



A Summary of US FDA LIB 4465: Collaboration of the QuEChERS Procedure for the Multiresidue Determination of Pesticides in Raw Agricultural Commodities by LC/MS/MS

UCT Product Numbers:

ECMSSC50CTFS-MP (6000 mg anhydrous magnesium sulfate, 1500 mg sodium chloride)

CUMPS2CT (150 mg anhydrous magnesium sulfate, 50 mg PSA)

ECMS12CPSA415CT (1200 mg anhydrous magnesium sulfate, 400 mg PSA)

March 2013

Method Summary

The analysis of fruits and vegetables for 173 pesticides using a single level calibration standard has been demonstrated to be an effective screening tool and can be completed in less than 20 minutes with overall accuracy of 105% and precision of 3% RSD. Pesticides are selected from a broad range of classes representing *carbamates*, *mectins*, *azoles*, *neonicotinoids*, *benzimidazoles*, *phenylureas*, *strobilurins*, *organophosphorous*, *anilides*, *tetrazines*, *anilides*, *benzoylphenylureas*, and *others*.

Procedure

Sample Preparation

Samples are composited by grinding in a vertical cutter mixed with dry ice

1. Sample Extraction

- a) Weigh 15 g of hydrated sample into the 50 ml centrifuge tube
- a) Add 15 mL acetonitrile (ACN)

Note: Adjust ACN volume of spike samples to account for spike solution volume to maintain ratio of 1g sample/mL of ACN, e.g. for 5 ml spike volume add 10 mL ACN to 15 g sample

- b) Shake for 1 min
- c) Add internal standard
- d) Add spike standard if needed

- e) Add the contents of pouch **ECMSSC50CTFS**
- f) Shake 1 min
- g) Centrifuge @ ~4500 rpm for 5 min

2. PSA Cleanup

- a) Transfer 1.0 mL of extract to **CUMPS2CT** (or alternative, step b)
- b) Transfer all extract to **ECMS12CPSA415CT**
- c) Vortex and centrifuge
- d) Dilute 0.5 mL extract to 5.0 mL with LC-MS aqueous buffer
- e) Filter through 0.2 or 0.45 μm Nylon filter
- f) Sample is ready for analysis

LC-MS/MS---Instrumentation

- AB Sciex 4000 QTrap: scheduled MRM in the positive ionization mode
- Shimadzu High Pressure HPLC System
- LC-20AD Pump
- Sil-20AC Autosampler
- CTO-20AC Column oven

HPLC Columns

- Ultra Aqueous C18, 3 μm , 100 x 2.1 mm with 10 x 2.1 mm guard column (Restek)

HPLC Instrument Parameters

Equilibration time (min)	1.5
Injection volume (μL)	20
Total Flow (mL/min)	0.5
Rinsing volume (μL)	200
Rinsing speed ($\mu\text{L}/\text{sec}$)	35
Sampling speed ($\mu\text{L}/\text{sec}$)	15
Cooler temperature ($^{\circ}\text{C}$)	15
Column oven temp ($^{\circ}\text{C}$)	40

Standards

Pesticide standard mixes may be purchased from AccuStandards and consist of 9 mixes of 20-25 analytes (total of 196 compounds)

The following injection and spiking standards were prepared in acetonitrile from the 3.0 $\mu\text{g}/\text{mL}$ mixture of all standards:

Injection Standard: 200 ng/mL

Internal Standard: 200 ng/mL BDMC

Spike standards: 3000, 1200, 300, and 60 ng/mL

HPLC Mobile Phase Composition

Pump A: Water with 4 mM ammonium formate and 0.1 % formic acid

Pump B: Methanol with 4 mM ammonium formate and 0.1 % formic acid

Time	Parameter
Min	% B
0.0	5
1.0	5
9.0	95
11.3	95
12.0	5
13.4	5
13.5	stop

Mass Spectrometer Parameters

Typical MS Settings

MRM Detection Window (sec)	60
Target Scan Time (sec)	.5
Resolution Q1	unit
Resolution Q2	unit
MR Pause (msec)	5
Collision gas	med
Curtin gas (mL/min)	30
Exit Potential (volts)	10
Ion Source gas 1 (mL/min)	50
Ion Source gas 2 (mL/min)	50
Interface heater	on
Ion Spray (Volts)	5000
Turbo Spray T (°C)	400

MS/MS Transition Parameters

Compound	Transition 1					Transition 2				
	Q1	Q2	DP	CE	EXP	Q1	Q2	DP	CE	EXP
3-Hydroxycarbofuran	238.1	163	66	21	15	238.1	181	66	16	11
Acephate	184.1	143	61	13	5	184.1	49	61	33	6
Acetamiprid	223	126	60	29	10	223	99	60	51	14
Acibenzolar-S-methyl	211	136	46	39	8	211	140	46	31	8
Alanycarb	400.1	238.2	35	14	5	400.1	91.1	35	40	5
Aldicarb+NH4	208.1	116	35	11	10	208.1	89	35	23	16
AldicarbSulfoxide	207.1	132.1	30	10	8	207.1	89.1	30	19	6

Aldoxycarb	223.1	86.1	52	21	5	223.1	148	52	13	9
Aminocarb	209.1	152	71	21	8	209.1	137.1	71	35	10
Amitraz	294.2	163.2	46	21	4	294.2	107.1	46	57	4
AvermectinB1a+NH4	890.9	567.7	75	23	18	890.9	305.4	72	35	22
AvermectinB1b+Na	876.5	291	41	35	4	876.5	145	41	43	4
Azoxystrobin	404.1	372.1	51	19	5	404.1	344.1	51	27	5
BDMC	260	122	52	34	5	260	107	52	54	5
Benalaxyl	326.2	148.1	71	31	8	326.2	294.1	71	17	10
Bendiocarb	224.1	109	61	27	20	224.1	167.1	61	15	12
Benfuracarb	411.2	195.1	50	30	5	411.2	252.1	50	19	5
Bentazon	241	199	76	19	8	241	107	76	39	8
Benzoximate	364	199	51	13	13	364	105	51	35	4
Bifenazate	301.1	170.1	59	30	9	301.1	198.1	59	21	10
Bitertanol	338.2	70	51	31	12	338.2	269.2	48	13	14
Boscalid	343	307	90	27	7	343	140	90	27	6
BromuconazoleA	378	159	61	39	12	378	70	61	43	12
BromuconazoleB	378.1	159.1	61	39	12	378.1	70.1	61	43	12
Bupirimate	317	166.1	86	33	12	317	108	86	37	10
Buprofezin	306.2	201.1	46	17	5	306.2	116.2	46	21	5
Butafenacil+NH4	492.1	331	58	33	16	492.1	349	61	21	12
Butocarboxim+Na	213.1	75	50	21	6	213.1	116	50	13	6
Butoxycarboxim	223.1	106	45	15	8	223.1	166	45	11	5
Carbaryl	202.1	145	57	15	9	202.1	127	54	41	8
Carbendazim	192.2	160.2	80	24	10	192.2	132.1	80	41	7
Carbetamide	237.1	192	55	13	10	237.1	118.1	56	19	10
Carbofuran	222.1	123	66	31	19	222.1	165.1	66	19	11
Chlorantraniliprole	484	452.9	66	23	14	484	285.9	66	19	16
Chlorfluazuron	540	158	91	27	4	540	383	91	28	4
Chlorotoluron	213.1	72.2	61	31	5	213.1	46.2	61	27	5
Chloroxuron	291.1	72.4	65	34	5	291.1	218.1	65	30	5
Clethodim	360.1	164	61	28	9	360.1	268.1	61	17	8
Clofentezine	303	138	65	22	8	303	102	65	51	14
Clothianidin	250	169	51	17	4	250	132	51	21	10
Cyazofamid	325	108	60	20	9	325	261.1	60	15	13
Cycluron	199.1	89.1	50	21	5	199.1	72.2	50	21	4
Cyflufenamid	413.1	295.1	56	23	8	413.1	223.1	56	33	14
Cymoxanil	199	128	60	13	5	199	111	60	25	5
CyproconazoleA	292	70	63	37	10	292	125	63	43	8
CyproconazoleB	292.1	70.1	63	37	10	292.1	125.1	63	43	8
Cyprodinil	226	93	95	49	13	226	77	95	64	12
Cyromazine	167.1	85.1	62	27	15	167.1	125.1	62	27	8
Desmedipham+NH4	318.1	182	42	19	10	318.1	136	39	34	9
Diclobutrazol	328.1	70	81	49	12	328.1	158.9	81	49	10
Dicrotophos	238.1	112.1	66	19	8	238.1	193	66	15	13
Diethofencarb	268.1	226.1	60	15	12	268.1	124	61	45	8
Difenoconazole	406.1	251.1	80	37	13	408.2	253.1	76	33	5
Diflubenzuron	311	158.2	71	23	10	311	141.1	71	45	10
Dimethoate	230	199	49	16	12	230	125	50	27	8
DimethomorphA	388.1	301	66	25	5	388.1	165.1	66	45	5
DimethomorphB	388.2	301.1	66	25	5	388.2	165.2	66	45	5

Dimoxystrobin	327.1	205	40	15	5	327.1	116	40	35	5
Dinotefuran	203.1	129.2	51	19	8	203.1	157.2	51	13	14
Dioxacarb	224.1	167	51	13	10	224.1	123	51	23	21
Diuron	233.1	72	56	33	5	235.1	72.1	56	38	10
Doramectin+NH4	916.9	593.6	68	20	16	916.9	331.5	65	33	22
Emamectin	886.5	158.1	111	51	10	886.5	82.1	111	127	13
Eprinomectin	914.5	186.2	77	27	12	914.5	154.2	77	58	10
Ethaboxam	321	183.1	86	33	12	321	200.1	86	39	12
Ethiofencarb	226.1	106.9	41	21	5	226.1	164.1	41	11	5
Ethiprole	397.3	350.9	81	29	24	397.3	255.2	81	49	16
Ethirimol	210.2	140.1	81	31	8	210.2	98.1	81	39	18
Etoxazole	360.1	141	76	45	5	360.1	57.2	76	45	5
Famoxadone+NH4	392	331	32	15	6	392	238	37	23	6
Fenamidone	312.1	92	66	39	16	312.1	236.1	66	21	14
Fenazaquin	307.1	161.1	68	27	10	307.1	147	68	28	9
Fenbuconazole	337	124.9	81	41	8	337	70	81	39	12
Fenhexamid	302	97	75	34	14	302	55	75	67	9
Fenobucarb	208.1	95.1	61	21	18	208.1	152.1	61	13	10
Fenoxycarb	302.1	88	65	30	6	302.1	116.1	65	17	7
Fenpyroximate	422	366.1	56	23	5	422	135.1	56	43	5
Fenuron	165.1	72.1	56	25	5	165.1	46	56	29	5
Flonicamid	230.1	203.1	55	35	4	230.1	174	55	35	4
Flubendiamide	683	408	56	17	12	683	274	56	43	16
Fludioxinil+NH4	266	229	41	23	14	266	227.1	41	13	14
Flufenoxuron	489	158	86	29	10	489	141.1	86	63	8
Fluometuron	233.1	72.1	71	37	12	233.1	46	71	35	4
Fluoxastrobin	459.2	427.2	55	28	5	459.2	188	55	35	5
Flusilazole	316.1	247.1	78	27	14	316.1	165.1	78	38	9
Flutolanil	324.1	262.1	74	26	14	324.1	242.1	74	34	12
Flutolanil+NH4	341.1	242.1	61	35	4	341.1	262.1	61	35	4
Flutriafol	302.1	70.1	66	37	12	302.1	123	66	41	8
Forchlorfenuron	248	129.1	52	25	5	248	93.1	52	48	5
Formetanate	222.1	165	71	22	9	222.1	93	76	53	14
Fuberidazole	185	157	81	33	13	185	65	81	67	11
Furathiocarb	383.1	195.1	74	26	10	383.1	252.1	74	19	14
Halofenozide	331.1	275	41	11	16	331.1	105.1	41	25	8
Hexaflumuron	461.1	158.2	56	25	5	461.1	141.1	56	65	5
Hexythiazox	353.1	228	63	23	12	353.1	168	63	36	9
Hydramethylnon	495.2	323.2	146	45	18	495.2	151.1	146	95	8
Imazalil	297	159	65	34	12	297	201	65	29	10
Imidacloprid	256	209.1	61	23	10	256	175.1	61	28	10
Indoxacarb	528	203	89	54	10	528	218	86	33	14
Ipconazole	334.2	70	74	52	10	334.2	125	74	50	17
Iprovalicarb	321.2	119	66	29	8	321.2	203.1	66	13	13
Isoprocarb	194.1	95	60	23	13	194.1	137	60	13	10
Isoproturon	207.2	72.1	66	29	5	207.2	46.1	66	31	5
Isoxaflutole	360.1	251.1	62	24	9	360.1	220.1	62	50	9
Isoxaflutole+NH4	377	251.1	56	29	14	377	69	56	35	12
Ivermectin+NH4	892.8	569.7	70	21	20	892.8	713.8	71	15	24
Kresoxim-methyl	314	116	51	21	4	314	206	51	13	4

Linuron	249.1	160	60	23	5	249.1	182.1	60	21	5
Lufenuron	511.1	158.1	61	27	5	511.1	141.2	61	67	5
Malathion	331	127	71	19	8	331	285	71	11	16
Mandipropamide	412.1	328.1	81	21	10	412.1	356.1	81	17	10
Mepanipyrim	224	106	86	37	8	224	77	86	59	14
Metaflumizone	507.1	178.1	101	39	12	507.1	287.1	101	37	16
Metalaxyl	280.1	220.2	60	20	12	280.1	192.2	60	26	10
Metconazole	320.1	70	81	51	12	320.1	125	81	59	10
Methamidophos	142	94	54	20	5	142	125	54	19	7
Methiocarb	226.1	169.1	61	13	11	226.1	121.1	61	27	8
Methomyl	163.1	88.1	35	12	6	163.1	106	35	13	6
Methoxyfenozide	369.1	149.1	56	24	9	369.1	313.2	56	13	10
Metobromuron	259	170.2	56	23	4	259	148.2	56	21	4
Mevinphos-E	225.1	127.1	51	20	7	225.1	193.2	51	10	10
Mevinphos-Z	225	127	51	20	7	225	193.1	51	10	10
Mexacarbate	223.2	166.1	64	23	10	223.2	151	64	35	9
Monocrotophos	224.1	127.1	53	23	10	224.1	98	53	17	5
Monolinuron	215.1	126.1	51	23	5	215.1	99	51	41	5
Moxidectin	640.5	528.5	61	12	16	640.5	498.5	61	17	16
Myclobutanil	289	70	71	37	12	289	125	71	47	8
Novaluron	493	158.1	71	27	5	493	141.1	71	69	5
Nuarimol	315	252.1	75	31	13	315	81	75	44	12
Omethoate	214	124.9	46	29	5	214	182.8	46	17	5
Oxadixyl	279.1	219.1	61	17	13	279.1	132.1	61	43	21
Oxamyl+NH₄	237.1	72.1	36	25	5	237.1	90.1	36	12	6
Paclobutrazol	294	70	62	46	10	294	125	58	49	8
Pencycuron	329.1	125	76	37	22	329.1	218.1	76	25	14
Phenmedipham	301.1	136	50	26	5	301.1	168.1	50	14	4
Phorate Sulfone	293.1	97.1	36	41	5	293.1	171.1	36	17	5
Picoxystrobin	368	145	56	27	4	368	205	56	15	4
PiperonylButox+NH₄	356.2	177.2	49	22	9	356.2	119.1	49	46	8
Pirimicarb	239.2	72.1	64	35	10	239.2	182.1	64	23	10
Prochloraz	376	308	45	17	10	376	70	45	44	12
Promecarb	208.1	109	37	23	8	208.1	151	37	13	10
Propamocarb	189.2	102	60	25	8	189.2	144	61	19	13
Propargite+NH₄	368.2	231.1	46	15	13	368.2	175.1	46	23	12
Propiconazole	342.1	159	62	40	9	342.1	69	62	36	10
Propoxur	210.1	111	39	19	6	210.1	168.1	39	11	10
Pymetrozine	218	105	71	27	5	218	78	71	47	5
Pyracarbolid	218.1	125	59	27	8	218.1	97	59	40	14
Pyraclostrobin	388	194	31	19	5	388	163	31	29	5
Pyridaben	365	147	46	31	5	365	309	46	19	5
Pyrimethanil	200	107	71	33	5	200	82	71	35	5
Pyriproxyfen	322	96	45	21	5	322	185	45	29	5
Rotenone	395.1	213.1	90	32	12	395.1	192.1	90	34	10
Siduron	233.3	137.2	66	21	5	233.3	94	66	31	5

Spinetoram A	748.5	142.2	86	45	8	748.5	98.1	86	109	18
Spinetoram B	760.5	142.2	96	41	10	760.5	98.1	96	101	18
SpinosynA	732.5	142.2	111	43	10	732.5	98.1	111	103	16
Spirodiclofen	411.3	313.3	72	23	8	411.3	71.3	71	33	10
Spiromesifen	371.2	273.2	73	16	6	371.2	255.2	74	33	4
Spiromesifen+NH₄	388.2	273.2	41	19	12	388.2	255.2	41	39	16
Spirotetramat	374.2	330.2	66	23	8	374.2	302.2	66	25	20
Spiroxamine	298.2	144.2	72	28	10	298.2	100.1	72	46	14
Sulfentrazone	387	307.1	81	27	5	387	146	81	57	5
Tebuconazole	308.2	70	81	49	11	308.2	125	81	51	8
Tebufenozide	353.2	133	54	24	9	353.2	297.2	54	14	9
Tebuthiuron	229.1	172.4	46	21	5	229.1	116.1	46	35	5
Teflubenzuron	381.1	141.2	66	52	5	381.1	158.2	66	23	5
Temephos	467	419.1	101	29	12	467	405	101	23	12
Thiabendazole	202.1	175.1	84	35	10	202.1	131.2	84	45	8
Thiacloprid	253	126	68	30	9	253	99	68	60	14
Thiamethoxam	292	211	64	18	10	292	181	64	32	10
Thidiazuron	221.1	102.1	57	28	6	221.1	128.2	57	22	7
Thiophanate-methyl	343	151.1	61	29	14	343	311	61	17	10
Triadimefon	294	197.1	63	22	12	294	225	63	19	8
Triadimenol	296.1	70	46	31	12	296.1	227.1	46	19	14
Trichlorfon	256.9	109.1	66	25	20	256.9	127	66	25	8
Tricyclazole	190	163	81	33	10	190	136	81	41	11
Trifloxystrobin	409	186	31	23	5	409	206	31	21	5
Triflumizole	346.1	278.1	51	15	8	346.1	73	51	27	6
Triflumuron	359.1	156.2	52	23	6	359.1	139	52	44	6
Triticonazole	318.1	70	63	42	10	318.1	125	63	41	8
Vamidotion	288	146	61	19	10	288	118	61	33	10
Zoxamide	336.1	187	55	33	11	336.1	159	53	39	12

Adapted from: Sack, Chris*, Smoker, Michael, KAN, Lenexa, Chamkasem, Narong, SRL, Thompson, Richard, Satterfield, Greg, ARL, MacMahon, Shaun, Masse, Claude NERL, Mercer, Greg, Neuhaus, Barbara, PRL-NW, Cassias, Irene, Chang, Eugene, Lin, Yi, PRL-SW, Wong, Jon, Zhang, Kai, CFSAN, *Development and Validation of a Multiresidue Determination for Pesticides by LC-MS/MS* DFS/ORAFDA No. 4464 Pesticides and *Collaboration of the QuEChERS Procedure for the Multiresidue Determination of Pesticides by LC-MS/MS In Raw Agricultural Commodities*, DFS/ORAFDA, No. 4465 Pesticides

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