263	281			0.44		
Bromacil	FV-2	39.17	205	207			0.97		
Flurochloridone 1	FV-2	39.19	311	187			2.48		

Table 1. (*continued*)

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Triadimenol	FV-2	39.22	112	168			0.45		
Profenofos	FV-1	39.28	339	337			1.06		
o,p′-DDD	FV-1	39.67	235	237			0.64		
Flurochloridone 2	FV-2	39.67	311	187			1.85		
Ethylan	FV-2	39.78	223	165			0.10		
Cyanazine	FV-1	40.04	225	240			0.49		
Chlorfenson	FV-1	40.09	302	175			6.83		
TCMTB	FV-2	40.40	238	180			6.23		
o,p′-DDT	FV-1	40.71	235	237			0.63		
Oxadiazon	FV-2	40.89	258	175			3.48		
Carbetamide	FV-2	41.06	119	120	236		0.22	0.04	
Tetrasul	FV-2	41.13	252	324			0.52		
Imazalil	FV-1	41.15	215	173	217		0.98	0.61	
Aramite 1	FV-1	41.17	185	319			0.18		
Fenamiphos	FV-2	41.48	303	217			0.59		
Erbon	FV-1	42.08	169	171			0.64		
Aramite 2	FV-1	42.13	185	319			0.08		
Methoprotryne	FV-2	42.18	256	213			0.37		
Chloropropylate	FV-1	42.24	251	139	253		1.14	0.63	
Methyl trithion	FV-2	42.40	157	314			0.10		
Nitrofen	FV-1	42.42	283	202			0.73		
Chlorobenzilate	FV-2	42.55	251	139			1.26		
Carboxin	FV-2	42.81	143	235			0.29		
Flamprop-methyl	FV-1	42.89	105	77	276		0.29	0.04	
Bupirimate	FV-2	43.17	273	316	208		0.16	0.94	
beta-Endosulfan	FV-1	43.36	241	237			1.06		
p,p-DDD	FV-2	43.62	235	237			0.64		
Oxyfluorfen	FV-2	43.82	252	300			0.27		
Chlorthiophos	FV-1	43.92	325	360			0.46		
Ethion	FV-1	44.42	231	153	384		0.76	0.04	
Etaconazole 1	FV-1	44.42	245	173			1.51		
Sulprofos	FV-2	44.47	322	156	140		1.83	2.14	
Etaconazole 2	FV-1	44.60	245	173			1.70		
Flamprop-isopropyl	FV-2	44.85	105	276	363		0.07	0.01	
p,p′-DDT	FV-1	44.96	235	237			0.64		
Carbophenothion	FV-1	45.17	157	342	121		0.13	0.54	
Fluorodifen	FV-2	45.19	190	328	162			0.15	
Myclobutanil	FV-2	46.02	179	288			0.06		
Benalaxyl	FV-1	46.15	148	206	325		0.16	0.02	
Edifenphos	FV-1	46.84	173	310	201		0.27	0.27	
Propiconazole 1	FV-2	47.25	259	261			0.61		
Fensulfothion	FV-2	47.52	293	308			0.16		
Mirex	FV-1	47.61	272	274	237		0.80	0.62	

Table 1. (*continued*)

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Propargite	FV-2	47.63	135	350	150	201	0.02	0.12	0.03
Propiconazole 2	FV-2	47.63	259	261			0.64		
Diclofop-methyl	FV-1	47.64	253	340	281		0.40	0.34	
Propetamphos	FV-2	48.22	124	208			2.24		
Triazophos	FV-2	48.40	162	161			1.54		
Benodanil	FV-1	48.92	231	323	203		0.17	0.21	
Nuarimol	FV-1	49.15	314	235	203		3.39	3.03	
Bifenthrin	FV-2	49.19	181	165	166		0.27	0.27	
Endosulfan sulfate	FV-1	49.43	272	387			0.27		
Bromopropylate	FV-2	50.26	341	183			1.11		
Oxadixyl	FV-2	50.29	163	132	278		0.79	0.06	
Methoxychlor	FV-1	50.41	227	228			0.16		
Benzoylprop-ethyl	FV-2	50.84	105	77	292		0.26	0.04	
Tetramethrin 1	FV-2	50.89	164	123			0.28		
Fenpropathrin	FV-1	51.21	181	265			0.33		
Tetramethrin 2	FV-2	51.25	164	123			0.29		
Leptophos	FV-2	51.51	171	377			0.29		
EPN	FV-1	51.70	169	157			2.46		
Norflurazon	FV-2	51.87	303	145			2.49		
Hexazinone	FV-1	52.08	171	128			0.13		
Phosmet	FV-1	52.16	160	161	317		0.12	0.02	
Iprodione	FV-2	52.30	314	316	187		0.64	1.31	
Tetradifon	FV-1	52.47	229	356			0.40		
Bifenox	FV-2	52.65	341	173			0.54		
Oxycarboxin	FV-2	53.16	175	267			0.26		
Phosalone	FV-1	53.43	182	367			0.08		
Chloridazon	FV-2	53.48	221	220			0.51		
Azinphos-methyl	FV-2	53.49	160	132			0.79		
Nitralin	FV-2	53.59	274	316			0.95		
cis-Permethrin	FV-1	53.69	183	163	165		0.22	0.18	
Fenarimol	FV-2	53.79	219	139			2.18		
trans-Permethrin	FV-1	54.05	183	163	165		0.30	0.23	
Pyrazophos	FV-1	54.06	232	221	373		3.77	0.20	
Azinphos-ethyl	FV-1	54.37	160	132			1.18		
Dialifos	FV-2	54.40	210	208			3.13		
Cyfluthrin 1	FV-2	55.79	226	206			1.08		
Prochloraz	FV-2	55.80	180	308	310		0.33	0.32	
Coumaphos	FV-2	56.02	362	210			1.20		
Cypermethrin 1	FV-1	56.03	181	163			1.59		
Cyfluthrin 4	FV-2	56.33	226	206			1.24		
Cypermethrin 4	FV-1	56.58	181	163			1.91		
Fenvalerate 1	FV-2	57.67	167	225	419		0.44	0.06	

Table 1. (*continued*)

Compound[b]	Method	Rt, min	Ions monitored, m/z				Abundance ratio of qualifier ion/target ion		
			Target	Q1	Q2	Q3	Q/tgt	Q2/tgt	Q3/tgt
Fenvalerate 2	FV-2	58.16	167	225	419		0.44	0.06	
Deltamethrin	FV-2	59.50	181	251			0.51		

[a] Q = qualifier ion; tgt = target ion.
[b] A compound name followed by a number indicates that this particular compound gives more than 1 GC peak. These are numbered according to their order of elution. The numbering is an internal convention. In some cases, up to 4 peaks are observed, but only 2 are monitored (e.g., cyfluthrin, cypermethrin).
[c] degr. = degradation product.
[d] Internal standard.

retention times, the acquisition method used in analysis (labeled as FV-1 or FV-2), the target and qualifier ions, as well as the abundance ratios of qualifier ions to target ion. The target ion is used for quantitation. Quantitation is based on a standard prepared in blank matrix extract, in order to compensate for the matrix effect (2, 7, 8) and to obtain a more accurate quantitation. The concentrations of standard and spike are the same, routinely 0.2 mg/kg (0.5 or 1.0 mg/kg for a few compounds).

The analytical procedure used for carbamate analysis has been reported previously (9). An internal standard is used (isoprocarb), and 2 new compounds have been added (methiocarb sulfone and methiocarb sulfoxide).

Quality Control

Our laboratory is ISO-25 accredited under the Standards Council of Canada Laboratory Accreditation Program for Pesticide Residues, which requires strict quality control procedures and participation in a regular check-samples program for pesticide residues.

Routine analyses are performed in sets consisting of 10 samples, 1 spike, and 1 blank (also used to prepare a standard in matrix). Two spiking solutions include all compounds determined by the 2 GC/MSD methods, and 2 spiking solutions include the 12 *N*-methyl carbamates determined by LC. Each spiking solution is added alternately to consecutive sets of the same commodity, so that recovery data for all compounds can be monitored on an on-going basis. The routine spiking level is 0.2−1.0 mg/kg.

Results and Discussion

The recoveries used to generate the limits of detection (LODs) of the method were obtained by spiking 3 or more different crops at 0.1−1.0 mg/kg, depending on the sensitivity of the compound. Recoveries of 90% of the pesticides were between 70 and 120%; the method is considered a screening procedure for the few compounds giving recoveries of ≤50% (mirex, EPTC, butylate, hexachlorobenzene, folpet, oxycarboxin, and chlorthiamid). Because of their low recoveries, folpet and oxycarboxin were not included in the total number of compounds, although their ions were monitored.

The LOD is defined as 3 times the standard deviation of a minimum of 7 replicate analyses of samples fortified at 2–3 times the estimated LOD. The LODs for most compounds range between 0.02 and 1.0 mg/kg, with 80% of the compounds having LODs of ≤0.04 mg/kg. Recovery data for all compounds, as well as LODs, are shown in Table 2.

The previous procedure (2) included a cleanup on charcoal:Celite minicolumns. Replacing these columns with the Envi-Carb SPE tubes allowed better recoveries for chlorothalonil, dicloran, diphenylamine, hexachlorobenzene, and propanil. However, because the cleanup on Envi-Carb alone was not sufficient, the carbon tube was coupled with an amino propyl cartridge and a C_{18} cleanup was added. The addition of the C_{18} and amino propyl cleanup did not compromise recoveries for most of the compounds. Two exceptions are mirex and folpet. Recoveries for mirex were higher (ca 100%) without the C_{18} cleanup, and folpet gave good recoveries (ca 90%) when the amino propyl cartridge was not used in the cleanup. Acephate gave acceptable recoveries with the amino propyl cartridge from the listed supplier; however, amino propyl tubes from other suppliers were found to give 0% recovery of acephate.

All compounds elute from the carbon/amino propyl cartridges with only 5 mL acetonitrile−toluene (3 + 1), except for the following: acephate (20–25 mL), bromophos-ethyl (10 mL), captan (10 mL), chlorthiophos (10 mL), coumaphos (15 mL), dichlofluanid (10 mL), hexachlorobenzene (20–25 mL), iodofenphos (10 mL), leptophos (15 mL), pyrazophos (15 mL), quintozene (10 mL), simetryn (10 mL), tetrasul (10 mL), and tolylfluanid (15 mL). It is possible to take advantage of these differences to adapt the method to analysis for specific target compounds.

In the process of expanding the scope of this method, other compounds were tested, but they were not added to the method for various reasons. Benzoximate gave 4 peaks; chloroxuron, metoxuron, and oxydemeton-methyl gave 3 peaks of degradation products; fluazinam and fluvalinate showed many degradation peaks as well as poor sensitivity;

Table 2. Recovery data for compounds determined by the multiresidue method

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Acephate[d]	0.5	44	61.9	18.6	30.1	0.31
Alachlor[e]	0.1	8	91.6	7.3	8.0	0.02
Aldicarb[e,f]	0.1	9	94.3	22.1	23.5	0.07
Aldicarb sulfone[e,f]	0.1	9	111.1	10.9	9.8	0.04
Aldicarb sulfoxide[e,f]	0.1	9	94.2	9.0	9.6	0.03
Allethrin[e]	0.1	8	83.1	2.2	2.6	0.02
Allidochlor[g]	0.1	9	66.9	7.9	11.8	0.03
Ametryn[e]	0.1	8	95.4	2.8	2.9	0.02
Aminocarb[g,h]	0.1	9	85.9	11.1	13.0	0.04
Aminocarb degradation[g]	0.1	9	87.4	21.1	24.1	0.07
Aramite 1[g]	0.1	9	90.4	8.6	9.5	0.03
Aramite 2[g]	0.1	9	92.7	8.4	9.1	0.03
Aspon[e]	0.1	8	80.0	4.2	5.3	0.02
Atrazine[e]	0.1	8	97.9	6.5	6.7	0.02
Atrazine, desethyl[e]	0.1	8	95.0	7.7	8.1	0.03
Azinphos-ethyl[e]	0.1	8	81.8	16.8	20.6	0.06
Azinphos-methyl[e]	0.25	8	79.9	10.8	13.5	0.09
Benalaxyl[g]	0.1	9	96.2	7.1	7.4	0.02
Bendiocarb[g,h]	0.1	9	95.6	5.1	5.4	0.02
Bendiocarb degradation[g]	0.1	9	104.1	11.6	11.2	0.04
Benfluralin[e]	0.1	8	75.8	6.0	7.9	0.02
Benodanil[g]	0.1	9	97.7	9.6	9.8	0.03
Benzoylprop-ethyl[e]	0.1	8	90.8	2.5	2.7	0.02
BHC, alpha-[e]	0.1	8	78.5	5.6	7.1	0.02
BHC, beta-[e]	0.1	8	92.8	4.3	4.7	0.02
Bifenox[e]	0.1	8	74.9	10.8	14.4	0.04
Bifenthrin[g]	0.1	9	75.3	9.7	12.8	0.03
Bromacil[e]	0.5	8	78.6	7.5	9.6	0.12
Bromophos[e]	0.1	8	83.4	8.5	10.2	0.03
Bromophos-ethyl[e]	0.1	8	77.1	7.1	9.2	0.02
Bromopropylate[e]	0.1	8	82.9	3.8	4.5	0.02
Bufencarb degradation[g]	0.1	9	99.9	12.8	12.8	0.04
Bupirimate[g]	0.1	9	96.2	6.3	6.5	0.02
Butachlor[g]	0.1	9	94.1	47.6	50.6	0.16
Butralin[e]	0.1	8	80.0	5.3	6.6	0.02
Butylate[e]	0.1	8	47.0	8.5	18.1	0.03
Captafol degradation[e]	0.5	5	68.0	13.6	19.9	0.22
Captan[d]	1.0	45	72.5	24.2	33.4	0.80
Captan degradation[e]	0.5	5	90.4	23.5	26.0	0.39
Carbaryl[e,f]	0.1	9	103.9	9.9	9.6	0.03
Carbetamide[g]	0.1	9	98.2	7.7	7.8	0.03
Carbofuran[e,f]	0.1	9	105.0	11.0	10.5	0.04
Carbophenothion[e]	0.1	8	79.4	9.9	12.4	0.03
Carboxin[e]	0.1	8	77.3	6.9	8.9	0.02

Table 2. (*continued*)

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Chlorbenside[e]	0.125	8	77.8	9.1	11.7	0.04
Chlorbromuron[e]	0.25	8	89.4	5.6	6.3	0.05
Chlorbufam[g]	0.1	9	98.4	6.8	6.9	0.02
cis-Chlordane[e]	0.1	8	79.8	4.8	6.1	0.02
trans-Chlordane[e]	0.1	8	78.5	5.1	6.5	0.02
Chlordimeform[e]	0.1	8	90.4	2.2	2.4	0.02
Chlorfenson[e]	0.1	8	89.9	8.4	9.4	0.03
Chlorfenvinphos (E)[e]	0.1	8	87.9	12.2	13.9	0.04
Chlorfenvinphos (Z)[e]	0.1	8	84.1	11.7	13.9	0.04
Chlorflurecol-methyl[e]	0.1	8	89.4	7.7	8.6	0.03
Chloridazon[g]	0.1	9	96.7	8.3	8.6	0.03
Chlormephos[e]	0.1	8	56.1	11.4	20.3	0.04
Chlorobenzilate[e]	0.1	8	91.4	4.6	5.0	0.02
Chloroneb[g]	0.1	9	73.3	7.0	9.6	0.02
Chloropropylate[g]	0.1	9	93.6	6.1	6.5	0.02
Chlorothalonil[d]	1.0	41	86.7	37.2	42.9	1.22
Chlorpropham[e]	0.1	8	86.0	6.0	7.0	0.02
Chlorpyrifos[e]	0.1	8	84.5	6.1	7.2	0.02
Chlorpyrifos-methyl[e]	0.1	8	84.1	6.3	7.5	0.02
Chlorthal-dimethyl[e]	0.1	8	90.4	5.4	6.0	0.02
Chlorthiamid[g]	0.1	3	37.7	6.8	18.1	0.02
Chlorthiamid degradation[g]	0.1	9	116.7	39.3	33.7	0.13
Chlorthion[g]	0.1	9	94.6	12.2	12.9	0.04
Chlorthiophos[e]	0.1	8	80.3	8.8	11.0	0.03
Chlozolinate[e]	0.1	8	71.8	16.9	23.6	0.06
Clomazone[e]	0.1	8	92.4	2.8	3.1	0.02
Coumaphos[e]	0.25	8	86.5	9.5	10.9	0.08
Crotoxyphos[e]	0.1	8	84.9	10.8	12.8	0.04
Crufomate[e]	0.25	8	81.0	8.2	10.2	0.07
Cyanazine[e]	0.1	8	79.0	26.6	33.6	0.09
Cyanophos[e]	0.1	8	89.9	7.0	7.8	0.02
Cycloate[e]	0.1	8	70.4	4.2	6.0	0.02
Cyfluthrin 1[e]	0.5	8	80.9	11.9	14.8	0.20
Cyfluthrin 4[e]	0.5	8	86.1	7.4	8.6	0.12
Cypermethrin 1[e]	0.5	8	80.4	6.2	7.7	0.10
Cypermethrin 4[e]	0.5	8	83.0	6.3	7.6	0.10
Cyprazine[e]	0.1	8	96.4	2.1	2.2	0.02
o,p′-DDD[g]	0.1	9	90.1	5.3	5.9	0.02
p,p′-DDD[e]	0.1	8	88.6	3.3	3.7	0.02
p,p′-DDE[e]	0.1	8	75.3	5.0	6.7	0.02
o,p′-DDT[e]	0.1	8	72.0	6.9	9.7	0.02
p,p′-DDT[e]	0.1	8	74.8	8.6	11.5	0.03
Deltamethrin[e]	0.5	8	83.4	20.2	24.2	0.33
Demeton-*S*[e]	0.1	8	54.8	12.5	22.8	0.04

Table 2. (*continued*)

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Demeton-*O*[e]	0.1	8	80.1	13.6	17.0	0.04
Demeton-*S*-methyl[e]	0.1	8	84.8	6.2	7.3	0.02
Desmetryn[e]	0.1	8	92.4	7.1	7.7	0.02
Dialifos[e]	0.1	8	87.1	9.9	11.4	0.03
Di-allate 1[e]	0.1	8	71.1	5.9	8.2	0.02
Di-allate 2[e]	0.1	8	73.6	5.6	7.6	0.02
Diazinon[e]	0.1	8	84.0	5.0	6.0	0.02
Dichlobenil[e]	0.1	8	56.4	10.7	19.0	0.04
Dichlofenthion[e]	0.1	8	81.5	4.9	6.0	0.02
Dichlofluanid[d]	0.25	45	84.9	25.3	29.8	0.21
Dichlormid[e]	0.1	8	63.6	10.8	17.0	0.04
Dichlorvos-naled[e]	0.1	8	52.6	9.4	17.9	0.03
Diclofop-methyl[g]	0.1	9	95.6	6.2	6.5	0.02
Dicloran[e]	0.125	8	85.6	10.5	12.3	0.04
Dicofol[e]	0.1	8	80.3	9.1	11.3	0.03
Dicrotophos[e]	0.1	8	84.5	10.7	12.7	0.04
Dieldrin[e]	0.1	8	87.0	5.8	6.6	0.02
Dimethachlor[e]	0.1	8	94.8	2.7	2.8	0.02
Dimethoate[e]	0.1	8	90.5	9.6	10.6	0.03
Dinitramine[e]	0.1	8	92.1	3.8	4.2	0.02
Dioxathion[e]	0.1	8	86.6	6.7	7.7	0.02
Diphenamid[e]	0.1	8	97.5	2.1	2.1	0.02
Diphenylamine[e]	0.1	5	78.4	6.2	7.9	0.02
Disulfoton[e]	0.1	8	65.5	10.7	16.3	0.04
Edifenphos[g]	0.1	9	92.6	12.8	13.8	0.04
Endosulfan sulfate[e]	0.2	8	87.4	11.7	13.4	0.08
Endosulfan, alpha-[e]	0.1	8	85.0	6.9	8.1	0.02
Endosulfan, beta-[e]	0.1	8	92.5	4.0	4.3	0.02
Endrin[e]	0.1	8	82.4	6.0	7.3	0.02
EPN[e]	0.1	8	85.0	9.7	11.4	0.03
EPTC[e]	0.1	8	49.0	9.2	18.7	0.03
Erbon[e]	0.1	8	74.0	9.9	13.4	0.03
Etaconazole 1[g]	0.1	9	90.3	6.6	7.3	0.02
Etaconazole 2[g]	0.1	9	93.1	7.7	8.3	0.03
Ethalfluralin[e]	0.1	8	75.9	6.2	8.2	0.02
Ethion[e]	0.1	8	80.5	10.2	12.7	0.03
Ethofumesate[g]	0.1	9	99.4	4.9	4.9	0.02
Ethoprophos[e]	0.1	8	87.1	2.0	2.2	0.02
Ethylan[e]	0.1	8	85.5	2.7	3.2	0.02
Etridiazole[e]	0.1	8	60.6	5.2	8.5	0.02
Etrimfos[e]	0.1	8	87.4	2.3	2.6	0.02
Fenamiphos[e]	0.1	8	80.4	8.5	10.5	0.03
Fenarimol[e]	0.1	8	92.3	5.9	6.4	0.02
Fenchlorphos[e]	0.1	8	81.9	6.2	7.5	0.02

Table 2. (*continued*)

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Fenitrothion[e]	0.1	8	90.8	9.0	9.9	0.03
Fenpropathrin[g]	0.1	9	87.4	13.2	15.0	0.04
Fenson[e]	0.1	8	95.4	1.6	1.7	0.02
Fensulfothion[e]	0.25	8	89.9	9.3	10.3	0.08
Fenthion[e]	0.1	8	85.3	10.4	12.2	0.03
Fenvalerate 1[e]	0.1	8	82.5	11.4	13.9	0.04
Fenvalerate 2[e]	0.1	8	82.8	9.6	11.6	0.03
Flamprop-isopropyl[g]	0.1	9	96.4	6.1	6.3	0.02
Flamprop-methyl[e]	0.1	8	94.4	2.9	3.1	0.02
Fluchloralin[e]	0.1	8	84.0	10.3	12.2	0.03
Flumetralin[g]	0.1	9	91.3	9.0	9.9	0.03
Fluorodifen[g]	0.1	9	98.2	7.7	7.8	0.03
Flurochloridone 1[g]	0.1	9	97.0	8.9	9.2	0.03
Flurochloridone 2[g]	0.1	9	98.6	6.8	6.9	0.02
Folpet[d]	1.0	37	27.9	12.8	45.6	0.42
Fonofos[e]	0.1	8	77.8	6.1	7.9	0.02
HCH, delta-[e]	0.1	8	96.8	5.6	5.8	0.02
Heptachlor[e]	0.1	8	69.5	4.8	6.8	0.02
Heptachlor epoxide[e]	0.25	8	88.3	2.4	2.7	0.05
Heptenophos[e]	0.1	8	89.4	2.8	3.1	0.02
Hexachlorobenzene[e]	0.1	8	33.5	8.9	26.7	0.03
Hexazinone[e]	0.1	8	87.0	15.8	18.2	0.05
3-Hydroxycarbofuran[e,f]	0.1	9	116.2	13.2	11.4	0.04
Imazalil[g]	0.25	9	87.0	10.0	11.5	0.08
Iodofenphos[e]	0.1	8	81.1	9.5	11.8	0.03
Iprodione[e]	0.1	8	75.5	26.8	35.5	0.09
Isazofos[g]	0.1	9	96.8	6.1	6.3	0.02
Isofenphos[e]	0.1	8	87.8	8.1	9.3	0.03
Isopropalin[g]	0.1	9	82.0	9.0	11.0	0.03
Leptophos[e]	0.1	8	74.4	3.9	5.3	0.02
Lindane[e]	0.1	8	83.5	4.8	5.7	0.02
Linuron[e]	0.5	8	90.5	5.7	6.3	0.10
Malaoxon[d]	0.2	47	98.3	19.6	20.0	0.13
Malathion[e]	0.1	8	89.3	12.9	14.5	0.04
Metalaxyl[e]	0.1	8	94.6	5.7	6.0	0.02
Metazachlor[e]	0.1	8	94.8	3.9	4.1	0.02
Methamidophos[e]	0.5	8	59.8	2.0	3.3	0.1
Methidathion[e]	0.1	8	87.6	12.8	14.7	0.04
Methiocarb[e,f]	0.1	9	82.3	18.0	21.9	0.06
Methiocarb sulfone[f,g]	0.1	8	96.7	17.3	17.9	0.06
Methiocarb sulfoxide[f,g]	0.1	8	96.7	11.3	11.7	0.04
Methomyl[e,f]	0.1	9	108.1	10.7	9.9	0.04
Methoprotryne[e]	0.1	8	88.1	7.1	8.0	0.02
Methoxychlor[e]	0.1	8	85.4	11.9	13.9	0.04

Table 2. (*continued*)

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Methyl trithion[e]	0.1	8	86.4	5.2	6.2	0.02
Metobromuron[e]	0.1	8	89.8	5.9	6.6	0.02
Metolachlor[e]	0.1	8	90.6	7.3	8.1	0.02
Metribuzin[e]	0.1	8	88.3	10.6	12.0	0.03
cis-Mevinphos[e]	0.1	8	79.8	5.8	7.3	0.02
trans-Mevinphos[e]	0.1	8	68.6	21.4	31.2	0.07
Mexacarbate[g,h]	0.1	9	87.2	9.9	11.3	0.03
Mexacarbate degradation[g]	0.1	9	95.8	12.3	12.8	0.04
Mirex[e]	0.1	8	50.5	4.1	8.2	0.02
Monocrotophos[e]	0.1	8	81.4	4.1	5.0	0.02
Monolinuron[e]	0.1	8	89.6	5.0	5.5	0.02
Myclobutanil[e]	0.1	8	92.1	4.9	5.4	0.02
Nitralin[e]	0.1	8	81.9	9.8	11.9	0.03
Nitrapyrin[e]	0.1	8	62.0	5.4	8.7	0.02
Nitrofen[e]	0.1	8	87.0	8.5	9.8	0.03
Nitrothal-isopropyl[e]	0.1	8	82.8	4.9	5.9	0.02
Norflurazon[e]	0.1	8	89.0	10.2	11.5	0.03
Nuarimol[g]	0.1	8	86.6	20.8	24.0	0.07
Omethoate[e]	0.25	8	59.0	30.5	51.6	0.25
Oxadiazon[e]	0.1	8	88.6	2.0	2.3	0.02
Oxadixyl[g]	0.1	9	98.3	5.3	5.4	0.02
Oxamyl[e,f]	0.1	9	112.8	10.0	8.9	0.03
Oxycarboxin[e]	0.1	2	25.0	12.7	50.9	0.04
Oxychlordane[e]	0.25	8	82.0	3.1	3.8	0.05
Oxyfluorfen[e]	0.1	8	85.3	7.2	8.5	0.02
Paraoxon[e]	0.25	8	87.4	3.7	4.3	0.05
Parathion[e]	0.1	8	89.0	9.2	10.4	0.03
Parathion-methyl[e]	0.1	8	88.4	9.5	10.7	0.03
Pebulate[e]	0.1	8	62.5	5.2	8.3	0.02
Penconazole[g]	0.1	9	88.9	7.8	8.8	0.03
Pendimethalin[e]	0.1	8	81.8	4.0	4.8	0.02
cis-Permethrin[e]	0.1	8	74.6	11.2	15.1	0.04
trans-Permethrin[e]	0.1	8	76.4	11.9	15.6	0.04
Phenthoate[e]	0.1	8	89.6	6.5	7.2	0.02
o-Phenylphenol[e]	0.1	8	86.9	3.8	4.4	0.02
Phorate[e]	0.1	8	69.4	7.7	11.1	0.03
Phosalone[e]	0.1	8	83.8	14.5	17.4	0.05
Phosmet[e]	0.1	8	81.6	21.5	26.3	0.07
Phosphamidon[e]	0.1	8	88.5	14.3	16.1	0.05
Pirimicarb[e]	0.1	8	106.8	8.9	8.4	0.03
Pirimiphos-ethyl[e]	0.1	8	86.3	7.5	8.6	0.02
Pirimiphos-methyl[e]	0.1	8	86.9	6.1	7.1	0.02
Prochloraz[g]	0.1	9	79.7	8.4	10.5	0.03
Procymidone[e]	0.1	8	93.8	7.8	8.3	0.03

Table 2. (*continued*)

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Profenofos[e]	0.1	8	81.4	15.5	19.1	0.05
Profluralin[e]	0.1	8	82.8	4.6	5.6	0.02
Promecarb[h] degradation 1[g]	0.1	9	102.4	19.1	18.6	0.06
Promecarb degradation 2[g]	0.1	9	98.4	6.9	7.0	0.02
Prometon[e]	0.1	8	96.8	2.4	2.5	0.02
Prometryn[e]	0.1	8	93.0	6.7	7.2	0.02
Pronamide[e]	0.1	8	92.1	6.9	7.4	0.02
Propachlor[g]	0.1	9	92.7	4.4	4.8	0.02
Propanil[e]	0.1	8	93.6	6.6	7.1	0.02
Propargite[e]	0.1	5	80.6	2.7	3.4	0.02
Propazine[e]	0.1	8	95.3	5.2	5.4	0.02
Propetamphos[e]	0.1	8	80.6	9.4	11.7	0.03
Propham[g]	0.1	9	84.9	5.7	6.7	0.02
Propiconazole 1[e]	0.1	8	81.5	5.0	6.2	0.02
Propiconazole 2[e]	0.1	8	84.1	10.4	12.3	0.03
Propoxur[e]	0.1	9	96.0	11.8	12.3	0.04
Prothiofos[e]	0.25	8	76.1	2.5	3.3	0.05
Pyrazophos[e]	0.1	8	81.6	13.9	17.0	0.05
Quinalphos[e]	0.1	8	89.1	10.2	11.5	0.03
Quintozene[e]	0.1	8	71.0	5.3	7.5	0.02
Schradan[e]	0.1	8	69.1	3.5	5.1	0.02
Secbumeton[g]	0.1	9	97.9	5.9	6.1	0.02
Simazine[e]	0.1	8	95.8	6.1	6.4	0.02
Simetryn[g]	0.1	9	97.2	4.9	5.0	0.02
Sulfallate[g]	0.1	9	74.4	6.0	8.1	0.02
Sulfotep[e]	0.1	8	79.8	8.3	10.4	0.03
Sulprofos[g]	0.1	9	82.8	21.8	26.3	0.07
TCMTB[e]	0.1	8	78.3	9.7	12.3	0.03
Tecnazene[e]	0.1	8	60.8	7.8	12.8	0.03
Terbacil[e]	0.25	8	87.0	4.6	5.3	0.05
Terbufos[e]	0.1	8	72.6	6.1	8.5	0.02
Terbumeton[g]	0.1	9	98.0	4.2	4.3	0.02
Terbutryn[e]	0.1	8	91.6	7.3	8.0	0.02
Terbuthylazine[e]	0.1	8	93.9	6.2	6.6	0.02
Tetrachlorvinphos[e]	0.1	8	82.8	21.7	26.2	0.07
Tetradifon[e]	0.1	8	85.6	10.2	11.9	0.03
Tetramethrin 1[e]	0.1	8	82.8	5.9	7.1	0.02
Tetramethrin 2[e]	0.1	8	80.6	5.9	7.3	0.02
Tetrasul[g]	0.1	9	64.3	4.9	7.6	0.02
Thiobencarb[g]	0.1	9	93.4	5.3	5.7	0.02
Tolylfluanid[d]	0.25	46	81.4	19.1	23.5	0.16
Triadimefon[e]	0.1	8	95.4	8.0	8.4	0.03
Triadimenol[e]	0.1	8	90.8	4.5	5.0	0.02
Tri-allate[e]	0.1	8	72.4	5.6	7.7	0.02

Table 2. (*continued*)

Compound	Spiking level, mg/kg	*n*	Mean recovery, %	SD[a]	CV, %[b]	LOD, mg/kg[c]
Triazophos[e]	0.1	8	87.3	5.6	6.4	0.02
Tribufos[g]	0.1	9	77.4	8.5	11.0	0.03
Trifluralin[e]	0.1	8	76.1	5.5	7.3	0.02
Vernolate[e]	0.1	8	61.8	5.9	9.6	0.02
Vinclozolin[e]	0.1	8	89.8	6.8	7.6	0.02

[a] SD = standard deviation.
[b] CV = coefficient of variation.
[c] LOD = limit of detection.
[d] Recovery data for apple, banana, cabbage, carrot, cucumber, lettuce, orange, pear, and pineapple.
[e] Recovery data for apple, carrot, and lettuce.
[f] LC analysis for *N*-methyl carbamates.
[g] Recovery data for carrot, banana, and pear.
[h] Analysis by GC/MSD, but also detected by LC under conditions for determination of carbamates.

dichlone showed poor sensitivity; ditalimfos was not recovered through the method; and vamidothion (in solution) degraded over time.

With the high number of compounds being monitored, data analysis was automated to let the analyst examine the large volume of data in the most efficient manner. Because recovery data and positive sample results are calculated automatically by the custom report software (using Microsoft Excel), verification of results is simplified for the analyst. Extracted ion chromatograms of each compound monitored during a run are printed in a format set up by the analyst (typically 12 compounds per page) via a macro. Evaluation of the data still requires analyst scrutiny.

Typically, a technician can prepare 42 samples (including blanks and spikes) for analysis each week (37.5 h/week). Analysis of rush samples can be completed within 1 day.

Conclusions

This method shows good sensitivity and recoveries and allows for rapid sample analysis. It requires only small volumes of solvent per sample and does not use any chlorinated solvents. It covers a wide range of pesticides, is applicable to various fruits and vegetables, and is ideally suited for use in a regulatory laboratory.

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