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Application News

SGLC-GC/MS-004-EN

Triple Quadrupole Mass Spectrometer Shimadzu GCMS-TQ8050

Analysis of 208 Residual Pesticides and Metabolites in Plant-Derived Food Using SHIMSEN QuEChERS and SH-1701 GC Column

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User Benefits

- Established an effective, fast, simple sample preparation method of plant-derived food.
- Realized simultaneous quantitative analysis of multi pesticides and metabolites, such as organophosphates, organochlorines, pyrethroids, triazoles, amides, triazines and carbamate esters.
- SHIMSEN QuEChERS provides centrifuge tubes containing prefilled amounts of salts and SPE sorbents, used in formalized EN and AOAC method, to improve laboratory efficiency and throughput.

■ Introduction

Fruits and vegetables are people daily food. In order to ensure yield and quality, pesticides are usually used in the planting process of fruits and vegetables. Therefore, pesticide residues in fruits and vegetables have always been a food safety issue of concern to people, and detection criteria for pesticide residues has been established to protect food safety

In QuEChERS method, the use of loose extraction salts and cleanup SPE sorbents in combination with shaking and centrifugation steps result in a Quick, Easy, Cheap, Effective, Rugged and Safe sample preparation technique[1]. QuEChERS has been used in analysis of multi pesticides, PAH, PCB, PBDE and flame retardants, etc., and been formalized in worldwide.

In this method, we realized a simultaneous quantitative analysis of multi pesticides in plant-derived food, that is pear, leek, tea and rice, using Shimadzu GCMS-TQ8050. The samples were pretreated by SHIMSEN QuEChERS extraction salts and dispersive SPE sorbents and separated by SH-1701 GC column.

Fig. 1 SHIMSEN QuEChERS Extraction Salt and Dispersive Tube

■ Instrument and Materials

Instrument: Shimadzu GCMS-TQ8050;

GC Column: SH-1701 Cap. Column, 0.25 µm, 30 m × 0.25 mm (P/N: R221-75777-30);

SHIMSEN QuEChERS Extract Salt Ⅰ (P/N: 380-00148);

SHIMSEN QuEChERS Extract Salt Ⅰ (P/N: 380-00151);

SHIMSEN QuEChERS Dispersive Tube Ⅰ (P/N: 380-00123);

SHIMSEN QuEChERS Dispersive Tube Ⅱ (P/N: 380-00124);

SHIMSEN QuEChERS Dispersive Tube Ⅲ (P/N: 380-00129);

SHIMSEN QuEChERS Dispersive Tube Ⅳ (P/N: 380-00145);

Filter and Vial: SHIMSEN Arc Disc HPTFE needle filter (P/N: 380-00341-05); LabTotal Vial (P/N: 227-34001-01);

Pipet: SHIMSEN Pipet PMII-10 (P/N: 380-00751-02); SHIMSEN Pipet PMII-100 (P/N: 380-00751-04); SHIMSEN Pipet PMII-1000 (P/N: 380-00751-06).

Fig. 2 SHIMSEN Arc Disc Filter, SHIMSEN Pipet and LabTotal Vial

■ Analytical Conditions

The GC and MS conditions are shown in Table 1.

Table 1 Analytical Conditions

GC		
Column	:	SH-1701 Cap. Column, df = 0.25 µm, 30 m × 0.25 mm (P/N: R221-75777-30)
Flow rate	:	1.0 mL/min
Injection volume	:	1 mL, Splitless
Injector temperature	:	280 ℃
Carrie Gas	:	He
Column oven temperature	:	40 ℃ (hold 1.0 min) to 120 ℃ at 40 ℃/min, 120 ℃ to 240 ℃ at 50 ℃/min, 240 ℃ to 300 ℃ at 12 ℃/min (hold 10 min)
MS		
Electron ionization mode	:	EI
Scan mode	:	MRM
Ion source temperature	:	230 ℃
Interface temperature	:	280 ℃
Solvent delay	:	3 min
Scan mode	:	MRM

■ Compound List for Pesticides

Table 2, split into 6 parts, shows the compound list of pesticides used in rice and pear sample matrix. Except for the compounds list in Table 3, the MRM information we used in the analysis of leek and tea is the same as rice and pear.

Table 2 List of Pesticides Used in Rice and Pear Sample Matrix (part 1)

No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
Group A (109 pesticides)					
1	Dichlorvos	109.00>79.00	8	185.00>93.00	14
2	Methamidoph-os	141.00>95.00	8	141.00>79.00	22
3	Dichlorobenzo-nitrile	170.90>136.00	14	170.90>100.00	24
4	Mevinphos	127.00>109.00	12	192.00>127.00	12
5	Methacrifos	208.00>180.00	8	240.00>208.00	4
6	Molinate	187.10>126.10	6	126.10>55.00	14
7	Acephate	136.00>94.00	14	94.00>64.00	6
8	Isoprocarb	136.00>121.00	10	121.00>77.00	22
9	Cycloate	154.00>83.00	10	83.00>55.00	10
10	Hexachlorobe-nzene	283.80>248.80	24	283.80>213.80	28
11	Ethoprophos	200.00>158.00	6	158.00>97.00	18
12	Ethalfluralin	276.00>202.00	18	316.10>276.00	10
13	Propoxur	152.10>110.10	8	110.10>64.00	18
14	Sulfotep	322.00>202.00	10	322.00>174.00	18
15	alpha-BHC	180.90>144.90	16	218.90>182.90	8
16	Atrazine-desethyl	187.00>172.10	6	172.00>69.10	18

Table 2 List of Pesticides Used in Rice and Pear Sample Matrix (part 2)

No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
17	Terbufos	231.00>128.90	26	231.00>174.90	14
18	Dioxathion	152.90>96.90	10	185.00>129.00	12
19	Profluralin	318.10>199.10	16	318.10>55.00	22
20	Triallate	268.10>184.00	20	270.10>186.00	20
21	Fonofos	137.10>109.10	8	246.00>137.10	6
22	Pirimiphos-ethyl	261.10>137.10	18	318.10>152.10	14
23	Propazine	229.10>58.00	14	229.10>187.10	6
24	Dicloran	206.00>176.00	10	176.00>148.00	12
25	Propetamphos	236.10>194.00	6	194.00>166.00	8
26	Iprobenfos	204.00>91.00	8	204.00>122.00	12
27	Monocrotophos	127.10>109.00	12	127.10>95.00	16
28	Dichlofenthion	279.00>222.90	14	222.90>204.90	14
29	Pirimicarb	238.10>166.10	12	166.10>55.00	20
30	Dimethoate	125.00>47.00	14	125.00>79.00	8
31	Acetochlor	174.10>146.10	12	223.10>132.10	22
32	Alachlor	188.10>160.10	10	188.10>132.10	18
33	Paraoxon-methyl	230.00>136.10	8	230.00>106.10	22
34	Pirimiphos-methyl	290.10>125.00	22	290.10>233.10	12
35	Vinclozolin	212.00>172.00	16	285.00>212.00	12
36	Metribuzin	198.10>82.00	14	198.10>110.10	10
37	Metalaxyl	249.20>190.10	8	206.10>132.10	20
38	Thiobencarb	257.10>100.00	8	125.00>89.00	18
39	Formothion	170.00>93.00	8	224.00>125.00	18
40	Metolachlor	162.10>133.10	16	238.10>162.10	12
41	Dicofol	139.00>111.00	16	139.00>75.00	28
42	Fenthion	278.00>109.00	20	278.00>169.00	14
43	Paraoxon	109.00>91.00	6	148.90>119.00	5
44	Bromophos	330.90>315.90	14	328.90>313.90	18
45	Triadimefon	208.10>181.00	10	208.10>111.00	22
46	Allethrin	123.00>81.10	8	136.00>93.10	12
47	Parathion	291.10>109.00	14	139.00>109.00	8
48	Isofenphos-methyl	199.00>121.00	14	241.10>121.10	22
49	Isofenphos	213.00>121.00	15	213.00>185.00	6
50	Quinalphos	146.10>118.00	10	146.10>91.00	24
51	alpha-Endosulfan	194.90>160.00	8	194.90>125.00	24
52	Penconazole	248.10>157.10	26	159.10>123.10	22
53	Phorate Sulfoxide	153.00>97.00	12	199.00>171.10	6
54	Fosthiazate	195.00>103.00	10	195.00>60.00	22
55	p,p'-DDE	246.00>176.00	30	317.90>248.00	24
56	Fenothiocarb	160.10>72.00	10	160.10>106.10	12
57	Bromacil	204.90>187.90	14	206.90>189.90	16
58	Terbufos sulfone	153.00>97.00	21	199.00>97.00	21
59	Phorate sulfone	153.00>97.00	12	153.00>125.00	6
60	Mepanipyrim	222.10>221.10	6	223.10>222.10	10
61	DEF	202.00>147.00	6	202.00>113.00	20
62	Triadimenol	168.10>70.00	10	128.10>65.00	22
63	Bromfenvinfos	266.90>159.00	14	268.90>161.00	16
64	Pretilachlor	262.10>202.10	10	238.10>162.10	10
65	Oxadiazon	258.00>175.00	8	302.00>175.00	14
66	o,p'-DDD	235.00>165.00	24	237.00>165.00	28
67	Kresoxim-methyl	206.10>131.10	14	206.10>116.10	6
68	Ditalimfos	271.00>243.00	6	299.00>243.00	8

Table 2 List of Pesticides Used in Rice and Pear Sample Matrix (part 3)

No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
69	Endrin	262.90>191.00	30	244.90>173.00	32
70	o,p'-DDT	235.00>165.00	24	237.00>165.00	28
71	Imazalil	215.00>173.00	6	215.00>159.00	6
72	Mephosfolan	196.00>140.00	12	196.00>168.00	6
73	Cyflufenamid	412.10>295.10	8	294.10>237.10	6
74	Bupirimate	273.10>108.10	16	273.10>193.10	8
75	Chlorthiophos	324.90>268.90	14	268.90>205.00	18
76	Oxyfluorfen	252.00>196.00	22	361.00>300.00	14
77	Flutolanil	173.00>145.00	14	173.00>95.00	26
78	p,p'-DDD	235.00>165.00	24	237.00>165.00	28
79	beta-Endosulfan	194.90>160.00	8	194.90>125.00	24
80	Quinoxyfen	237.10>208.10	28	307.10>237.10	22
81	Trifloxystrobin	222.10>190.10	4	222.10>130.10	12
82	Aclonifen	212.00>182.10	15	264.00>194.10	18
83	Carbophenothion	157.00>45.00	18	341.90>157.00	14
84	Isoxathion	177.10>130.10	10	177.10>116.10	12
85	Piperonyl-butoxide	176.10>131.10	12	176.10>117.10	20
86	Edifenphos	173.00>109.00	10	310.00>173.00	14
87	Fensulfothion	293.00>125.00	14	293.00>153.00	8
88	Triazophos	161.00>134.00	8	161.00>106.00	14
89	Bifenthrin	181.10>166.10	12	181.10>179.10	12
90	Tebufenpyrad	333.10>171.10	20	333.10>276.10	8
91	Bromopropylate	340.90>182.90	18	340.90>184.90	20
92	Tetramethrin	164.10>107.10	14	164.10>77.00	22
93	Epoxiconazole	192.00>138.00	14	192.00>111.00	26
94	Tebuconazole	250.10>125.10	22	125.10>89.00	18
95	Pyriproxyfen	136.10>78.00	20	136.10>96.00	14
96	Piperophos	320.10>122.10	14	140.10>98.00	12
97	EPN	156.90>77.00	24	169.00>77.10	25
98	Hexazinone	171.10>71.00	16	171.10>85.00	16
99	Fenamidone	238.10>103.10	22	268.10>180.10	16
100	Tetradifon	226.90>199.00	16	355.90>159.00	18
101	Anilofos	226.10>157.00	14	226.10>184.00	6
102	Permethrin	183.10>153.10	14	183.10>168.10	14
103	Pyrazophos	221.10>193.10	12	221.10>149.10	14
104	Fenarimol	251.00>139.00	14	330.00>139.00	8
105	Pyridaben	147.10>117.10	22	147.10>132.10	14
106	Cypermethrin	163.10>127.10	6	163.10>91.00	14
107	Boscalid	140.10>112.10	12	140.10>76.00	24
108	Fenvalerate	225.10>119.10	20	225.10>147.10	10
109	Deltamethrin	180.90>151.90	22	252.90>93.00	20
Group B (113 pesticides)					
1	Ethiolate	100.00>72.10	6	161.00>100.10	9
2	Biphenyl	154.10>128.10	22	154.10>115.10	24
3	Etridiazole	210.90>182.90	10	182.90>139.90	18
4	Chloroneb	206.00>141.00	20	193.00>113.00	18
5	Tecnazene	260.90>202.90	14	202.90>142.90	22
6	Thionazin	143.00>79.10	12	175.00>79.10	12
7	Diphenylamine	169.10>66.00	24	167.10>139.10	28
8	Fenobucarb	121.10>77.00	20	150.10>121.10	10
9	Benfluralin	292.10>264.00	8	292.10>160.00	22
10	Naled	109.00>79.00	8	145.00>109.00	15
11	Phorate	260.00>75.00	8	231.00>129.00	24

Table 2 List of Pesticides Used in Rice and Pear Sample Matrix (part 4)

No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
12	Chlorpropham	127.10>65.00	22	213.10>171.10	6
13	Pentachloronitrobenzene	264.80>236.80	10	294.80>236.80	16
14	Omethoate	156.00>110.00	8	110.00>79.00	10
15	Atratone	211.00>169.20	6	211.00>154.10	15
16	Diazinon	304.10>179.10	10	179.10>137.10	18
17	Dicrotofos	127.10>109.00	12	127.10>95.00	18
18	Clomazone	204.10>107.00	20	204.10>78.00	26
19	Pyrimethanil	198.10>183.10	14	198.10>118.10	28
20	delta-BHC	180.90>144.90	16	218.90>182.90	8
21	Carbofuran	164.10>149.10	8	149.10>121.10	10
22	Etrimfos	181.10>153.10	10	292.10>181.10	8
23	Atrazine	215.10>58.00	14	215.10>173.10	6
24	Simazine	201.10>173.10	6	201.10>186.10	6
25	Terbuthylazine	229.10>173.10	6	214.10>71.00	16
26	Monolinuron	214.00>61.00	10	126.00>99.00	15
27	Pronamide	172.90>144.90	16	172.90>109.00	26
28	Isazofos	257.00>162.00	8	257.00>119.00	18
29	Pentachloroaniline	262.90>191.90	22	264.90>193.90	18
30	Chlorpyrifos-methyl	285.90>93.00	22	287.90>93.00	22
31	Aldrin	262.90>191.00	34	262.90>193.00	28
32	Desmetryn	213.00>171.10	6	213.00>58.10	18
33	Ronnel	284.90>269.90	16	286.90>271.90	18
34	Tolclofos-methyl	264.90>249.90	14	264.90>93.00	24
35	Prometryn	226.10>184.10	10	241.20>184.10	12
36	beta-BHC	180.90>144.90	16	218.90>182.90	8
37	Ametryn	227.10>185.10	6	227.10>58.00	14
38	Terbutryn	241.20>185.10	6	241.20>170.10	14
39	Chlorpyrifos	196.90>168.90	14	313.90>257.90	14
40	Malaoxon	127.00>99.00	10	268.00>127.00	10
41	Phosphamidon	127.10>109.10	12	127.10>95.10	18
42	Dipropetryn	255.00>222.20	9	255.00>180.20	18
43	Parathion-methyl	263.00>109.00	14	125.00>47.00	12
44	Trichloronat	297.00>269.00	15	299.00>271.00	15
45	gamma-BHC	180.90>144.90	16	218.90>182.90	8
46	Pirimiphos-ethyl	304.00>168.00	10	318.00>166.00	15
47	Malathion	173.10>99.00	14	173.10>127.00	6
48	Methoprene	153.00>111.00	5	111.10>55.00	18
49	Fenitrothion	277.00>260.00	6	277.00>109.10	14
50	Ethofumesate	207.10>161.10	8	207.10>137.10	12
51	Cyprodinil	224.10>208.10	16	224.10>197.10	22
52	Isofenphos-oxon	229.10>201.00	10	201.00>121.00	20
53	Pendimethalin	252.10>162.10	10	252.10>191.10	8
54	E-Chlorfenvinphos	323.00>267.00	16	267.00>159.00	18
55	Propanil	217.00>161.00	10	160.90>99.00	24
56	o,p'-DDE	246.00>176.00	30	248.00>176.00	28
57	Bromophos-ethyl	358.90>302.90	16	302.90>284.90	18
58	Isocarbophos	289.10>136.00	14	230.00>212.00	10
54	Z-Chlorfenvinphos	323.00>267.00	16	267.00>159.00	18
59	Chlordane-trans	374.80>265.90	26	372.80>263.90	28
60	Tetraconazole	336.00>204.00	28	336.00>218.00	14

Table 2 List of Pesticides Used in Rice and Pear Sample Matrix (part 5)

No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
61	Butachlor	176.10>147.10	14	188.10>160.10	12
62	Prothiofos	266.90>238.90	10	309.00>238.90	14
63	Beflubutamid	176.00>91.10	15	221.00>193.00	12
64	Tetrachlorvinphose	328.90>109.00	20	330.90>109.00	22
65	Procymidone	283.00>96.00	10	285.00>96.00	10
66	Dieldrin	276.90>241.00	8	262.90>193.00	34
67	Methidathion	145.00>85.00	8	145.00>58.00	14
68	Profenofos	338.90>268.90	18	336.90>266.90	14
69	Napropamide	128.10>72.00	6	100.00>72.00	8
70	Hexaconazole	214.00>159.00	20	214.00>172.00	20
71	Butamifos	286.10>202.10	14	200.10>65.00	22
72	Paclobutrazol	236.10>125.00	14	236.10>167.00	10
73	Chlorfenson	175.00>111.00	12	175.00>75.00	28
74	Fluazifop-butyl	282.00>91.10	18	282.00>238.10	18
75	Isoprothiolane	231.10>189.00	10	290.10>118.00	14
76	Phosfolan	255.00>227.00	6	255.00>140.00	22
77	Chlorobenzilate	139.00>111.00	16	251.00>139.00	14
78	Nitrofen	202.00>139.00	24	282.90>253.00	12
79	Ethion	153.00>97.00	14	230.90>129.00	24
80	Fluorodifen	190.00>126.00	12	190.00>75.00	21
81	Fipronil	366.90>212.90	30	368.90>214.90	30
82	Diniconazole	268.00>232.00	12	270.00>234.00	10
83	Myclobutanil	179.10>125.00	14	179.10>152.00	8
84	Cyproconazole-1	139.10>111.10	16	222.10>125.10	24
85	p,p'-DDT	235.00>165.00	24	237.00>165.00	28
86	Cyproconazole-2	222.10>125.10	24	139.10>111.10	16
84	Methoxychlor	227.10>121.10	16	121.10>78.00	22
87	Benalaxyl	148.10>105.10	16	148.10>79.10	24
88	Propiconazole	173.00>145.00	16	259.00>69.00	14
89	Diclofop-methyl	340.00>253.00	14	253.00>162.00	22
90	Fenthion-sulfoxide	278.00>108.90	18	278.00>125.10	24
91	Fenthion-sulfone	310.00>105.20	12	310.00>109.00	21
92	Fludioxonil	248.00>127.00	26	248.00>154.00	20
93	Oxadixyl	163.10>132.10	8	132.10>117.10	18
94	Iprodione	314.00>245.00	12	314.00>56.00	22
95	Etoxazole	359.10>187.10	14	359.10>340.10	12
96	Famphur	218.00>109.00	16	218.00>79.00	24
97	Fenpropathrin	181.10>152.10	22	265.10>210.10	12
98	Pyridaphenthion	340.00>199.10	8	199.10>92.00	16
99	Leptophos	376.90>361.90	24	374.90>359.90	24
100	Phosmet	160.00>77.00	24	160.00>133.00	14
101	Bifenox	340.90>309.90	10	340.90>188.90	20
102	lambda-Cyhalothrin	208.00>181.00	8	197.00>141.00	12
103	Acrinathrin	289.10>93.00	14	289.10>77.00	26
104	Phosalone	182.00>111.00	14	182.00>138.00	8
105	Mefenacet	192.00>136.00	14	192.00>109.00	24
106	Azinphos-ethyl	160.10>132.10	4	132.10>77.00	14
107	Fluquinconazole	340.00>298.00	20	340.00>313.00	14
108	Cyfluthrin	226.10>206.10	14	198.90>170.10	25
109	Coumaphos	362.00>109.00	16	362.00>226.00	14
110	Flucythrinate	199.10>157.10	10	157.10>107.10	12

Table 2 List of Pesticides Used in Rice and Pear Sample Matrix (part 6)

No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
111	Fenbuconazole	198.10>129.10	10	129.10>102.10	18
112	Fluvalinate	250.10>55.00	20	250.10>200.00	20
113	Difenoconazole	323.00>265.00	14	265.00>202.00	20
Internal standard, IS					
1	Heptachlor-epoxide (exo)	352.80>262.90	14	354.80>264.90	20

Table 3 MRM information of Pesticides Used in Leek and Tea

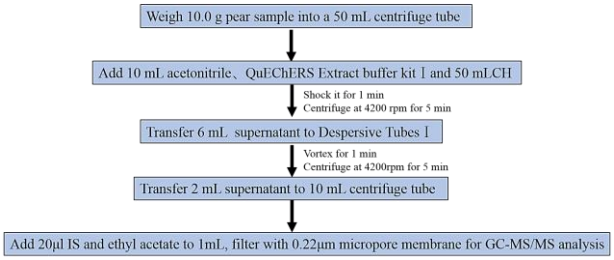
No.	Pesticides	Quantitative ion pair	CE1	Qualitative ion pair	CE2
Leek					
1	Dichlorvos	185.00> 93.00	14	109.00>79.00	8
2	Fonofos	246.00>137.10	6	137.10>109.10	8
3	Dioxathion	185.00>129.00	12	152.90>96.90	10
4	Fenthion	278.00>169.00	14	278.00>109.00	20
5	Allethrin	136.00> 93.10	12	123.00>81.10	8
6	Ethiolate	161.00>100.10	9	100.00>72.10	6
Tea					
1	Acetochlor	223.10>132.10	22	174.10>146.10	12
2	Dicofol	139.00> 75.00	28	139.00>111.00	16
3	Methoprene	111.10> 55.00	18	153.00>111.00	5
4	Allethrin	136.00> 93.10	12	123.00>81.10	8
5	Fonofos	246.00>137.10	6	137.10>109.10	8

■ Sample preparation

Pear

Weigh 10.0 g homogeneous pear sample into a 50 mL centrifuge tube, add 10 mL acetonitrile, a piece of QuEChERS Extract Salt Ⅰ (P/N: 380-00148; SHIMSEN QuEChERS Extraction Salts Packets with 50mL Centrifuge Tube, 4 g $MgSO_4$, 1 g NaCl, 0.5 g disodium hydrogen citrate, 1 g sodium citrate, 50/p) and a piece of ceramic homogenizer, CH, shake it for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 6 mL supernatant to SHIMSEN QuEChERS Dispersive Tube Ⅰ (P/N: 380-00123; SHIMSEN QuEChERS dSPE, 15mL, 150mg PSA, 900mg $MgSO_4$, 50/p), vortex for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 2 mL supernatant to a 10 mL centrifuge tube. Concentrate with nitrogen at 35 ℃ till nearly-dried. Add 20 µL Internal standard, IS, solution (5 µg/mL), and then add ethyl acetate to 1 mL, vortex to mix, filter through a 0.22 µm micropore HPTFE membrane. The sample preparation process of pear is shown in Fig. 3.

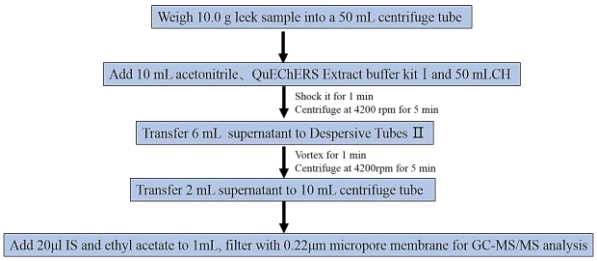
Fig. 3 The Sample Preparation Process of Pear



Leek

Weigh 10.0 g homogeneous pear sample into a 50 mL centrifuge tube, add 10 mL acetonitrile, a piece of QuEChERS Extract Salt Ⅰ (P/N: 380-00148; SHIMSEN QuEChERS Extraction Salts Packets with 50mL Centrifuge Tube, 4 g $MgSO_4$, 1 g NaCl, 0.5 g disodium hydrogen citrate, 1 g sodium citrate, 50/p) and a piece of ceramic homogenizer, CH, shake it for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 6 mL supernatant to SHIMSEN QuEChERS Dispersive Tube Ⅱ (P/N: 380-00124; SHIMSEN QuEChERS dSPE, 15mL, 150mg PSA, 15mg GCB, 885mg $MgSO_4$, 50/P), vortex for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 2 mL supernatant to a 10 mL centrifuge tube. Concentrate with nitrogen at 35℃ till nearly-dried. Add 20 µL IS solution (5 µg/mL), and then add ethyl acetate to 1 mL, vortex to mix, filter through a 0.22 µm micropore HPTFE membrane. The sample preparation process of leek is shown in Fig. 4.

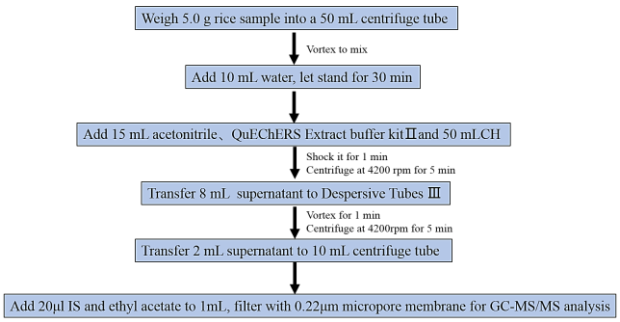
Fig. 4 The Sample Preparation Process of Leek



Rice

Weigh 5.0 g homogeneous pear sample into a 50 mL centrifuge tube, add 10 mL water, vortex to mix for 30 min, add 15 mL acetonitrile containing 1% acetic acid, a piece of QuEChERS Extract Salt Ⅱ (P/N: 380-00151; SHIMSEN QuEChERS Extraction Salts Packets with 50mL Centrifuge Tube, 6g $MgSO_4$, 1.5g NaOAC, 50/P) and a piece of ceramic homogenizer, CH, shake it for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 8 mL supernatant to SHIMSEN QuEChERS Dispersive Tube Ⅲ (P/N: 380-00129; SHIMSEN QuEChERS dSPE, 15mL, 400mg PSA, 400mg C18, 1200mg $MgSO_4$, 50/P), vortex for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 2 mL supernatant to a 10 mL centrifuge tube. Concentrate with nitrogen at 35 ℃ till nearly-dried. Add 20 µL IS solution (5 µg/mL), and then add ethyl acetate to 1 mL, vortex to mix, filter through a 0.22 µm micropore HPTFE membrane. The sample preparation process of rice is shown in Fig. 5.

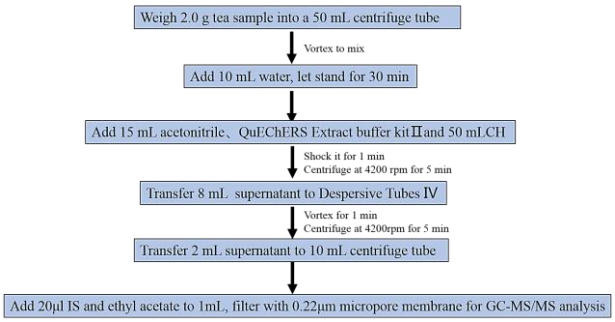
Fig. 5 The Sample Preparation Process of Rice



Tea

Weigh 2.0 g homogeneous pear sample into a 50 mL centrifuge tube, add 10 mL water, vortex to mix for 30 min, add 15 mL acetonitrile containing 1% acetic acid, a piece of QuEChERS Extract Salt Ⅱ (P/N: 380-00151; SHIMSEN QuEChERS Extraction Salts Packets with 50mL Centrifuge Tube, 6g $MgSO_4$, 1.5g NaOAC, 50/P) and a piece of ceramic homogenizer, CH, shake it for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 8 mL supernatant to SHIMSEN QuEChERS Dispersive Tube Ⅳ (P/N: 380-00145; SHIMSEN QuEChERS dSPE, 15mL, 400mg PSA, 400mg C18, 200mg GCB, 1200mg $MgSO_4$, 50/P), vortex for 1 min. Centrifuge at 4200 rpm for 5 min, transfer 2 mL supernatant to a 10 mL centrifuge tube. Concentrate with nitrogen at 35 ℃ till nearly-dried. Add 20 µL IS solution (5 µg/mL), and then add ethyl acetate to 1 mL, vortex to mix, filter through a 0.22 µm micropore HPTFE membrane. The sample preparation process of tea is shown in Fig. 6.

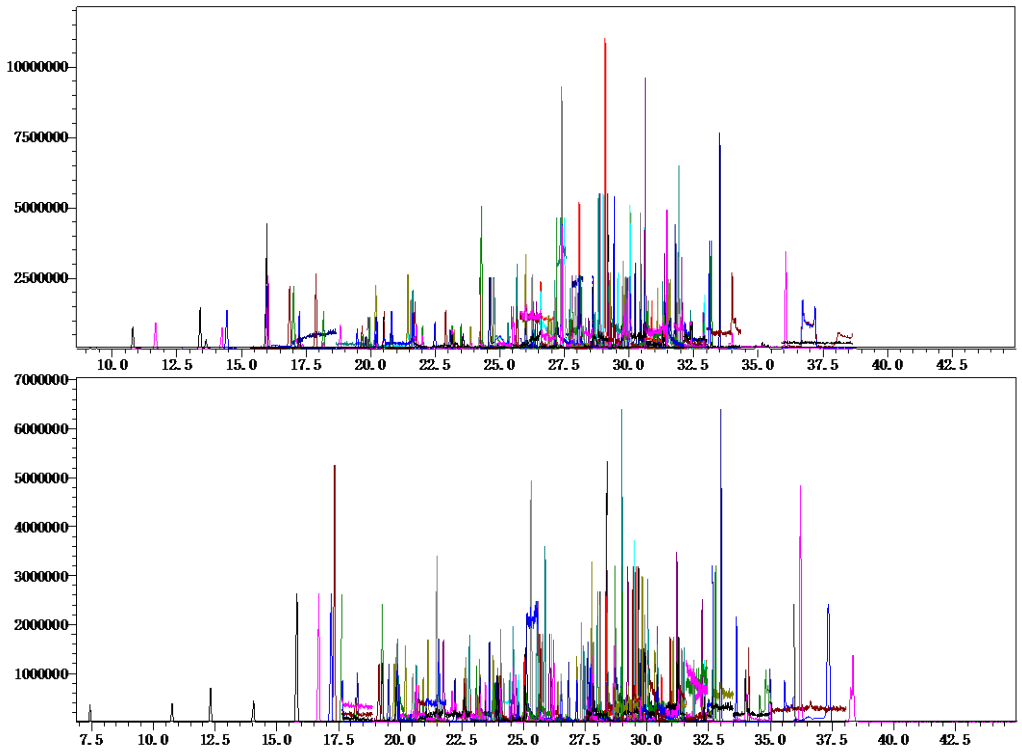
Fig. 6 The Sample Preparation Process of Tea



■ MRM Chromatogram

Fig. 7 shows MRM chromatogram, split into 2 groups, of pesticides standard mixture solution.

Fig. 7 MRM Chromatogram of Pesticides Standard Mixture Solution,
A, Group A, 109 Pesticides standard mixture solution; B, Group B, 113 Pesticides standard mixture solution



■ Spike and Recovery Test

Validation parameters like recovery and precision were studied using pear, leek, rice and tea sample extracts spiked with 40 µg/kg, 40 µg/kg, 100 µg/kg, and 250 µg/kg respectively. Three replicates of spiked samples were evaluated against matrix-matched calibration curve.

Good recovery rate and reproducibility were obtained without significant matrix effect.

Results have been showed in Table 4, which was split into 5 parts due to the limited space.

The break down of recovery rate of each sample matrix is shown in Fig. 8.

Table 4 Recovery Rate and Reproducibility (%RSD, n=3) (part 1)

No.	Pesticides	Pear		Leak		Tea		Rice	
		spiked level (40 µg/kg)		spiked level (40 µg/kg)		spiked level (250 µg/kg)		spiked level (100 µg/kg)	
		Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Group A (109 pesticides)									
1	Dichlorvos	115.38%	3.98%	117.33%	4.24%	107.90%	3.40%	102.32%	2.94%
2	Methamidophos	73.75%	0.49%	84.55%	2.95%	90.71%	7.49%	90.77%	2.86%
3	Dichlorobenzonitrile	98.32%	3.50%	99.44%	2.29%	93.22%	4.93%	90.69%	2.47%
4	Mevinphos-1	104.02%	3.39%	100.63%	2.96%	96.88%	1.66%	98.26%	2.44%
5	Mevinphos-2	108.49%	2.00%	100.15%	3.96%	98.25%	2.91%	95.80%	2.33%
6	Methacrifos	104.74%	2.22%	95.64%	4.03%	96.59%	3.16%	97.30%	2.94%
7	Molinate	105.34%	0.90%	96.52%	3.54%	91.45%	3.71%	91.33%	2.67%
8	Acephate	118.44%	5.73%	94.66%	3.44%	94.81%	8.98%	98.76%	1.57%
9	Isoprocarb	104.61%	2.99%	100.33%	2.57%	99.60%	6.35%	94.91%	2.88%
10	Cycloate	102.41%	3.25%	98.27%	2.39%	84.87%	6.80%	91.89%	2.51%
11	Hexachlorobenzene	103.85%	2.75%	91.10%	3.15%	60.24%	4.86%	83.54%	2.87%
12	Ethoprophos	108.61%	2.65%	97.98%	3.89%	92.02%	4.16%	99.22%	2.57%
13	Ethalfluralin	110.50%	2.69%	108.44%	1.92%	93.29%	4.24%	108.44%	2.88%
14	Propoxur	112.65%	0.61%	98.42%	3.88%	90.17%	6.57%	77.56%	6.98%
15	Sulfotep	106.57%	2.47%	99.86%	2.62%	96.55%	4.48%	99.89%	2.34%
16	alpha-BHC	107.01%	2.83%	100.95%	2.16%	91.30%	4.68%	97.41%	2.09%
17	Atrazine-desethyl	105.01%	2.26%	104.53%	2.83%	86.35%	15.51%	96.91%	2.94%
18	Terbufos	106.25%	3.50%	101.89%	3.19%	89.32%	4.40%	110.46%	3.42%
19	Dioxathion	104.01%	2.92%	101.05%	5.94%	87.62%	3.63%	110.42%	2.94%
20	Profluralin	113.93%	2.18%	109.43%	2.72%	93.93%	4.48%	106.62%	2.57%
21	Triallate	107.14%	3.54%	99.67%	1.88%	84.30%	3.79%	94.28%	2.75%
22	Fonofos	106.74%	2.80%	99.07%	2.83%	91.29%	4.94%	97.38%	2.84%
23	Pirimiphos-ethyl	107.88%	2.78%	99.72%	1.66%	89.84%	3.15%	96.97%	2.46%
24	Propazine	107.99%	3.09%	99.20%	2.37%	81.96%	9.36%	100.07%	3.18%
25	Dicloran	111.41%	2.20%	102.47%	2.61%	83.66%	5.95%	111.84%	1.06%
26	Propetamphos	107.51%	3.08%	98.20%	3.30%	93.97%	4.47%	101.58%	3.64%
27	Iprobenfos	108.81%	1.99%	98.60%	2.99%	89.09%	2.48%	101.78%	2.89%
28	Monocrotophos	102.80%	1.13%	94.25%	4.48%	94.12%	2.81%	98.69%	3.06%
29	Dichlofenthion	106.58%	2.73%	98.22%	2.87%	87.88%	4.45%	96.89%	2.22%
30	Pirimicarb	106.95%	3.58%	97.69%	3.49%	82.56%	6.69%	98.62%	2.66%
31	Dimethoate	114.69%	0.48%	97.76%	3.15%	112.83%	1.04%	108.07%	5.48%
32	Acetochlor	107.47%	4.49%	102.70%	2.18%	94.23%	5.42%	97.21%	4.54%
33	Alachlor	110.63%	3.29%	101.01%	3.19%	89.01%	6.37%	99.29%	2.15%
34	Paraoxon-methyl	113.65%	1.98%	92.77%	10.60%	96.14%	4.35%	101.79%	2.77%
35	Pirimiphos-methyl	108.43%	3.86%	97.09%	1.43%	89.02%	2.44%	97.38%	3.34%
36	Vinclozolin	104.19%	7.44%	99.51%	2.89%	91.38%	2.67%	88.54%	0.89%
37	Metribuzin	105.64%	4.10%	99.26%	1.23%	97.51%	5.84%	95.18%	0.41%
38	Metalaxyl	101.99%	8.04%	100.60%	3.61%	92.47%	6.36%	94.58%	7.18%
39	Thiobencarb	98.92%	5.56%	99.36%	2.81%	84.54%	3.69%	88.86%	2.80%
40	Formothion	101.43%	9.60%	87.79%	1.71%	88.97%	8.41%	86.94%	2.79%
41	Metolachlor	108.80%	2.78%	102.39%	2.06%	86.30%	5.83%	99.52%	2.66%
42	Dicofol	104.82%	2.63%	111.92%	6.70%	87.32%	9.68%	85.20%	3.56%
43	Fenthion	99.65%	3.34%	99.85%	3.40%	83.59%	4.49%	87.20%	5.46%
44	Paraoxon	108.50%	4.21%	94.03%	3.15%	100.92%	8.28%	94.58%	2.82%
45	Bromophos	103.94%	5.17%	90.67%	3.20%	82.47%	1.21%	91.34%	1.35%
46	Triadimefon	103.04%	3.17%	106.60%	1.82%	91.07%	4.15%	98.93%	3.22%
47	Allethrin	100.69%	3.14%	110.07%	7.84%	86.19%	12.15%	90.46%	2.47%
48	Parathion	116.34%	1.66%	109.46%	1.22%	92.55%	4.38%	118.37%	2.17%
49	Isofenphos-methyl	102.28%	2.88%	101.87%	1.82%	91.22%	4.10%	98.02%	1.52%
50	Isofenphos	108.12%	3.00%	100.44%	1.75%	91.34%	6.32%	100.25%	2.40%

Table 4 Recovery Rate and Reproducibility (%RSD, n=3) (part 1)

No.	Pesticides	Pear		Leak		Tea		Rice	
		spiked level (40 µg/kg)		spiked level (40 µg/kg)		spiked level (250 µg/kg)		spiked level (100 µg/kg)	
		Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Group A (109 pesticides)									
51	Quinalphos	100.54%	3.16%	98.89%	3.48%	79.15%	1.22%	88.32%	1.95%
52	alpha-Endosulfan	104.26%	4.95%	104.33%	5.69%	87.70%	7.64%	96.55%	5.16%
53	Penconazole	101.25%	2.76%	100.39%	2.57%	85.74%	4.53%	91.29%	3.30%
54	Phorate Sulfoxide	102.71%	2.53%	101.34%	3.80%	92.40%	3.43%	93.40%	4.33%
55	Fosthiazate -1	113.72%	3.01%	98.46%	3.46%	99.15%	5.34%	94.33%	6.09%
56	Fosthiazate-2	111.61%	5.03%	99.84%	3.77%	95.80%	0.39%	88.07%	6.28%
57	p,p'-DDE	102.57%	2.80%	100.23%	2.12%	73.76%	4.44%	86.80%	1.66%
58	Fenothiocarb	103.72%	2.58%	100.21%	2.98%	88.48%	4.05%	91.98%	3.73%
59	Bromacil	79.17%	7.78%	104.55%	1.52%	88.19%	6.88%	78.90%	4.44%
60	Terbufos sulfone	107.87%	3.40%	100.19%	2.38%	94.26%	1.21%	99.05%	3.93%
61	Phorate sulfone	108.23%	3.12%	101.14%	2.39%	94.32%	3.37%	96.82%	2.20%
62	Mepanipyrim	101.08%	2.64%	97.12%	3.55%	79.52%	2.58%	97.01%	3.85%
63	DEF	105.82%	2.60%	98.79%	2.89%	76.82%	4.10%	92.73%	0.60%
64	Triadimenol-1	100.23%	2.06%	102.31%	3.23%	83.69%	6.36%	89.36%	5.83%
65	Bromfenvinfos	103.63%	2.99%	102.46%	2.40%	92.63%	3.66%	98.66%	2.86%
66	Pretilachlor	105.14%	2.37%	103.16%	3.27%	91.71%	5.50%	97.42%	4.43%
67	Triadimenol-2	112.65%	0.28%	109.48%	5.48%	88.41%	6.44%	95.99%	4.83%
68	Oxadiazon	105.68%	1.76%	101.38%	1.77%	91.14%	4.46%	95.48%	4.18%
69	o,p'-DDD	99.48%	3.47%	103.63%	2.40%	72.61%	5.81%	93.91%	3.24%
70	Kresoxim-methyl	105.05%	3.01%	98.03%	2.95%	92.15%	5.08%	100.99%	3.63%
71	Ditalimfos	88.81%	5.07%	78.10%	8.96%	78.46%	6.27%	84.03%	5.08%
72	Endrin	104.93%	5.42%	97.33%	0.33%	92.30%	2.50%	94.58%	2.16%
73	Imazalil	102.46%	3.67%	91.09%	4.52%	---[2]	---[2]	88.32%	4.00%
74	o,p'-DDT	117.20%	4.42%	76.76%	6.20%	74.54%	10.09%	66.61%	5.56%
75	Mephosfolan	108.64%	2.12%	97.43%	3.36%	89.42%	7.54%	107.97%	3.78%
76	Cyflufenamid	109.55%	1.13%	102.38%	4.46%	101.54%	6.30%	87.76%	5.35%
77	Bupirimate	104.37%	2.20%	98.25%	2.35%	77.42%	11.84%	94.48%	2.50%
78	Chlorthiophos-2	106.53%	3.19%	100.77%	3.43%	88.21%	2.14%	94.73%	2.49%
79	Oxyfluorfen	111.08%	1.54%	111.51%	0.89%	96.99%	2.72%	114.88%	2.89%
80	Flutolanil	103.99%	3.48%	103.35%	2.43%	93.56%	5.03%	97.26%	3.45%
81	Chlorthiophos-2	109.14%	3.37%	99.63%	3.89%	87.89%	2.77%	92.22%	2.81%
82	p,p'-DDD	100.00%	3.26%	102.18%	2.35%	78.75%	5.95%	88.62%	2.48%
83	beta-Endosulfan	105.18%	3.13%	101.81%	3.22%	82.96%	12.28%	92.73%	2.62%
84	Quinoxyfen	106.07%	2.98%	98.23%	2.72%	63.99%	16.80%	93.26%	3.52%
85	Trifloxystrobin	109.52%	2.80%	98.79%	2.07%	92.29%	1.77%	104.48%	2.81%
86	Aclonifen	118.04%	2.08%	108.18%	1.41%	81.74%	2.97%	113.18%	2.20%
87	Carbophenothion	111.27%	2.71%	98.18%	1.71%	85.22%	3.44%	99.15%	3.79%
88	Isoxation	102.47%	3.43%	99.14%	3.27%	79.46%	1.86%	92.42%	1.67%
89	Piperonyl butoxide	107.63%	2.98%	100.56%	3.00%	80.90%	4.15%	97.04%	3.65%
90	Edifenphos	107.33%	2.46%	92.68%	4.21%	93.55%	3.78%	86.54%	5.38%
91	Fensulfothion	111.81%	2.43%	98.80%	2.41%	91.19%	4.53%	106.80%	2.58%
92	Triazophos	101.31%	1.60%	91.71%	11.11%	92.17%	4.92%	95.16%	1.71%
93	Bifenthrin	106.09%	2.77%	---[1]	---[1]	85.34%	3.12%	92.76%	3.21%
94	Tebufenpyrad	105.78%	2.95%	101.01%	2.98%	89.20%	3.94%	97.02%	3.61%
95	Bromopropylate	104.56%	3.44%	100.88%	2.67%	89.36%	3.26%	93.29%	1.64%
96	Tetramethrin-1	108.22%	5.98%	97.51%	2.73%	85.93%	2.93%	99.97%	1.20%
97	Epoxiconazole	107.31%	1.54%	104.50%	2.07%	86.08%	2.35%	92.72%	3.21%
98	Tebuconazole	105.32%	3.72%	100.95%	1.97%	88.51%	3.69%	96.14%	2.95%
99	Tetramethrin-2	104.49%	2.34%	99.87%	3.65%	85.79%	3.02%	97.14%	3.59%
100	Pyriproxyfen	103.57%	2.86%	97.92%	2.97%	83.55%	3.06%	98.56%	1.95%

Table 4 Recovery Rate and Reproducibility (%RSD, n=3) (part 1)

No.	Pesticides	Pear		Leak		Tea		Rice	
		spiked level (40 μg/kg)		spiked level (40 μg/kg)		spiked level (250 μg/kg)		spiked level (100 μg/kg)	
		Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Group A (109 pesticides)									
101	Piperophos	108.04%	2.03%	101.90%	2.11%	93.50%	2.95%	101.12%	3.25%
102	EPN	114.94%	1.34%	111.44%	1.00%	91.23%	4.27%	110.25%	1.78%
103	Hexazinone	106.31%	3.11%	99.77%	2.78%	87.54%	22.65%	96.21%	1.68%
104	Fenamidone	106.32%	3.32%	101.74%	1.78%	93.85%	3.28%	97.96%	2.37%
105	Tetradifon	106.77%	3.86%	99.95%	1.88%	84.57%	4.33%	96.65%	5.22%
106	Anilofos	107.77%	2.77%	91.82%	2.64%	97.04%	6.49%	101.94%	3.33%
107	Permethrin-1	105.87%	3.41%	99.90%	4.58%	94.06%	10.51%	93.66%	0.73%
108	Pyrazophos	107.52%	2.57%	92.89%	2.44%	93.03%	1.55%	100.82%	2.54%
109	Permethrin-2	102.52%	3.08%	99.56%	1.93%	81.58%	5.22%	94.14%	5.19%
110	Fenarimol	106.27%	3.10%	98.26%	2.40%	86.86%	1.69%	95.92%	2.91%
111	Pyridaben	106.42%	2.64%	103.05%	2.39%	82.25%	4.69%	96.38%	2.80%
112	Cypermethrin-1	108.49%	2.67%	103.47%	2.66%	93.91%	2.43%	96.05%	2.71%
113	Cypermethrin-2	108.21%	4.96%	112.83%	5.67%	98.19%	3.01%	96.88%	8.82%
114	Cypermethrin-3	113.75%	6.81%	122.11%	3.25%	94.27%	2.05%	93.86%	13.55%
115	Cypermethrin-4	117.23%	2.36%	125.81%	3.24%	97.44%	3.94%	89.03%	5.94%
116	Boscalid	106.04%	2.89%	106.81%	0.47%	77.85%	12.98%	95.27%	4.19%
117	Fenvalerate-1	115.79%	2.04%	108.14%	1.83%	90.66%	5.39%	92.99%	4.29%
118	Fenvalerate-2	108.62%	1.35%	114.76%	3.29%	91.60%	1.70%	89.25%	3.58%
119	Deltamethrin-1	101.86%	5.30%	---[2]	---[2]	90.84%	40.49%	91.12%	5.63%
120	Deltamethrin-2	106.61%	2.10%	134.98%	4.76%	95.78%	8.66%	87.54%	9.61%
Group B (113 pesticides)									
1	Ethiolate	92.04%	2.21%	87.18%	4.20%	89.54%	5.68%	91.93%	7.30%
2	Biphenyl	97.83%	1.14%	90.37%	2.96%	80.11%	4.42%	88.71%	4.79%
3	Etridiazole	114.06%	1.47%	90.39%	2.54%	89.28%	4.48%	72.05%	1.87%
4	Chloroneb	104.92%	2.24%	94.96%	2.33%	88.39%	4.25%	96.31%	2.57%
5	Tecnazene	106.28%	1.78%	97.02%	2.20%	81.25%	3.54%	103.06%	2.74%
6	Thionazin	107.65%	1.98%	102.69%	1.36%	92.26%	4.90%	101.41%	1.46%
7	Diphenylamine	105.89%	3.02%	100.49%	0.35%	88.57%	7.53%	75.19%	0.51%
8	Fenobucarb	107.96%	2.04%	98.24%	1.79%	92.34%	5.79%	94.01%	1.32%
9	Benfluralin	110.86%	2.98%	105.75%	1.17%	87.49%	4.85%	106.77%	2.54%
10	Naled	98.68%	6.66%	---[2]	---[2]	---[2]	---[2]	86.78%	2.67%
11	Phorate	106.36%	2.09%	99.71%	0.81%	84.77%	5.40%	108.73%	1.83%
12	Chlorpropham	105.75%	2.00%	103.51%	2.11%	89.72%	4.86%	100.41%	0.89%
13	Pentachloronitrobenzene	110.43%	2.88%	99.30%	1.98%	73.19%	7.73%	102.71%	3.20%
14	Omethoate	91.43%	0.93%	84.23%	9.01%	101.07%	11.87%	82.17%	0.48%
15	Atratone	106.81%	1.75%	97.96%	2.34%	77.15%	5.65%	100.76%	0.99%
16	Diazinon	108.36%	1.81%	98.70%	2.83%	77.64%	6.54%	100.58%	2.07%
17	Dicrotofos	105.19%	0.96%	98.27%	7.36%	88.98%	5.62%	101.65%	1.12%
18	Clomazone	107.72%	2.60%	96.76%	2.77%	90.94%	5.91%	98.85%	1.83%
19	Pyrimethanil	107.82%	2.70%	95.90%	4.14%	75.99%	8.82%	99.01%	3.01%
20	delta-BHC	108.83%	1.93%	97.19%	1.79%	88.19%	5.88%	97.62%	2.82%
21	Carbofuran	114.76%	2.33%	100.70%	3.95%	101.22%	5.64%	53.34%	12.24%
22	Etrimfos	108.89%	2.12%	100.44%	2.00%	79.40%	7.83%	99.45%	2.27%
23	Atrazine	119.01%	3.29%	97.43%	1.81%	77.09%	12.45%	99.90%	0.90%
24	Simazine	108.26%	3.37%	98.69%	1.53%	71.42%	7.98%	99.41%	1.19%
25	Terbuthylazine	109.17%	3.18%	101.86%	2.47%	77.33%	9.89%	98.48%	1.41%
26	Monolinuron	112.27%	2.71%	90.78%	6.94%	63.71%	25.02%	99.59%	1.63%
27	Pronamide	109.55%	1.88%	101.56%	4.11%	87.97%	4.31%	100.73%	1.62%
28	Isazofos	106.72%	5.87%	96.61%	4.03%	96.93%	4.30%	104.78%	2.79%
29	Pentachloroaniline	113.39%	3.20%	96.03%	3.19%	68.67%	5.40%	95.09%	3.90%

Table 4 Recovery Rate and Reproducibility (%RSD, n=3) (part 1)

No.	Pesticides	Pear		Leak		Tea		Rice	
		spiked level (40 µg/kg)		spiked level (40 µg/kg)		spiked level (250 µg/kg)		spiked level (100 µg/kg)	
		Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Group B (113 pesticides)									
30	Chlorpyrifos-methyl	102.94%	2.42%	95.31%	3.14%	87.85%	4.80%	100.68%	3.96%
31	Aldrin	105.80%	3.77%	95.07%	3.28%	70.73%	6.02%	91.88%	2.94%
32	Desmetryn	112.21%	1.09%	100.57%	2.40%	81.36%	3.05%	95.25%	3.87%
33	Ronnel	108.12%	2.06%	92.06%	2.89%	89.19%	4.29%	97.85%	1.16%
34	Tolclofos-methyl	108.85%	1.48%	100.46%	4.94%	89.03%	5.83%	101.00%	0.93%
35	Prometryn	103.86%	4.96%	100.24%	1.92%	84.89%	5.72%	100.25%	0.77%
36	beta-BHC	105.17%	3.02%	99.71%	2.47%	90.49%	3.20%	103.44%	5.20%
37	Ametryn	103.37%	2.54%	100.71%	3.28%	83.92%	5.17%	99.78%	1.34%
38	Terbutryn	109.34%	2.21%	98.67%	2.21%	78.79%	5.33%	100.65%	0.94%
39	Chlorpyrifos	106.16%	4.84%	99.02%	1.20%	76.89%	8.00%	104.44%	4.50%
40	Malaoxon	114.25%	2.59%	104.27%	6.21%	---[1]	---[1]	81.83%	2.25%
41	Phosphamidon-1	123.38%	4.24%	101.10%	1.81%	---[1]	---[1]	91.87%	4.77%
42	Phosphamidon-2	103.35%	1.53%	105.00%	4.22%	---[1]	---[1]	97.52%	8.17%
43	Dipropetryn	108.22%	2.45%	101.73%	2.56%	83.78%	3.87%	99.43%	1.56%
44	Parathion-methyl	118.15%	1.15%	100.58%	1.93%	92.48%	5.47%	117.21%	3.82%
45	Trichloronat	108.61%	4.17%	98.59%	3.50%	72.58%	4.95%	96.62%	1.77%
46	gamma-BHC	106.23%	1.84%	98.06%	2.34%	91.01%	5.02%	102.16%	1.31%
47	Pirimiphos-ethyl	104.35%	2.27%	101.30%	1.52%	84.96%	2.46%	99.79%	1.49%
48	Malathion	104.89%	0.87%	98.06%	2.77%	93.80%	5.32%	102.03%	5.02%
49	Methoprene	106.19%	1.92%	---[1]	---[1]	68.25%	6.26%	97.68%	10.80%
50	Fenitrothion	108.75%	1.49%	99.44%	3.65%	92.63%	3.52%	118.60%	3.75%
51	Ethofumesate	103.81%	1.25%	99.07%	1.88%	89.39%	4.79%	100.08%	1.26%
52	Cyprodinil	104.73%	2.39%	97.26%	1.98%	75.99%	3.80%	97.69%	1.22%
53	Isofenphos oxon	105.57%	1.08%	98.36%	2.06%	87.95%	6.13%	101.41%	0.96%
54	Pendimethalin	111.82%	1.30%	107.92%	2.67%	82.02%	4.67%	107.31%	3.45%
55	E-Chlorfenvinphos	110.80%	1.78%	87.93%	10.34%	85.75%	5.53%	109.90%	3.99%
56	Propanil	103.47%	3.83%	97.56%	0.98%	83.48%	5.10%	102.74%	2.33%
57	o,p'-DDE	103.99%	2.55%	99.59%	1.80%	74.43%	3.36%	94.31%	3.03%
58	Bromophos-ethyl	105.06%	1.40%	98.88%	2.81%	80.09%	3.10%	96.79%	0.78%
59	Isocarbophos	107.97%	4.21%	99.84%	3.42%	92.42%	6.53%	88.26%	3.29%
60	Z-Chlorfenvinphos	107.35%	2.76%	97.49%	2.78%	88.32%	5.85%	99.60%	1.33%
61	Chlordane-trans	106.98%	0.11%	99.88%	3.53%	77.69%	3.61%	91.48%	1.37%
62	Tetraconazole	109.32%	2.23%	101.22%	1.67%	89.14%	5.58%	103.86%	1.04%
63	Butachlor	107.29%	3.54%	103.24%	1.89%	79.65%	5.45%	102.90%	2.48%
64	Prothiofos	104.05%	1.60%	100.04%	2.49%	77.95%	3.75%	94.84%	2.15%
65	Beflubutamid	104.10%	2.24%	101.82%	1.94%	89.97%	6.59%	102.45%	3.37%
66	Tetrachlorvinphose	108.99%	2.52%	94.59%	5.41%	96.67%	2.42%	90.62%	3.73%
67	Procymidone	105.59%	3.17%	92.82%	0.77%	88.19%	5.76%	99.24%	1.17%
68	Dieldrin	106.23%	2.45%	98.00%	1.78%	81.65%	1.50%	99.99%	2.50%
69	Methidathion	109.06%	2.39%	91.20%	5.40%	91.61%	2.32%	101.88%	1.59%
70	Profenofos	106.08%	1.88%	94.97%	4.38%	89.93%	2.52%	98.89%	0.62%
71	Napropamide	106.54%	2.09%	99.99%	1.50%	84.77%	6.36%	100.09%	0.94%
72	Hexaconazole	105.19%	0.62%	90.43%	0.41%	81.18%	3.52%	100.05%	2.97%
73	Butamifos	112.81%	2.48%	109.19%	1.55%	90.78%	5.02%	114.03%	2.93%
74	Paclobutrazol	108.29%	2.85%	99.86%	2.50%	84.44%	6.50%	99.60%	3.08%
75	Chlorfenson	106.64%	2.14%	98.50%	1.76%	85.18%	5.14%	101.36%	1.28%
76	Fluazifop-butyl	104.80%	2.18%	101.53%	1.83%	89.40%	5.80%	100.63%	3.84%
77	Isoprothiolane	104.43%	0.97%	102.17%	1.69%	88.01%	4.70%	100.81%	2.69%
78	Phosfolan	110.49%	3.66%	92.81%	4.43%	91.75%	6.76%	104.92%	3.74%
79	Chlorobenzilate	106.51%	2.01%	100.46%	2.25%	84.65%	4.92%	99.79%	0.62%

Table 4 Recovery Rate and Reproducibility (%RSD, n=3) (part 1)

No.	Pesticides	Pear		Leak		Tea		Rice	
		spiked level (40 μg/kg)		spiked level (40 μg/kg)		spiked level (250 μg/kg)		spiked level (100 μg/kg)	
		Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Group B (113 pesticides)									
80	Nitrofen	113.23%	2.81%	106.08%	0.81%	83.20%	3.24%	115.93%	3.19%
81	Ethion	110.46%	2.16%	100.23%	2.53%	81.38%	3.60%	101.66%	2.37%
82	Fluorodifen	124.82%	1.37%	109.14%	1.54%	92.67%	3.71%	94.28%	2.48%
83	Fipronil	111.66%	1.58%	102.04%	1.41%	91.11%	5.40%	98.22%	3.08%
84	Diniconazole	106.93%	2.12%	98.57%	2.33%	79.91%	4.47%	98.83%	0.38%
85	Myclobutanil	106.04%	1.91%	104.79%	2.44%	86.34%	4.34%	99.94%	1.78%
86	Cyproconazole-1	103.20%	1.67%	99.36%	5.20%	82.94%	2.63%	98.86%	2.71%
87	p,p'-DDT	92.04%	2.21%	118.61%	5.16%	82.31%	11.62%	70.30%	2.87%
88	Cyproconazole-2	105.21%	0.88%	106.10%	11.02%	81.38%	4.87%	99.85%	6.17%
89	Methoxychlor	---2	---2	---2	---2	---2	---2	---2	---2
90	Benalaxyl	105.54%	2.90%	101.16%	4.31%	86.25%	5.02%	98.80%	0.86%
91	Propiconazole-1	108.69%	2.83%	98.36%	4.36%	87.34%	3.06%	102.75%	1.49%
92	Diclofop-methyl	106.01%	2.42%	101.65%	1.43%	87.94%	4.78%	99.80%	1.88%
93	Propiconazole-2	114.08%	2.99%	97.93%	3.34%	85.03%	6.30%	98.22%	0.84%
94	Fenthion sulfoxide	95.17%	6.46%	76.47%	8.79%	111.16%	19.57%	85.00%	6.54%
95	Fenthion sulfone	105.98%	2.26%	80.80%	11.02%	100.82%	12.66%	98.88%	2.13%
96	Fludioxonil	108.97%	3.98%	97.05%	1.60%	86.09%	2.93%	71.71%	8.38%
97	Oxadixyl	107.12%	2.70%	101.12%	2.46%	90.82%	3.94%	100.58%	1.08%
98	Iprodione	122.58%	3.28%	102.14%	9.38%	68.78%	23.01%	95.41%	14.62%
99	Etoxazole	107.99%	1.52%	100.22%	2.34%	80.46%	2.34%	102.17%	1.95%
100	Famphur	107.00%	3.11%	83.28%	10.06%	100.86%	7.45%	99.15%	0.76%
101	Fenpropathrin	105.38%	2.84%	99.82%	2.11%	87.93%	3.30%	100.98%	3.14%
102	Pyridaphenthion	107.80%	2.77%	93.82%	3.47%	90.62%	2.61%	100.69%	0.97%
103	Leptophos	104.02%	2.96%	90.60%	5.12%	82.50%	3.77%	95.66%	1.97%
104	Phosmet	104.77%	2.96%	76.62%	11.66%	98.69%	9.00%	96.18%	1.83%
105	Bifenox	120.09%	0.44%	110.02%	1.26%	85.70%	1.57%	99.92%	2.44%
106	lambda-Cyhalothrin-1	119.45%	7.08%	77.81%	9.86%	100.33%	4.07%	78.86%	2.57%
107	Acrinathrin	102.89%	5.17%	104.45%	3.02%	93.94%	4.38%	103.74%	2.37%
108	lambda-Cyhalothrin-2	109.73%	4.82%	106.75%	4.58%	89.56%	1.97%	98.38%	4.14%
109	Phosalone	107.54%	3.09%	90.50%	5.18%	93.75%	2.66%	101.78%	1.47%
110	Mefenacet	108.45%	2.69%	101.64%	2.23%	82.50%	2.50%	102.68%	2.55%
111	Azinphos-ethyl	111.22%	1.59%	88.90%	4.67%	80.13%	15.91%	102.69%	1.37%
112	Fluquinconazole	105.35%	2.08%	100.68%	1.83%	68.61%	26.67%	101.82%	1.88%
113	Cyfluthrin-1	109.95%	6.85%	103.20%	1.34%	92.94%	4.16%	100.19%	2.49%
114	Cyfluthrin-2	109.25%	2.69%	106.83%	3.76%	88.86%	1.05%	92.68%	5.93%
115	Cyfluthrin-3	114.18%	6.25%	97.21%	5.26%	84.69%	2.31%	97.22%	5.03%
116	Coumaphos	106.65%	2.25%	87.18%	5.22%	92.28%	4.89%	101.58%	0.39%
117	Cyfluthrin-4	115.70%	5.43%	109.12%	4.39%	86.59%	3.89%	95.04%	1.02%
118	Flucythrinate-1	113.49%	4.27%	109.16%	0.05%	90.59%	4.80%	93.39%	2.60%
119	Flucythrinate-2	115.04%	2.99%	110.94%	2.75%	91.58%	5.55%	95.21%	1.10%
120	Fenbuconazole	107.30%	2.02%	98.42%	2.26%	83.10%	1.86%	102.83%	1.39%
121	Fluvalinate-1	105.99%	3.63%	105.49%	1.44%	87.34%	3.94%	97.07%	2.23%
122	Fluvalinate-2	105.99%	3.63%	105.88%	4.82%	91.08%	6.05%	97.07%	2.23%
123	Difenoconazole-1	106.23%	5.50%	100.85%	2.49%	85.99%	4.08%	108.71%	3.52%
124	Difenoconazole-2	113.12%	2.12%	100.59%	2.00%	75.63%	5.12%	100.48%	1.83%

Note:

---1: positive matrix, high content of pesticide in blank matrix, unable to calculate recovery rate and RSD.

---2: due to the matrix effect (deltamethrin-1 and diroteophos in leek, teromycin and diromate in tea), or standard (methoxy DDT) decomposition at high temperature, the peak is not detected, so the recovery and RSD can not be calculated.

Fig. 8 Breakdown of Recovery Rate of Each Sample Matrix

■ Conclusion

This method was established for the determination of multi pesticides and metabolites in plant-derived food by using Shimadzu GCMS-TQ8050. Samples were pretreated by SHIMSEN QuEChERS extraction salts and dispersive SPE sorbents and separated by SH-1701 GC column. The quantitation was performed using multiple reaction monitoring and the recovery and precision were studied. As shown above, mean recoveries for most of the compounds were found within 70-120%. 239 compounds were found to be reproducible with 20% RSD in all four sample.

This method turns out to be simple, effective, fast and shows good reproducibility and high accuracy, suitable for detection of pesticides at trace level.

<References>

1) M. Anastassiades, S. J. Lehotay, D. Štajnbaher, F. J. Schenck, 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., 86, 412–431, (2003)

<Related Applications>

1. Method for the determination of 313 Residual Pesticides in Black tea using LCMS-8045 and GCMS-TQ8040 NX, 06-ADC-F-01-EN

SGLC-GC/MS-004-EN First Edition: Dec. 2022

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