A New Multiresidue Method for Pesticides in Fruit and Vegetables Using LC-MS/MS detection. Part 2.

CHRISTER JANSSON, TUIJA PIHLSTRÖM, BRITA KAJRUP, EVA FLYGH, ANNA LIEDGREN
National Food Administration, Box 622, SE-751 26 Uppsala SWEDEN
E-mail: christer.jansson@slv.se

Results

Table 1. *Monitored ions together with recovery data. Dinocap is analysed using ES-, the other pesticides by using ES+. For each pesticide there is only one ion monitored for the recovery study, but it is possible to detect more ions for each pesticide for confirmation purpose. All recoveries are corrected for matrix effect.*

				0.01 mg/kg			0.05 mg/kg			0.01 mg/kg With NaOH			0.05 mg/kg With NaOH			Matrix effect			Matrix effect With NaOH		
Peak no.	Pesticide	Rt. min	MS/MS, m/z	Mean	RSD	n	Mean	RSD	n	Mean	RSD	n	Mean	RSD	n	Mean	RSD	n	Mean	RSD	n
18	Acetamiprid	10,9	223>126	90%	22%	21	88%	16%	21							102%	10%	16			
23	Aldicarb	12,7	208>116	94%	15%	44	93%	12%	44							107%	25%	44			
5	Aldicarb sulphone	5,9	223>148	94%	18%	44	93%	13%	44							111%	18%	44			
3	Aldicarb sulphoxide	4,6	207>89	83%	25%	33	86%	19%	25	70%	19%	22	73%	15%	22	105%	13%	45	99%	20%	24
30	Bendiocarb	14,2	224>167	93%	12%	44	91%	10%	44							101%	27%	44			
21	Butocarboxim	12,5	213>75	92%	18%	44	95%	13%	44							96%	44%	44			
1	Butocarboxim sulphoxide	4,0	207>75	81%	18%	23	80%	20%	25	79%	15%	22	82%	9%	22	107%	20%	45	101%	19%	24
4	Butoxycarboxim	5,6	223>106	92%	16%	44	93%	12%	44							108%	15%	44			
32	Carbaryl	14,8	202>145	94%	11%	45	94%	11%	44	86%	16%	22	87%	14%	22	99%	22%	45	105%	24%	24
19	Carbendazim	10,9	192>160	87%	18%	27	90%	18%	29	98%	20%	21	95%	13%	21	91%	24%	44	96%	37%	23
29	Carbofuran	14,1	222>165	95%	11%	44	93%	10%	44							100%	27%	44			
17	Carbofuran-3-OH	10,5	238>220	94%	19%	43	92%	13%	44							116%	27%	44			
57	Carbosulfan	24,2	381>118	43%	89%	36	50%	73%	25							87%	29%	36			
51	Clofentezine	19,8	303>138	79%	32%	42	81%	29%	43							88%	24%	44			
44	Demeton	16,8	259>89	85%	23%	36	76%	31%	35							101%	30%	35			
31	Demeton-S-methyl	14,4	231>89	90%	23%	36	90%	27%	35							107%	22%	35			
10	Demeton-S-methyl sulphone	7,6	263>169	99%	33%	36	102%	16%	35							111%	12%	36			
8	Demeton-S-methyl sulphoxide	6,9	247>169	76%	40%	36	71%	35%	25							104%	9%	36			
55	Dinocap	21,3	295>134	83%	34%	40	79%	27%	40							96%	23%	42			
52	Disulfoton	20,0	275>89	81%	23%	36	79%	31%	25							90%	16%	36			
38	Disulfoton sulphone	15,6	307>171	96%	27%	36	89%	19%	25							108%	22%	36			
35	Disulfoton sulphoxide	15,4	291>213	89%	21%	36	90%	12%	35							102%	20%	35			
34	Ethiofencarb	15,2	226>107	111%	19%	42	108%	17%	42							98%	24%	43			
12	Ethiofencarb sulphone	9,2	258>107	94%	12%	44	93%	11%	44							116%	28%	44			
13	Ethiofencarb sulphoxide	9,4	242>107	88%	22%	45	90%	21%	44							110%	21%	45			
49	Fenoxycarb	18,8	302>116	85%	21%	43	85%	20%	43							86%	21%	44			
53	Furathiocarb	20,6	383>195	83%	25%	36	82%	19%	35							96%	13%	35			
56	Hexythiazox	21,4	353>228	80%	27%	42	86%	26%	42							99%	19%	44			
45	Imazalil	17,1	297>159	68%	18%	22	70%	18%	22	88%	15%	20	89%	14%	21	94%	28%	41	98%	16%	22
14	Imidacloprid	9,8	256>209	90%	14%	39	91%	14%	37	99%	12%	22	99%	13%	22	123%	23%	44	120%	19%	24
40	Isoprocarb	15,8	194>95	91%	10%	44	91%	10%	44							103%	31%	44			
46	Linuron	17,4	249>160	80%	21%	43	83%	15%	43							94%	28%	44			
47	Methiocarb	17,4	226>169	84%	18%	43	86%	14%	43							91%	31%	44			
20	Methiocarb sulphone	11,2	258>122	100%	16%	44	98%	16%	44							149%	33%	42			
15	Methiocarb sulphoxide	10,0	242>122	118%	29%	43	110%	37%	42							139%	40%	43			
9	Methomyl	7,3	163>106	92%	12%	44	93%	11%	44							111%	19%	44			
6	Oxamyl	6,0	237>72	88%	18%	45	86%	31%	44	71%	39%	22	79%	28%	22	106%	8%	45	102%	20%	24
2	Oxamyl-oxime	4,3	163>72	95%	13%	42	93%	12%	43							123%	25%	44			
50	Phorate	19,8	261>75	79%	25%	36	74%	21%	25							108%	25%	36			
39	Phorate sulphone	15,7	293>247	90%	25%	22	74%	16%	4							97%	12%	4			
36	Phorate sulphoxide	15,4	277>199	93%	15%	36	93%	12%	35							102%	21%	35			
43	Phorate-O-analogue	16,4	245>75	91%	19%	26	n.a.	n.a.								n.a.	n.a.				
48	Promecarb	17,6	208>151	85%	14%	43	86%	13%	43							92%	31%	44			
27	Propoxur	14,0	210>111	96%	13%	45	96%	11%	44	90%	13%	22	93%	12%	22	103%	21%	45	104%	21%	24
54	Terbufos	20,9	289>103	81%	24%	36	78%	22%	35							92%	17%	35			
25	Terbufos-O-sulphone	13,1	305>203	93%	27%	26	n.a.	n.a.								n.a.	n.a.				
22	Thiabendazole	12,6	202>175	80%	21%	21	85%	19%	21	94%	10%	21	93%	11%	22	96%	30%	43	97%	32%	23
33	Thiodicarb	15,1	355>88	78%	32%	45	79%	31%	44							108%	23%	45			
37	Thiometon	15,6	247>89	94%	24%	36	87%	25%	25							99%	19%	36			
24	Thiometon sulphoxide	12,7	263>185	92%	26%	36	92%	14%	35							102%	18%	35			
26	Thiometon sulphone	13,1	279>143	99%	17%	36	94%	13%	25							113%	21%	36			
28	Thiophanate methyl	14,0	343>151	44%	82%	43	54%	56%	44							113%	86%	38			
41	Trimethacarb-2,3,5	16,2	194>122	89%	14%	44	89%	12%	44							100%	32%	44			
42	Trimethacarb-3,4,5	16,2	194>137	92%	11%	45	93%	11%	44	94%	12%	22	94%	13%	22	96%	18%	45	98%	13%	24
16	Vamidothion	10,4	288>146	89%	22%	35	87%	20%	25							103%	12%	36			
11	Vamidothion sulphone	7,7	320>178	101%	29%	33	87%	23%	25							119%	20%	36			
7	Vamidothion sulphoxide	6,6	304>201	55%	50%	36	59%	40%	35							104%	9%	36			

Included matrices: *Four recoveries from each commodity group are included in the test. The representative crops in each group were chosen according to the consumption pattern in Sweden, totally 31 different matrices. One determination of recovery from each matrix. Peak numbers refer to the chromatograms. Recoveries are calculated as the sum of parent compound and metabolite.*
n.a. Not analyzed.

Conclusions

The present multiresidue method is simple and gives quantitative results for most pesticides and pesticide metabolites tested at low level. In general the overall recoveries lie higher than 70% even at 0.01 mg/kg level. The higher RSD values for some pesticides can in many cases be explained by poor recoveries in more acidic fruits. However, acceptable recoveries, >70% were obtained, when sodium hydroxide was added before extraction. Compared to the previous methods, the analysis time has been shortened and the time consuming clean up step has been shown to be unnecessary. LC-MS is a sensitive technique and provides confirmation of identity, which is an important feature when low MRLs are introduced for certain commodities.

The use of the established ethyl acetate extraction makes it applicable and efficient for monitoring purposes and a number of different extraction systems can be replaced by using the proposed multiresidue method.

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