

# GC-MS/MS 法同时分析葡萄基质中 174 种农药残留

## GCMSMS-057

**摘要：**建立气相色谱 – 串联质谱 (GC-MS/MS) 同时分析葡萄基质中 174 种农药残留的方法。葡萄空白基质用乙腈提取后，用 QuEChERS 方法净化、氮气吹干后复溶于丙酮中，加 174 种农药混标 (加标浓度为 10  $\mu\text{g/L}$ )，采用 GC-MS/MS 的方法对多种农药残留进行灵敏度和重现性考察。结果表明：葡萄基质中 174 种农药残留色谱峰峰形好，信噪比高，连续进 6 针进行重复性实验，其峰面积的相对标准偏差 (RSD %) 均在 10 % 以下。

**关键词：**GC-MS/MS 农药残留 葡萄

农药残留的污染问题日益受到全球的关注，日本于 2006 年提出肯定列表制度，规定了数百种农业化学品在食品中的最高残留限量为 10  $\mu\text{g/L}$ 。欧盟于 2008 年实施欧洲议会第 396/2005 法令，统一了欧盟各成员国所规定的农药最高残留量，并设定 0.01 mg/kg 为最高残留限量农药的默认限值。

以往，由于 MRM 相关软件功能的限值及灵敏度的要求，分析 174 种农药残留需要设置几种不同的方法。

随着分析任务的增加，加大了分析实验室和分析人员的压力。

本文采用岛津公司三重四极杆气质联用仪 GCMS-TQ8040，结合 Smart MRM 数据库，使用岛津特有的 AART 功能，无需使用标准品即可建立葡萄中 174 种农药残留的检测方法。结果表明，使用岛津 GCMS-TQ8040 在 174 种农残同时分析时获得高灵敏度。

## 实验部分

### 1.1 仪器

三重四极杆气质联用仪：GCMS-TQ8030

### 1.2 分析条件

GC 条件

色谱柱：Rxi-5 Sil ms (30 m $\times$ 0.25 mm $\times$ 0.25 $\mu\text{m}$ )

进样口温度：250 $^{\circ}\text{C}$

柱温程序：50 $^{\circ}\text{C}$  (1 min)-(25 $^{\circ}\text{C}$  /min)-150 $^{\circ}\text{C}$  - (10 $^{\circ}\text{C}$  /min)-300 $^{\circ}\text{C}$  (15 min)

恒线速度方式：47.2 cm/sec

进样方式：不分流进样

进样量：1  $\mu\text{L}$

高压进样：250 kpa(1.5 min)

接口温度：250 $^{\circ}\text{C}$

离子源温度：200

检测器电压：调谐电压 +0.8 kv

溶剂延迟时间：4 min

采集方式：MRM，特征离子见表 1

表 1 农药组分名称、保留时间及 MRM 参数

NO	中文名称	英文名称	CAS号	保留时间	定量离子对	CE	定性离子对	CE
1	三丙烯草胺	Allidochlor	93-71-0	6.259	138.1>96.0	6	138.1>110.1	6
2	二氯丙烯酰胺	Dichlorimid	37764-25-3	6.912	172.00>108.10	6	172.00>136.10	6
3	联苯	Biphenyl	92-52-4	7.287	154.1>128.1	22	154.1>115.1	24
4	丁草特	Butylate	2008-41-5	7.686	174.1>146.1	6	174.1>75.0	4
5	依得利(土菌灵)	Etridiazole	2593-15-9	7.933	210.9>182.9	10	210.9>139.9	22
6	苯胺灵	propham	122-42-9	8.004	179>137	5	120>77	15
7	虫螨畏	Methacrifos	62610-77-9	8.410	240.0>208.0	4	240.0>180.0	10
8	地茂散	Chloroneb	2675-77-6	8.519	206.0>141.0	20	206.0>113.0	24
9	2-苯基苯酚(邻苯基苯酚)	2-Phenylphenol	90-43-7	8.691	170.1>141.1	24	170.1>115.1	28
10	庚烯磷	heptenophos	23560-59-0	9.204	124>89	15	215>200	10
11	四氯硝基苯	Teonazene	117-18-0	9.454	260.9>202.9	14	260.9>230.9	8
12	梨内二苯胺(二苯胺)	Diphenylamine	122-39-4	9.832	169.1>66.0	24	169.1>77.0	28
13	灭克磷(灭线磷)	Ethoprophos	13194-48-4	9.909	200.0>158.0	6	200.0>114.0	14
14	丁氟消草(乙丁烯氟灵)	Ethalfurailin	55283-68-6	10.039	316.1>276.0	10	316.1>202.0	24
15	氟苯胺灵	Chlorpropham	101-21-3	10.142	213.1>171.1	6	213.1>127.1	14
16	百治磷	Dicrotophos	141-66-2	10.207	127.1>109.0	12	127.1>95.0	18
17	氟乐灵	Trifluralin	1582-09-8	10.209	306.1>264.1	8	306.1>206.1	14
18	氟草胺(乙丁氟灵)	Benfluralin	1861-40-1	10.265	292.1>264.0	8	292.1>206.0	12
19	蔬果磷	Dioxabenzofos (Salithion)	3811-49-2	10.293	216.0>201.0	10	216.0>183.0	10
20	硫特普(治螟磷)	Sulfotep	36889-24-5	10.308	322.0>202.0	10	322.0>294.0	4
21	硫线磷	Cadusafos	95465-99-9	10.452	158.9>130.9	8	158.9>97.0	18
22	甲拌磷	Phorate	298-02-2	10.532	260.0>75.0	8	260.0>231.0	4
23	alpha-六六六	alpha-HCH	319-84-6	10.636	218.9>182.9	8	218.9>144.9	20

24	六氯苯	Hexachlorobenzene	118-74-1	10.706	283.8>248.8	24	283.8>213.8	28
25	甲基乙拌磷 ( 二甲基硫吸磷 )	Thiometon	640-15-3	10.779	125.0>47.0	14	125.0>79.0	10
26	五氯甲氧基苯 ( 五氯茴香醚 )	pentachloroanisole	1825-21-4	10.823	265>237	15	280>265	10
27	氯硝胺	Dicloran	99-30-9	10.892	206.0>176.0	10	206.0>160.0	16
28	绿谷隆	monoinuron	1746-81-2	11.133	126>99	15	214>61	10
29	beta-六六六	beta-HCH	319-85-7	11.135	218.9>182.9	8	218.9>144.9	20
30	噻节因	Dimethipin	55290-64-7	11.138	118.0>58.0	6	118.0>73	2
31	广灭灵 ( 异恶草松 )	Clomazone	81777-89-1	11.196	204.1>107.0	20	204.1>78.0	26
32	五氯硝基苯	Quintozene	82-68-8	11.215	294.8>236.8	16	294.8>264.8	12
33	gamma-六六六	gamma-HCH (Lindane)	58-89-9	11.316	218.9>182.9	8	218.9>144.9	20
34	特丁硫磷	Terbufos	13071-79-9	11.398	231.0>174.9	14	231.0>128.9	26
35	杀螟腈	Cyanophos	2636-26-2	11.399	243.0>109.0	14	243.0>116.0	6
36	大福松 (地虫磷) (地虫硫磷)	Fonofos	944-22-9	11.476	246.0>109.1	18	246.0>137.1	6
37	炔敌唑	Propyzamide	23950-58-5	11.478	172.9>144.9	16	172.9>74.0	28
38	二嗪农 ( 二嗪磷 )	Diazinon	333-41-5	11.533	304.1>179.1	10	304.1>162.1	8
39	磷胺-1	Phosphamidon-1	13171-21-6	11.616	264.1>127.1	14	264.1>193.1	8
40	百菌清	Chlorothalonil	1897-45-6	11.639	265.9>230.8	14	265.9>168.0	22
41	乙拌磷	Disulfoton	298-04-4	11.744	186.0>97.0	16	186.0>153.0	6
42	氰唑磷	Isazophos	42509-80-8	11.774	161.00>119.00	15	161.00>146.10	6
43	特草定	Terbacil	5902-51-2	11.774	161.0>144.0	14	161.0>118.0	14
44	七氟菊酯	Teftuthrin	79538-32-2	11.817	177.0>127.1	16	177.0>137.1	16
45	益多松 ( 乙噻硫磷 )	Erimfos	38260-54-7	11.862	292.1>181.1	8	292.1>153.1	20
46	delta-六六六	delta-HCH	319-86-8	11.864	218.9>182.9	10	218.9>144.9	20
47	野麦畏	Tri-allate	2303-17-5	11.902	268.1>226.0	14	268.1>184.0	20
48	福木松 ( 安硫磷 )	Formothion	2540-82-1	12.160	224.0>125.0	18	224.0>155.0	12
49	磷胺-2	Phosphamidon-2	13171-21-6	12.311	264.1>127.1	14	264.1>193.1	8

50	呋草黄 (呋草磺)	Benfuresate	68505-69-1	12.329	163.1>121.1	6	163.1>135.1	6
51	除线磷	Dichlorfenthion	97-17-6	12.351	279.0>222.9	14	279.0>250.9	8
52	汰草灭(二甲吩草胺)	Dimethenamid (Dimethenamid-P)	87674-68-8	12.369	230.0>154.1	10	230.0>137.1	20
53	敌稗	Propanil	709-98-8	12.388	160.9>99.0	24	160.9>90.0	22
54	甲基毒死蜱	Chlorpyrifos-methyl	5598-13-0	12.473	285.9>93.0	22	285.9>270.9	14
55	噁草酮	Metribuzin	21087-64-9	12.475	198.1>82.0	14	198.1>110.1	10
56	免克宁(乙烯菌核利)	Vinclozolin	50471-44-8	12.548	285.0>212.0	12	285.0>178.0	14
57	甲基对硫磷	Parathion-methyl	298-00-0	12.596	263.0>109.0	14	263.0>136.0	8
58	甲基立枯磷	Tolclofos-methyl	57018-04-9	12.618	264.9>249.9	14	264.9>93.0	24
59	七氟	Heptachlor	76-44-8	12.768	271.8>236.9	20	271.8>117.0	32
60	莠灭净	Ametryn	834-12-8	12.769	227.1>170.1	14	227.1>185.1	6
61	皮蝇磷	Fenchlorphos	299-84-3	12.811	284.9>269.9	16	284.9>93.0	24
62	扑草净	Prometryn	7287-19-6	12.825	241.2>199.1	6	241.2>58.0	14
63	氟硫酸定	Dithiopyr	97886-45-8	12.875	354.1>306.1	8	354.1>286.1	14
64	八氯二丙醚	S421	127-90-2	12.953	130>95	20	181>85	10
65	甲基噻啶磷	Pirimiphosmethyl	29232-93-7	13.043	305.1>180.1	8	305.1>290.1	12
66	杀螟硫磷	Fenitrothion	122-14-5	13.092	277.0>260.0	6	277.0>109.1	14
67	乙味草黄	Ethofumesate	26225-79-6	13.135	286.1>207.1	8	286.1>161.1	18
68	甲基五氯苯基硫醚	methyl pentachlorophenyl sulfide	1825-19-0	13.183	296<263	15	246>211	20
69	抑菌灵	Dichlofluanid	1085-98-9	13.231	223.9>123.1	8	223.9>77.0	28
70	甲拌磷亚矾	Phorate sulfoxide	2588-03-6	13.287	125.00>97.00	9	125.00>115.00	3
71	毒死蜱	Chlorpyrifos	2921-88-2	13.405	313.9>257.9	14	313.9>285.9	8
72	甲拌磷砒	Phorate sulfone	2588-04-7	13.415	153.00>97.00	15	153.00>125.00	6
73	(E)-甲基毒虫畏	(E)-Dimethylvinphos	2274-67-1	13.439	294.9>109.0	14	294.9>279.9	16
74	(Z)-甲基毒虫畏	(Z)-Dimethylvinphos	2274-67-1	13.439	294.9>109.0	14	294.9>279.9	16
75	艾氏剂	Aldrin	309-00-2	13.476	262.9>193.0	28	262.9>203.0	26

76	倍硫磷	Fenthion	55-38-9	13.484	278.0>109.0	20	278.0>125.0	20
77	氟酞酸甲酯	Chlorthal-dimethyl	1861-32-1	13.499	300.9>222.9	26	300.9>272.9	14
78	对硫磷	Parathion	56-38-2	13.552	291.1>109.0	14	291.1>137.0	6
79	三奈芬(三唑酮)	Triadimefon	43121-43-3	13.615	208.1>181.0	10	208.1>127.0	14
80	四克利(四氟醚唑)	Tetraconazole	112281-77-3	13.615	336.0>218.0	14	336.0>204.0	28
81	水胺硫磷	Isocarbophos	24353-61-5	13.634	289.1>136.0	14	289.1>113.0	6
82	三氯杀螨醇分解物(三氯杀螨醇)	Dicofol deg. (DCBP)	0-00-0	13.699	250.0>139.0	14	250.0>215.0	8
83	酞菌酯	Nitrothal-isopropyl	10552-74-6	13.705	254.1>212.0	10	254.1>165.0	22
84	氟咯草酮	Fluorochloridone	61213-25-0	13.711	311.00>174.10	15	311.00>103.10	18
85	乙基虫螨磷/噁啶磷	pirimiphos-ethyl	23505-41-1	13.828	304>168	10	318>166	15
86	溴硫磷	Bromophos	2104-96-3	13.829	330.9>315.9	14	330.9>285.9	28
87	牧草谢(双苯酰草胺)	Diphenamid	957-51-7	13.846	167.1>152.1	20	167.1>128.1	26
88	噻唑膦-1(噻唑膦)	Fosfthiazetel	98886-44-3	13.909	283.0>195.0	8	283.0>103.0	18
89	甲基异柳磷	Isofenphos-methyl	99675-03-3	13.944	199.0>121.0	14	241.1>121.1	22
90	二甲戊乐灵	Pendimethalin	40487-42-1	14.044	252.1>162.1	10	252.1>191.1	8
91	异艾氏剂	Isodrin	465-73-6	14.045	193.00>123.00	30	193.00>157.00	21
92	(E)-毒虫畏	(E)-Chlorfenvinphos	470-90-6	14.048	323.0>267.0	16	323.0>295.0	6
93	噁菌环胺	Cyprodinil	121552-61-2	14.065	224.1>208.1	16	224.1>197.1	22
94	氟虫腓	Fipronil	120068-37-3	14.132	366.9>212.9	30	366.9>254.9	22
95	平克座(戊菌唑)	Penconazole	66246-88-6	14.168	248.1>192.1	14	248.1>157.1	26
96	环氧七氯(exo)	Heptachlor-exo-epoxide	1024-57-3	14.196	352.8>262.9	14	352.8>281.9	12
97	乙菌利(克氯得)	Chlozolinate	84332-86-5	14.221	330.9>258.9	6	330.9>186.0	20
98	亚芬松(异柳磷)	Isofenphos	25311-71-1	14.222	213.1>1211	14	213.1>185.1	6
99	(Z)-毒虫畏	(Z)-Chlorfenvinphos	470-90-6	14.252	323.0>267.0	16	323.0>295.0	6
100	环氧七氯(endo)	Heptachlor-endo-epoxide	28044-83-9	14.253	352.8>289.0	6	352.8>253.0	26
101	吡蚜酮	Ethychlozate	27512-72-7	14.293	238.1>165.0	12	238.1>138.0	28

102	灭蚜磷	Mecarbam	2595-54-2	14.321	329.0>131.1	18	329.0>159.1	4
103	稻丰散	Phenthoate	2597-03-7	14.350	273.9>125.0	20	273.9>246.0	6
104	喹硫磷	Quinalphos	13593-03-8	14.370	157.1>129.0	14	146.1>1180	10
105	呋霜灵	furalaxyl	57646-30-7	14.394	242>95	15	301>224	20
106	克菌丹	Captan	133-06-2	14.405	149.1>105.1	4	149.1>79.1	14
107	腐霉利	Procyimdone	32809-16-8	14.432	283.0>96.0	10	283.0>255.0	12
108	乙基溴硫磷	Bromophos-ethyl	4824-78-6	14.634	358.9>302.9	16	358.9>330.9	10
109	反-氟丹	trans-Chlordane	5103-74-2	14.671	372.8>336.8	10	372.8>263.9	28
110	氟杀螨	Chlorbenside	103-17-3	14.683	125.0>89.0	16	125.0>99.0	18
111	加护松 (丙虫磷)	Propaphos	7292-16-2	14.688	304.1>140.1	26	304.1>220.1	14
112	o,p'-DDE	o,p'-DDE	3424-82-6	14.733	246.0>176.0	30	246.0>211.0	22
113	杀虫威 (杀虫畏)	Tetrachlorvinphos	22248-79-9	14.758	328.9>109.0	20	328.9>313.9	18
114	多效唑	Pacloutrazol	76738-62-0	14.790	236.1>125.0	14	236.1>167.0	10
115	丁基拉草 (丁草胺)	Butachlor	23184-66-9	14.820	188.1>160.1	12	188.1>146.1	14
116	顺-氟丹	cis-Chlordane	5103-71-9	14.936	372.8>336.8	10	372.8>263.9	28
117	alpha-硫丹	alpha-Endosulfan	959-98-8	14.943	338.9>160.0	18	338.9>266.9	8
118	克线磷 (苯线磷)	Fenamiphos	2222-492-6	15.042	303.1>195.1	8	303.1>154.1	18
119	秦丙酰草胺 (敌草胺)	Napropamide	15299-99-7	15.074	128.1>72.0	6	128.1>57.0	12
120	福多宁 (氟酰胺)	Flutolanil	66332-96-5	15.108	173.0>145.0	14	173.0>95.0	26
121	普硫松 (丙硫磷)	Prothiofos	34643-46-4	15.184	309.0>238.9	14	309.0>280.9	10
122	丙溴磷	Profenofos	41198-08-7	15.266	336.9>266.9	14	336.9>308.9	6
123	p,p'-DDE	p,p'-DDE	72-55-9	15.348	246.0>176.0	30	246.0>211.0	22
124	脱叶磷	Tribufos	78-48-8	15.392	258.0>202.0	4	258.0>147.0	10
125	灭克落	Myclobutanil	88671-89-0	15.418	179.1>125.0	14	179.1>152.0	8
126	狄氏剂 (地特灵)	Dieldrin	60-57-1	15.459	276.9>241.0	8	276.9>170.0	38
127	氟硅唑	Flusilazole	85509-19-9	15.459	233.1>165.1	14	233.1>152.1	14

180	氟唑唑	Fluquinconazole	136426-54-5	19.637	340.0>298.0	20	340.0>313.0	14
181	敌杀磷	Dioxathion	78-34-2	19.679	271.0>153.0	8	271.0>125.0	14
182	氟氯氰菊酯-1	Cyfluthrin-1	68359-37-5	20.033	226.1>206.1	14	226.1>199.1	6
183	氟氯氰菊酯-2	Cyfluthrin-2	68359-37-5	20.144	226.1>206.1	14	226.1>199.1	6
184	氟氯氰菊酯-3	Cyfluthrin-3	68359-37-5	20.201	226.1>206.1	14	226.1>199.1	6
185	氟氯氰菊酯-4	Cyfluthrin-4	68359-37-5	20.241	226.1>206.1	14	226.1>199.1	6
186	氯氰菊酯-1	Cypermethrin-1	52315-07-8	20.363	181.1>152.1	22	181.1>127.1	22
187	氯氰菊酯-2	Cypermethrin-2	52315-07-8	20.464	181.1>152.1	22	181.1>127.1	22
188	氯氰菊酯-3	Cypermethrin-3	52315-07-8	20.520	181.1>152.1	22	181.1>127.1	22
189	氟氰菊酯(氟氰戊菊酯)-1	Flucythrinate-1	70124-77-5	20.526	199.1>157.1	10	199.1>107.1	22
190	氯氰菊酯-4	Cypermethrin-4	52315-07-8	20.562	181.1>152.1	22	181.1>127.1	22
191	依芬宁(醚菊酯)	Etofenprox	80844-07-1	20.683	163.1>135.1	10	163.1>107.1	18
192	氟氰菊酯(氟氰戊菊酯)-2	Flucythrinate-2	70124-77-5	20.720	199.1>157.1	10	199.1>107.1	22
193	硅醚菊酯	Silaflufen	105024-66-6	20.822	286.1>258.1	14	286.1>207.1	14
194	氟啶草酮	Fluridone	59756-60-4	20.897	328.1>259.0	24	328.1>313.0	22
195	氟戊菊酯-1	Fenvalerate-1	51630-58-1	21.243	419.1>225.1	6	419.1>167.1	12
196	氟胺氰菊酯-1	Fluvalinate-1	102851-06-9	21.356	250.1>55.0	20	250.1>200.0	20
197	氟胺氰菊酯-2	Fluvalinate-2	102851-06-9	21.421	250.1>55.0	20	250.1>200.0	20
198	氟戊菊酯-2(S-氟戊菊酯)	Fenvalerate-2 (Esfenvalerate)	51630-58-1	21.444	419.1>225.1	6	419.1>167.1	12
199	溴氰菊酯-1	Deltamethrin-1 (Tralomethrin deg. 1)	52918-63-5	21.798	252.9>93.0	20	252.9>171.9	8
200	溴氰菊酯-2	Deltamethrin-2 (Tralomethrin deg. 2)	52918-63-5	22.002	252.9>93.0	20	252.9>171.9	8
201	恶唑酮菌(恶唑菌酮)	Famoxadone	131807-57-3	22.394	330.1>224.1	10	330.1>196.1	22

备注：中文名称中部分农药带（）为同一农药在岛津MRM农残数据库中的名称和在中国常用的农药名称

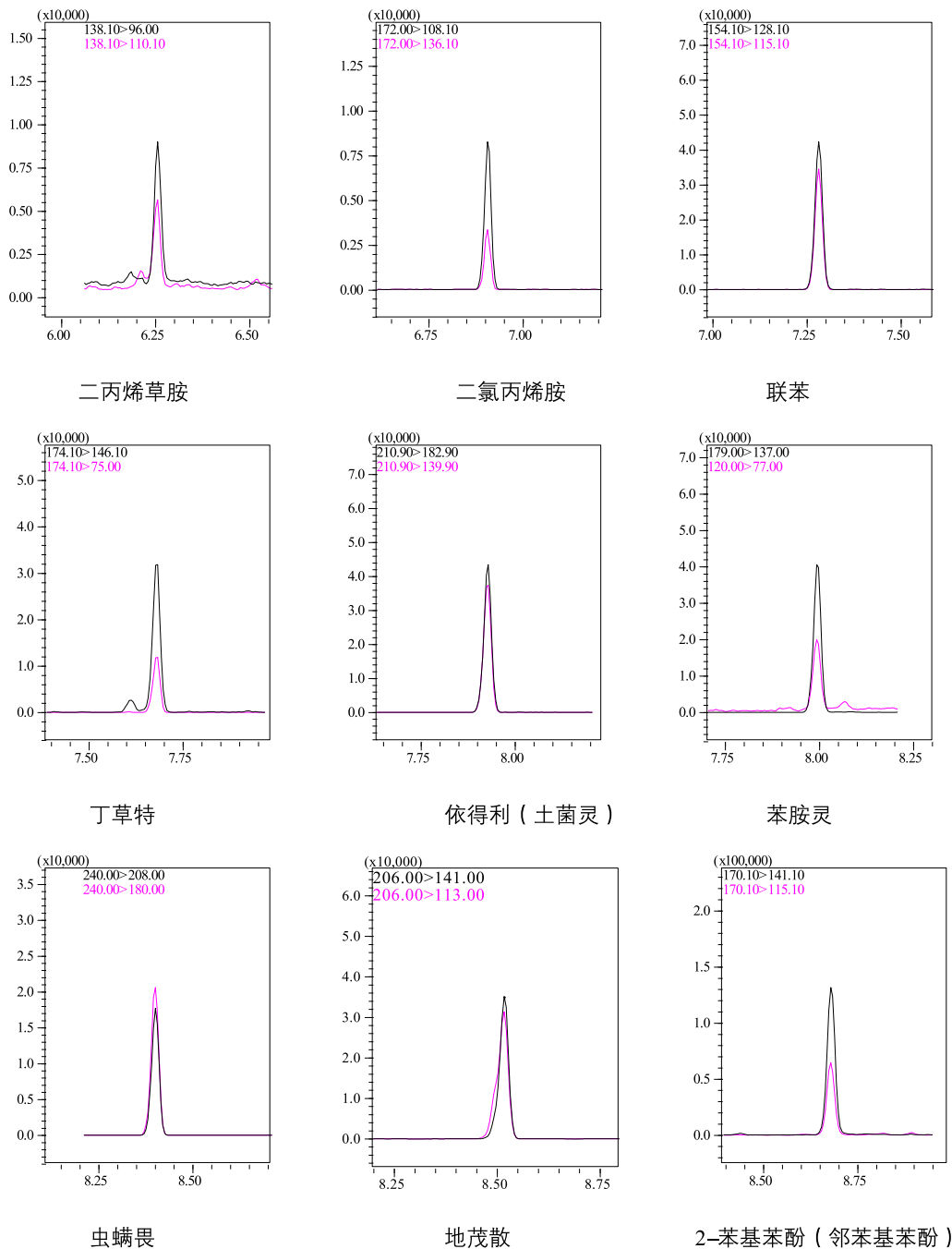
### 1.3 样品前处理

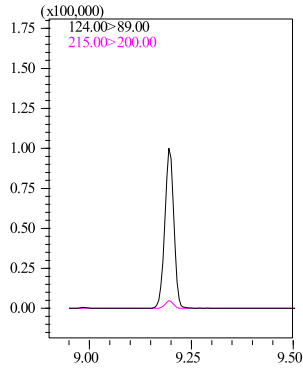
准确称取 10 g 试样，于 50 mL 离心管中，加入 10 mL 乙腈，用均质机高速匀浆 1 min。加入 8-12 g 氯化钠，旋涡混合后，静置 2 h，待分层。取 1 mL 上清液，QuEChERS 净化，过膜，氮吹至干，丙酮定容至 1 mL，加 174 种农药混标（加标浓度为 10 μg/L）。

## 结果讨论

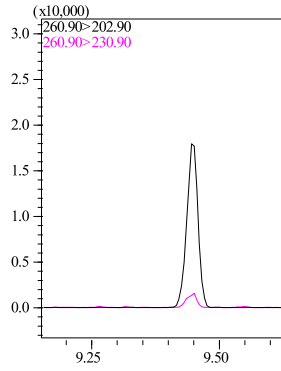
### 2.1 葡萄基质中 174 种农药残留（浓度为 10 μg/L）灵敏度考察

葡萄基质中 174 种农药残留（浓度为 10 μg/L）的质量色谱图见图 1。

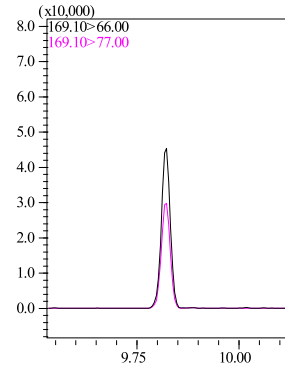




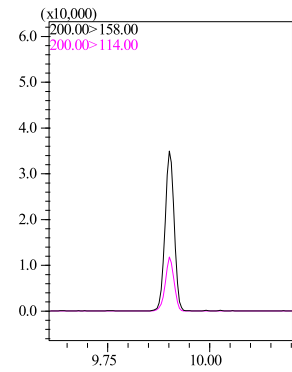
庚烯磷



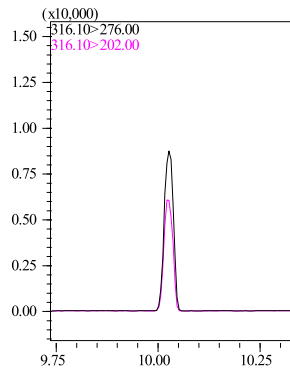
四氯硝基苯



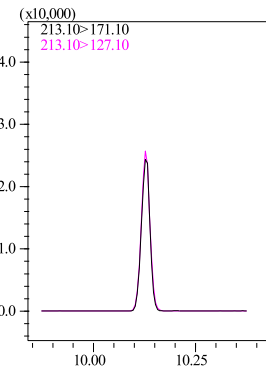
梨内二苯胺(二苯胺)



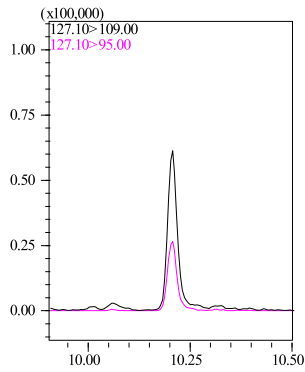
灭克磷 (灭线磷)



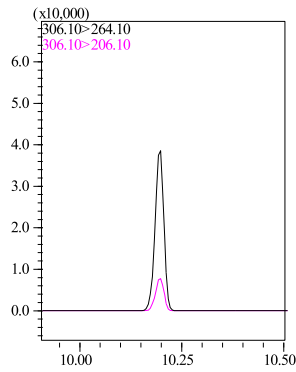
丁氟消草(乙丁烯氟灵)



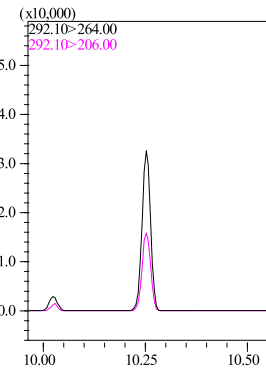
氯苯胺灵



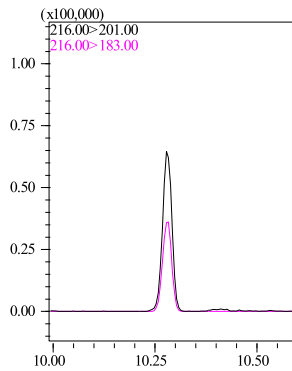
百治磷



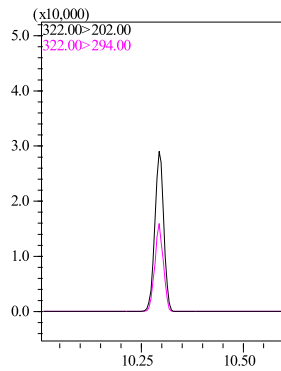
氟乐灵



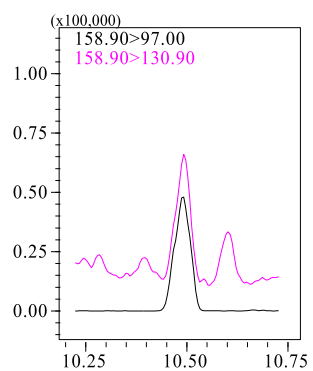
氟草胺 (乙丁氟灵)



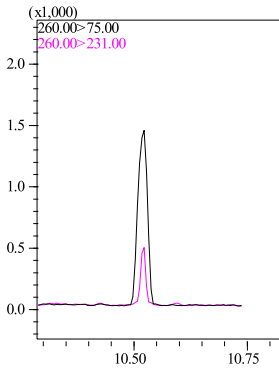
蔬果磷



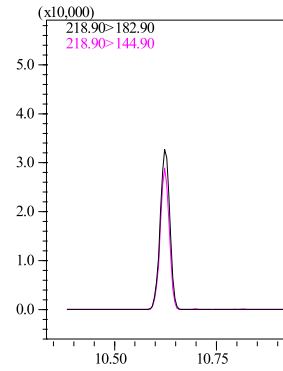
硫特普 (治螟磷)



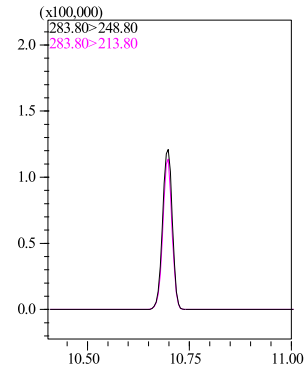
硫线磷



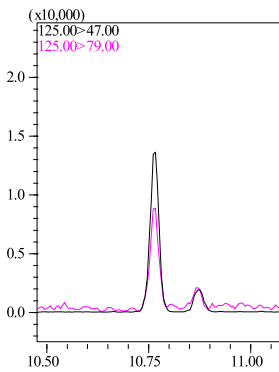
甲拌磷



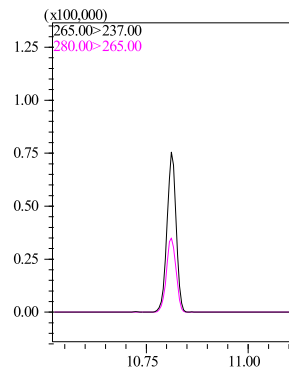
alpha-六六六



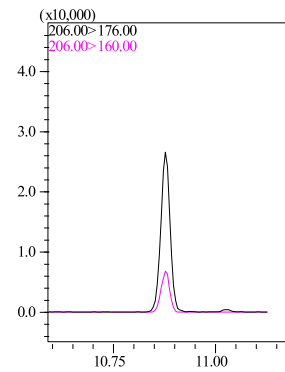
六氯苯



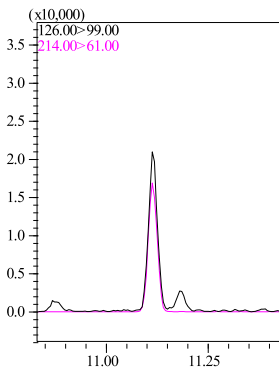
甲基乙拌磷 (二甲基硫吸磷)



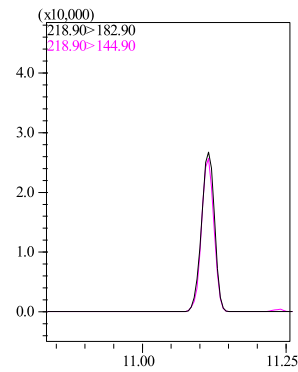
五氯甲氧基苯 (五氯茴香醚)



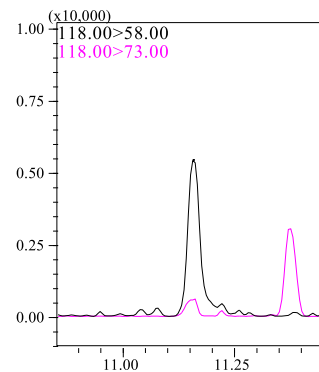
氯硝胺



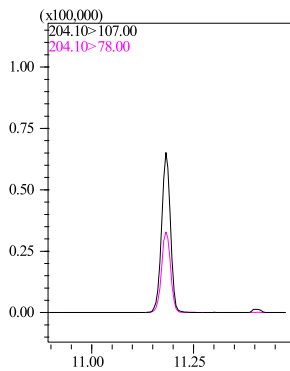
绿谷隆



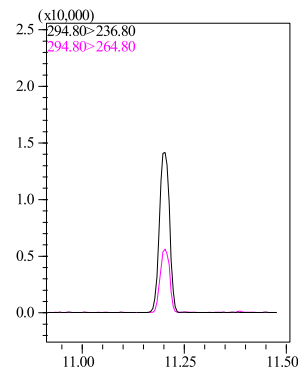
beta-六六六



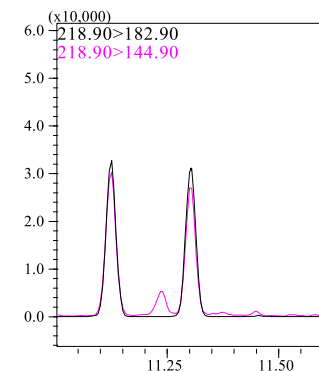
噻节因



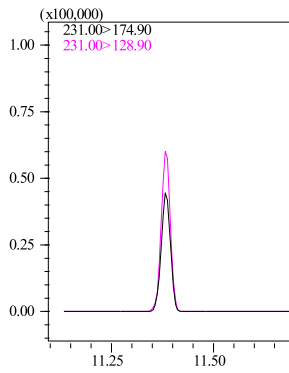
广灭灵 (异恶草松)



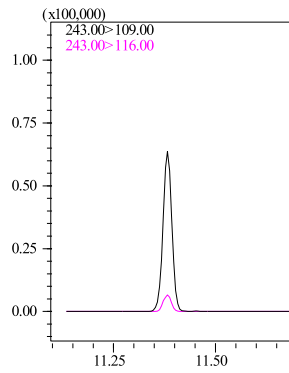
五氯硝基苯



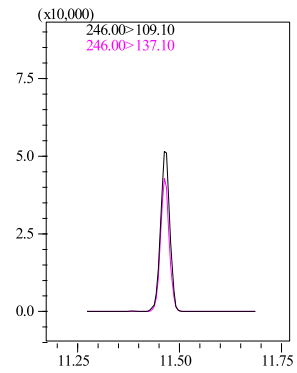
gamma-六六六



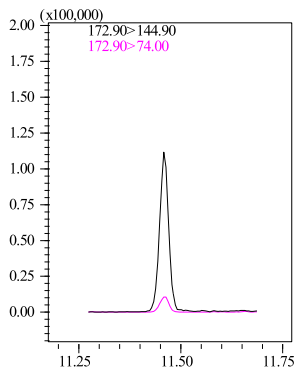
特丁硫磷



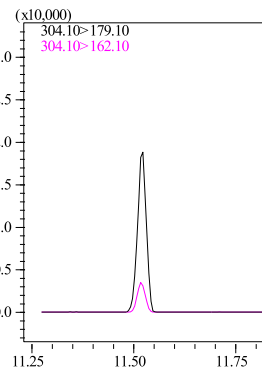
杀螟腈



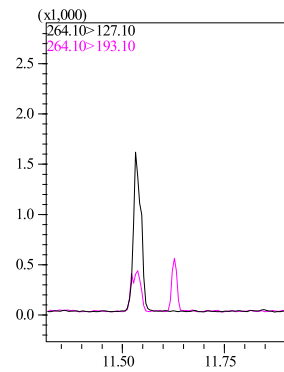
大福松(地虫磷) (地虫硫磷)



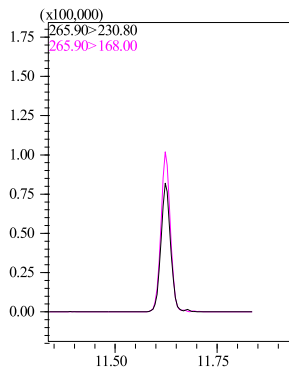
炔敌稗



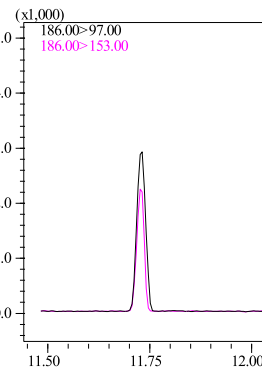
二嗪农 (二嗪磷)



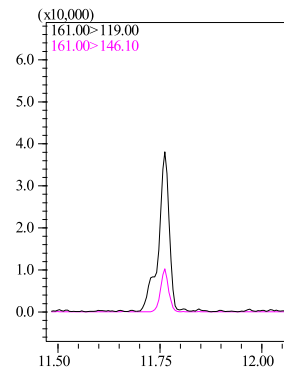
磷胺-1



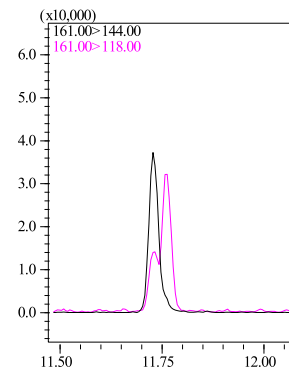
百菌清



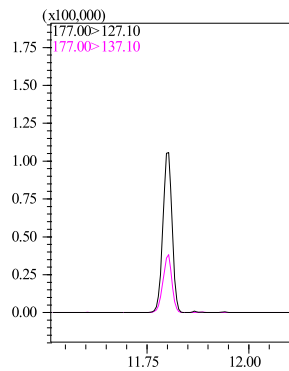
乙拌磷



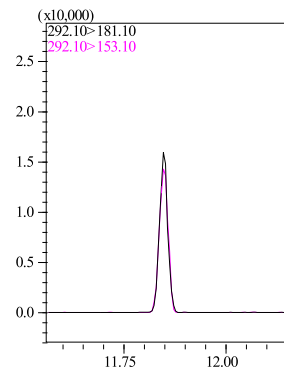
氯唑磷



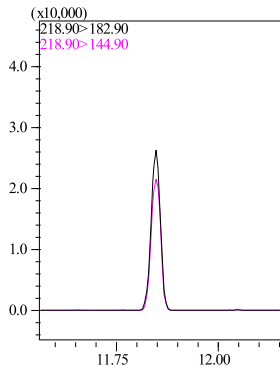
特草定



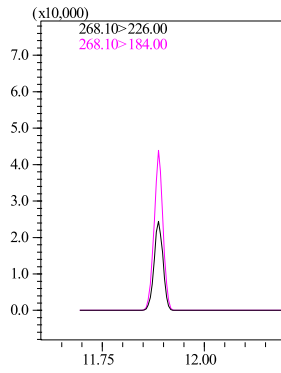
七氟菊酯



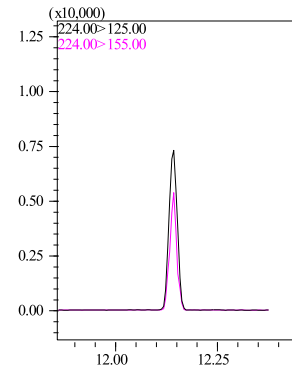
益多松 (乙噻硫磷)



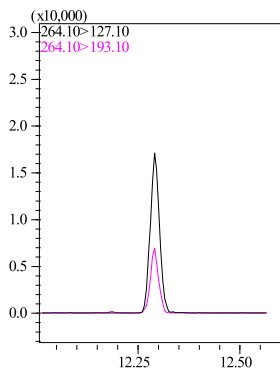
delta-六六六



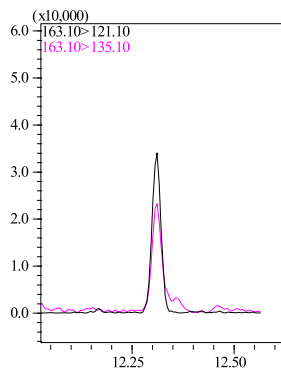
野麦畏



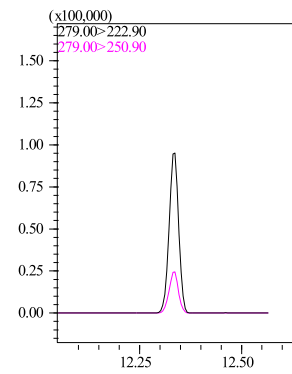
福木松 (安硫磷)



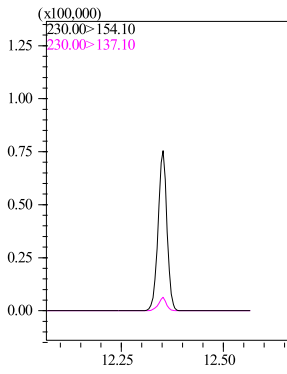
磷胺-2



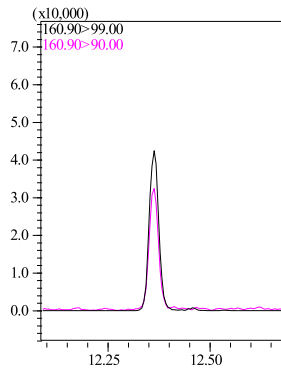
呋草黄 (呋草磺)



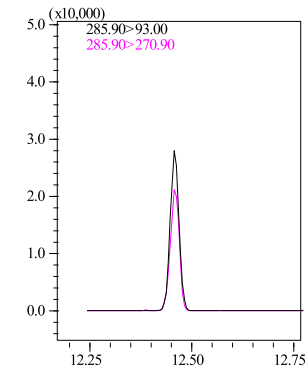
除线磷



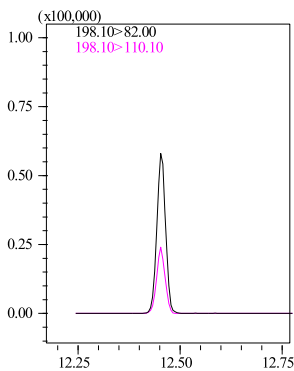
汰草灭(二甲吩草胺)



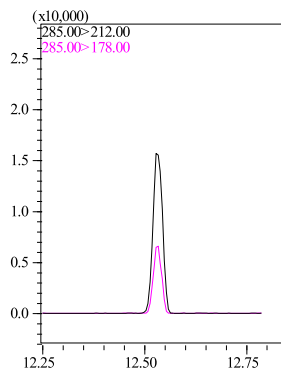
敌稗



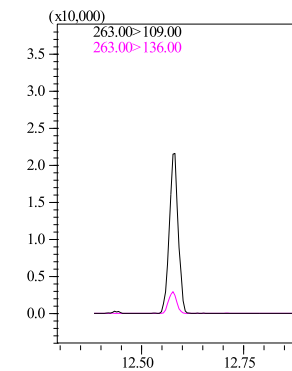
甲基毒死蜱



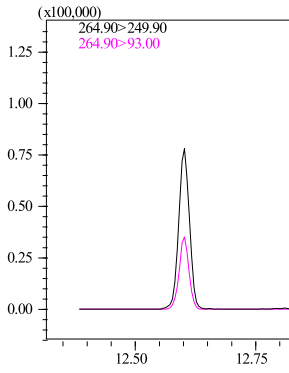
噻草酮



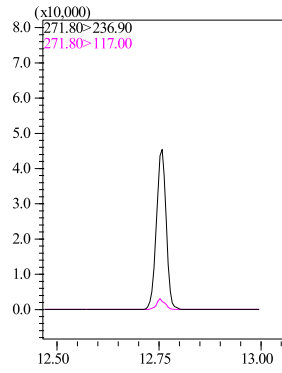
免克宁(乙烯菌核利)



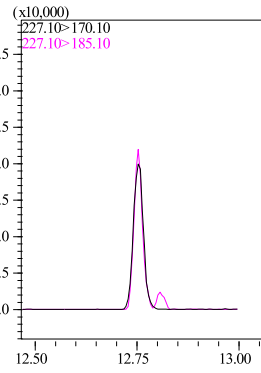
甲基对硫磷



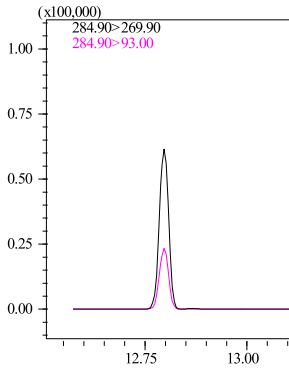
甲基立枯磷



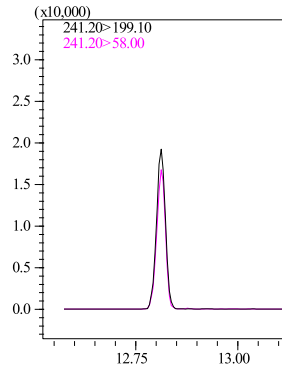
七氯



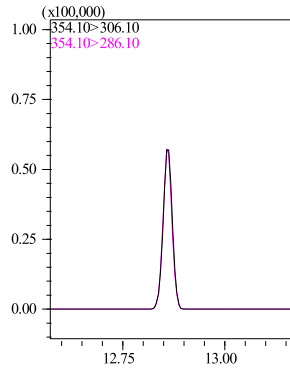
莠灭净



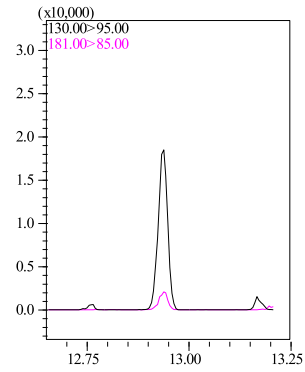
皮蝇磷



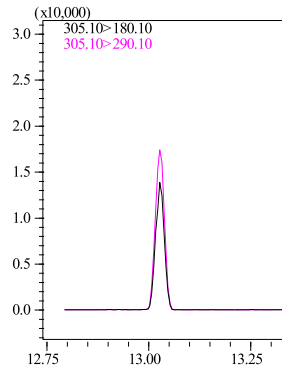
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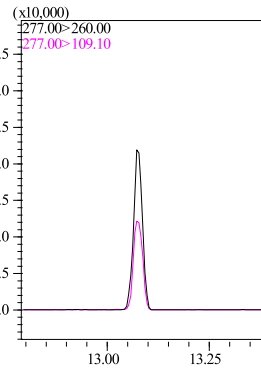
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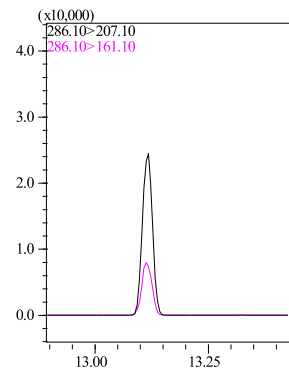
八氯二丙醚



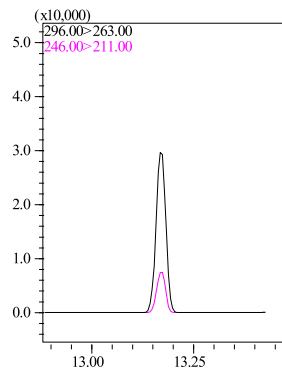
甲基嘧啶磷



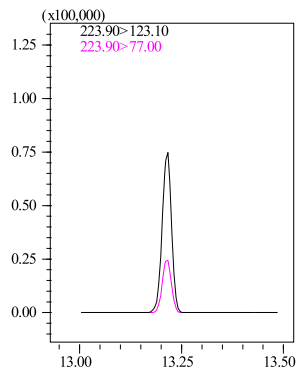
杀螟硫磷



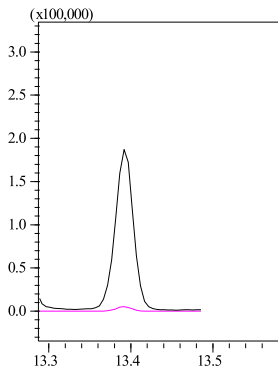
乙呋草黄



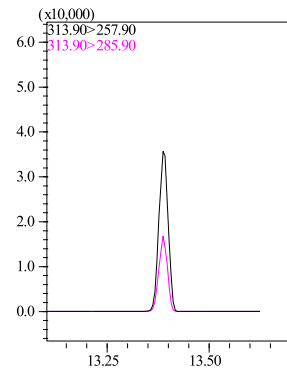
甲基五氯苯基硫醚



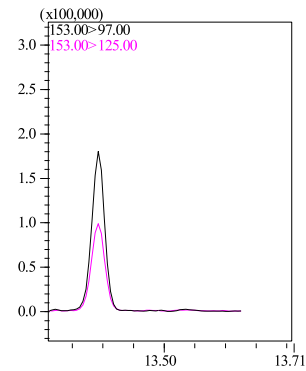
抑菌灵



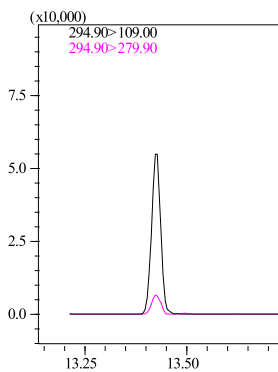
甲拌磷亚砷



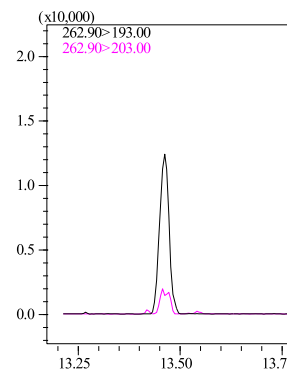
毒死蜱



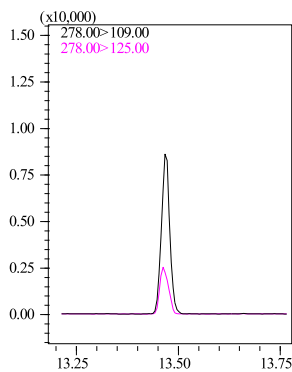
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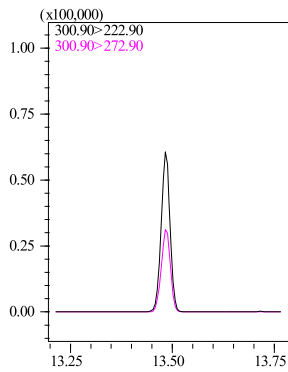
(E,Z)-甲基毒虫畏



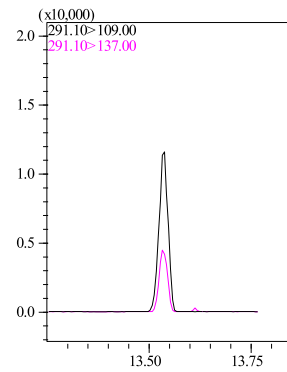
艾氏剂



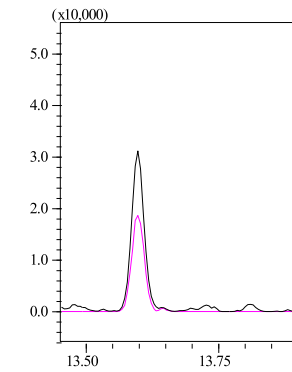
倍硫磷



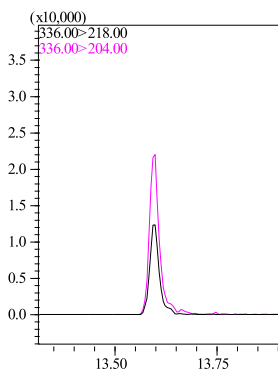
氯酞酸甲酯



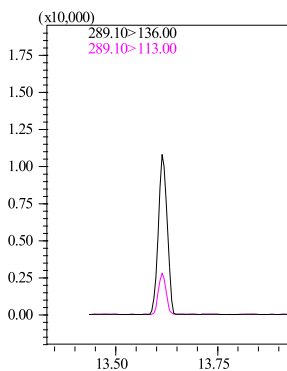
对硫磷



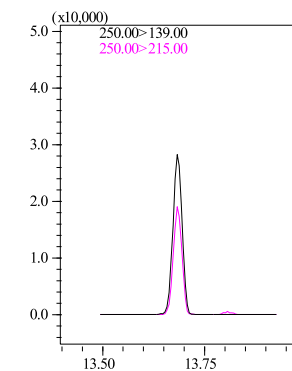
三泰芬(三唑酮)



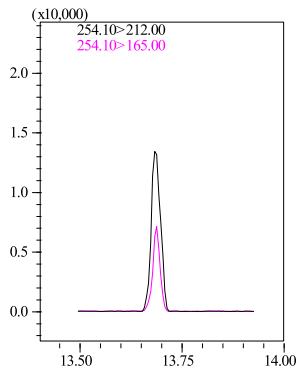
四克利(四氟醚唑)



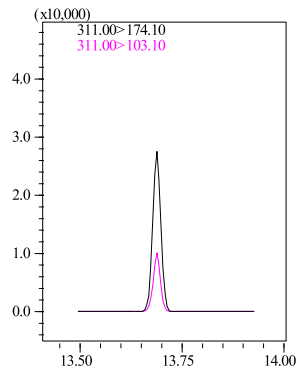
水胺硫磷



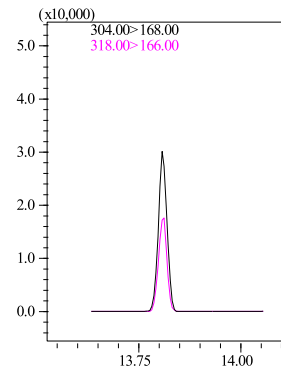
三氯杀螨醇 分解物(三氯杀螨醇)



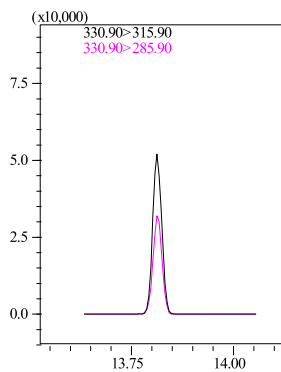
酞菌酯



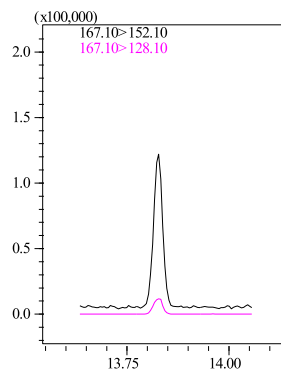
氟咯草酮



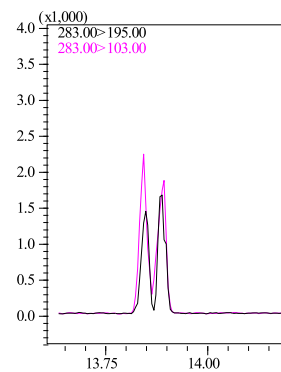
乙基虫磷/啉啶磷



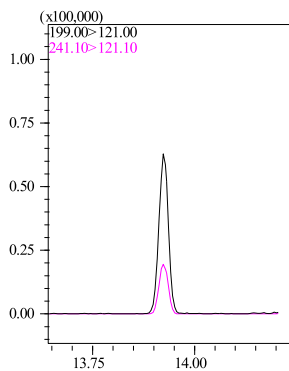
溴硫磷



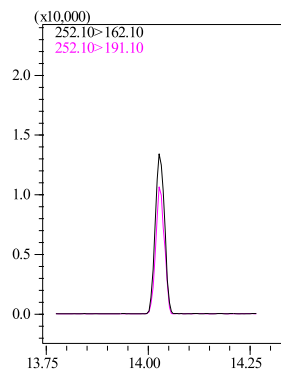
牧草谢 (双苯酰草胺)



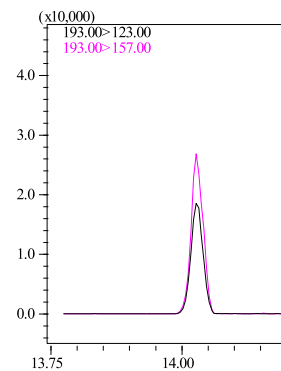
噻唑磷-1 (噻唑磷)



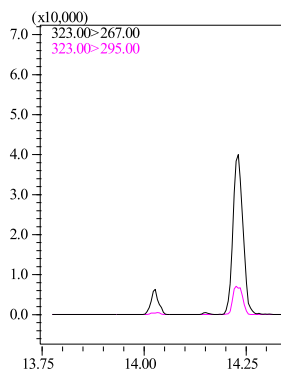
甲基异柳磷



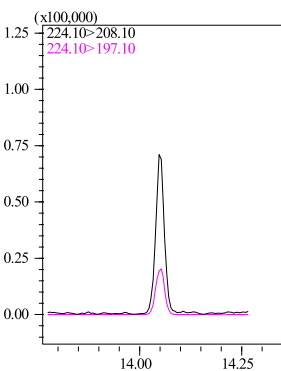
二甲戊乐灵



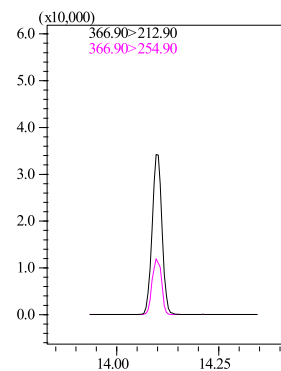
异艾氏剂



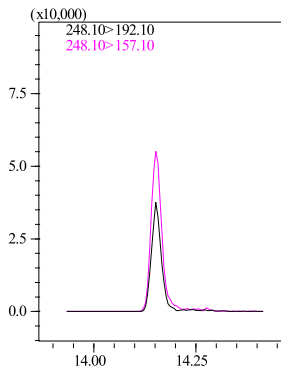
(E,Z)-毒虫畏



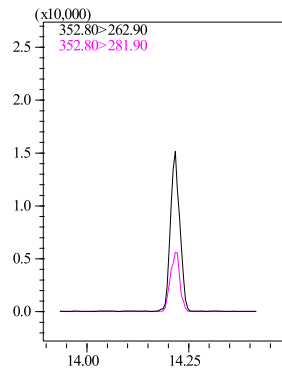
啉菌环胺



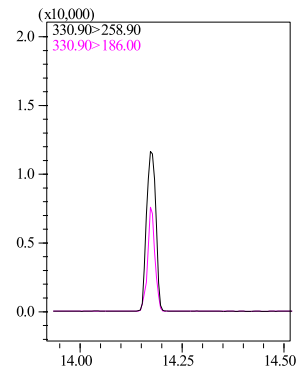
氟虫腈



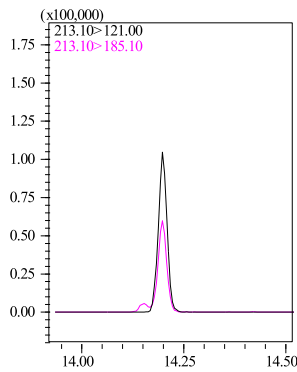
平克座 (戊菌唑)



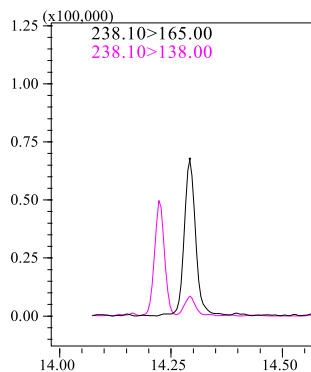
环氧七氯



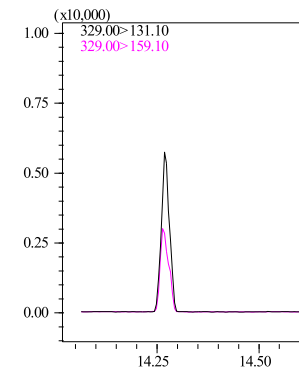
乙菌利 (克氯得)



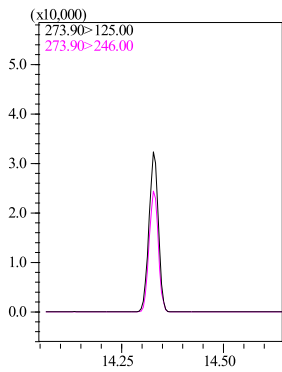
亚芬松 (异柳磷)



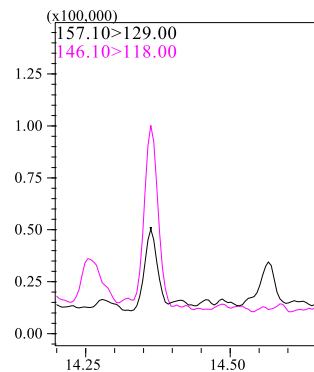
吡啶酯



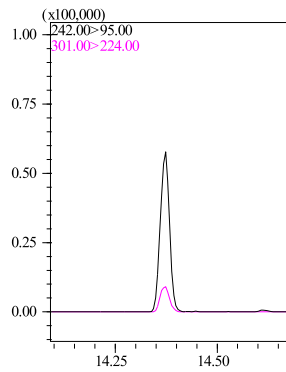
灭蚜磷



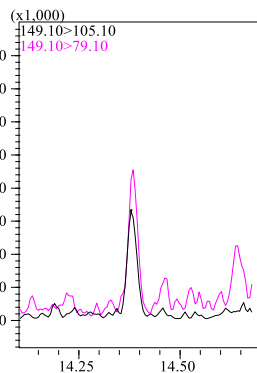
稻丰散



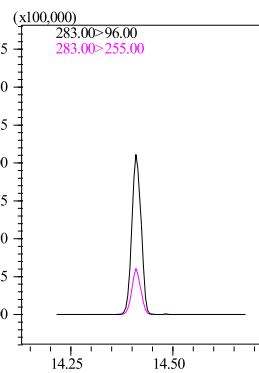
啶硫磷



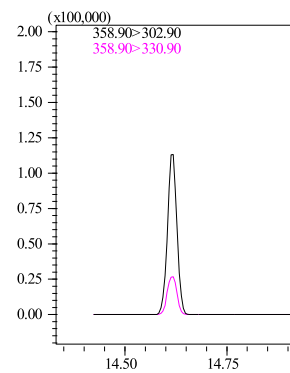
呋霜灵



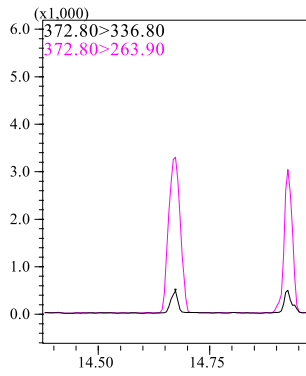
克菌丹



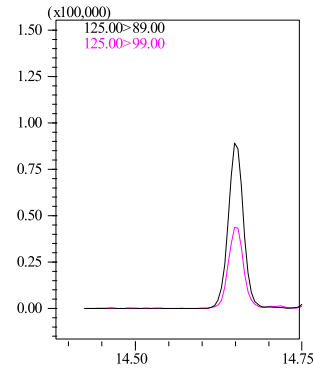
腐霉利



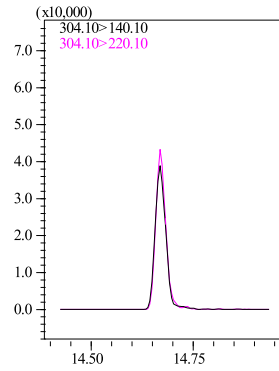
乙基溴硫磷



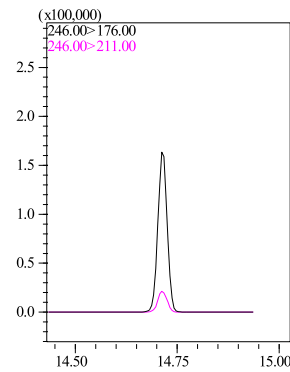
反,顺-氯丹



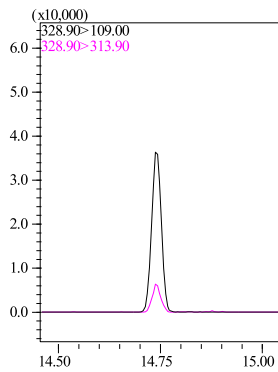
氯杀螨



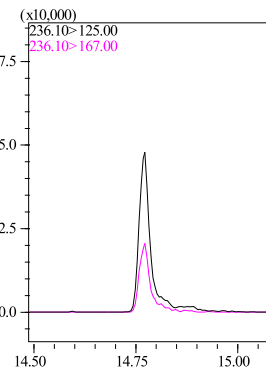
加护松 (丙虫磷)



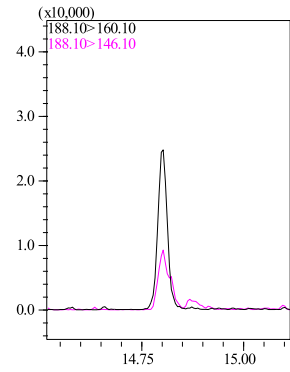
o,p'-DDE



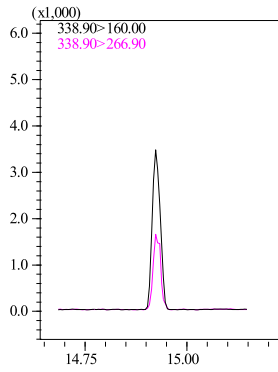
杀虫威 (杀虫畏)



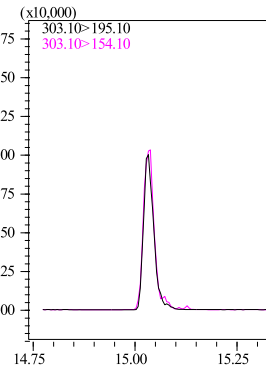
多效唑



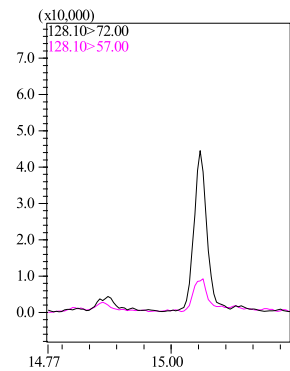
丁基拉草 (丁草胺)



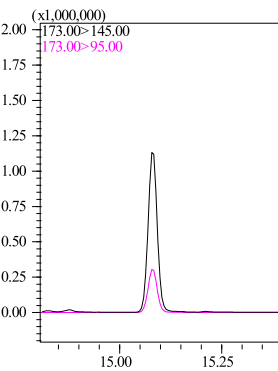
alpha-硫丹



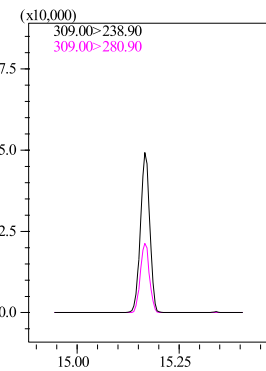
克线磷 (苯线磷)



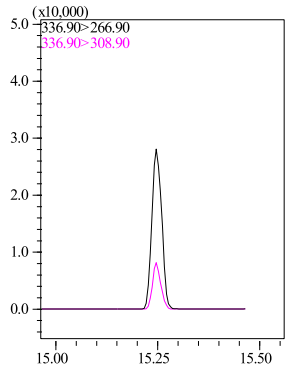
萘丙酰草胺 (敌草胺)



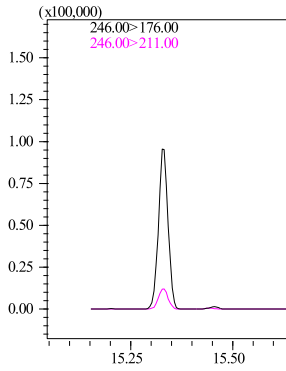
福多宁 (氟酰胺)



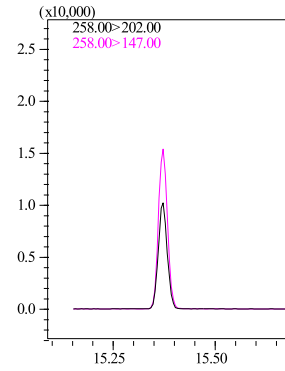
普硫松 (丙硫磷)



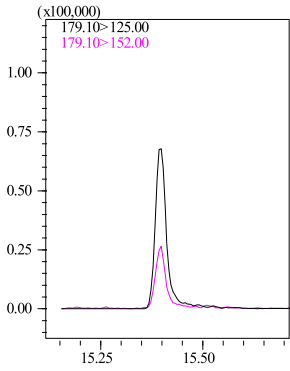
丙溴磷



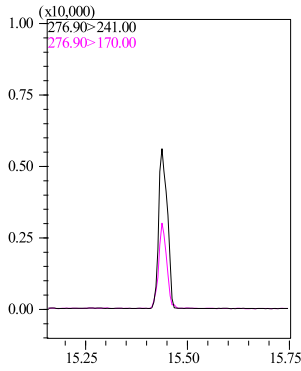
p,p'-DDE



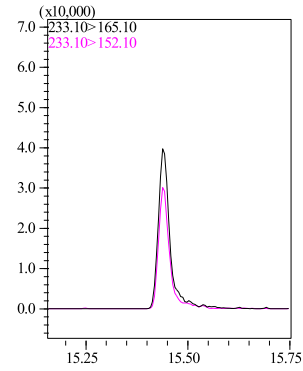
脱叶磷



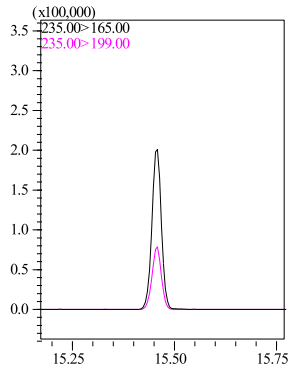
灭克落



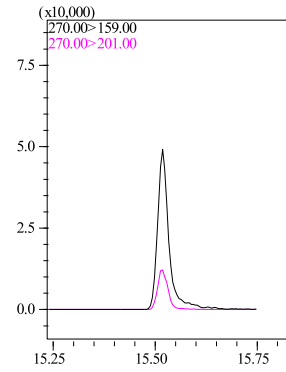
狄氏剂 (地特灵)



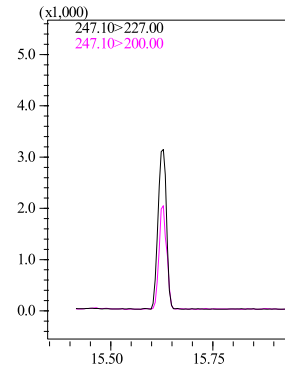
氟硅唑



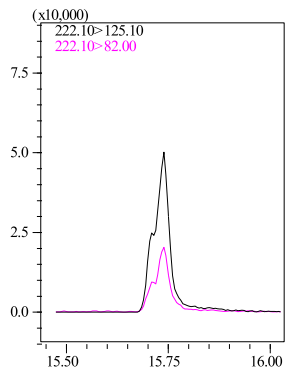
o,p'-DDD



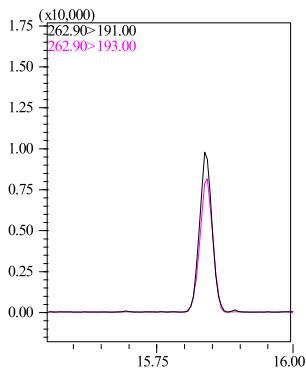
苯氧三唑醇



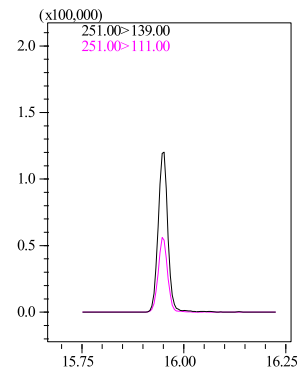
克凡派 (虫螨腈)



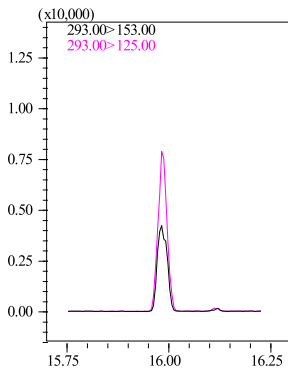
环唑醇-1,2



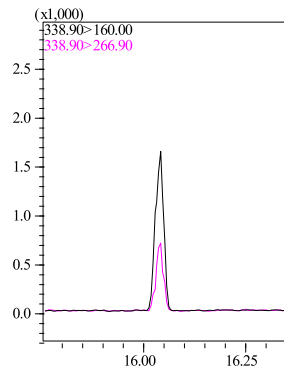
异狄氏剂



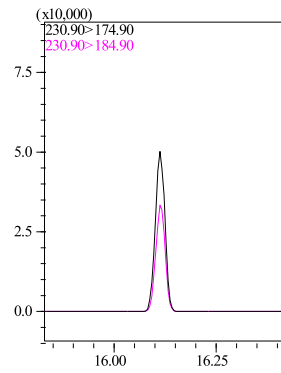
杀螨酯(乙酯杀螨醇)



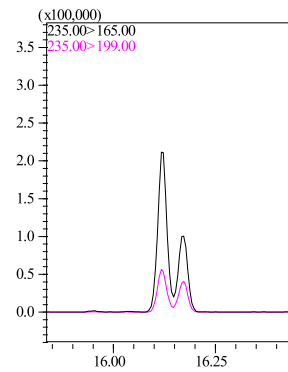
丰索磷



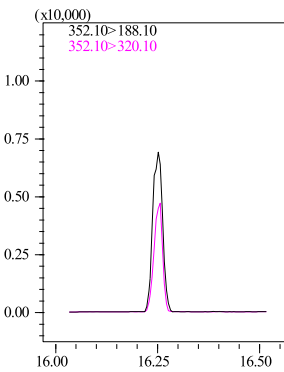
beta-硫丹



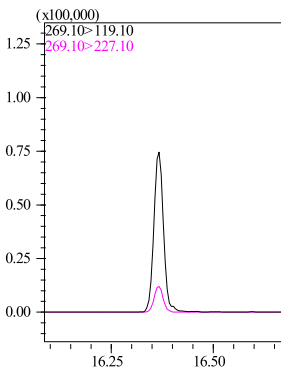
爱杀松(乙硫磷)



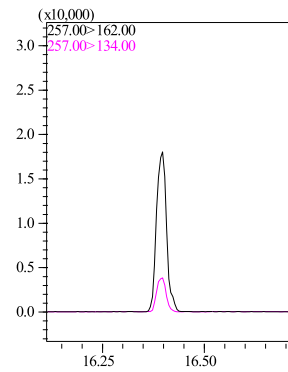
p,p'-DDD \ o,p'-DDT



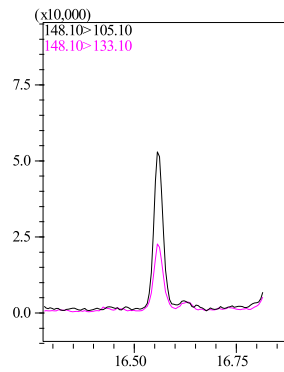
噻螨酯



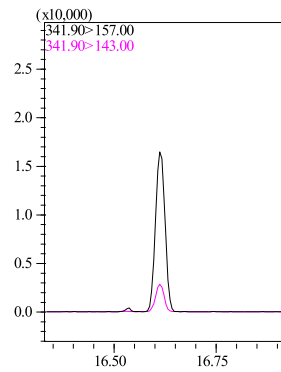
灭普宁(灭锈胺)



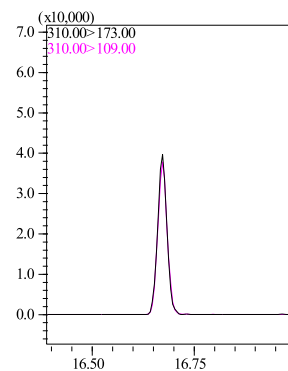
三唑磷



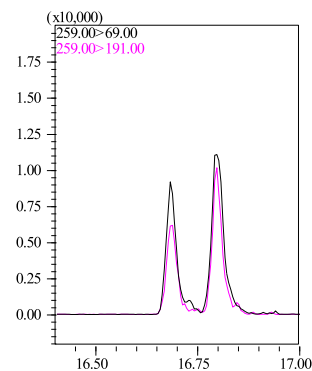
本达乐(苯霜灵)



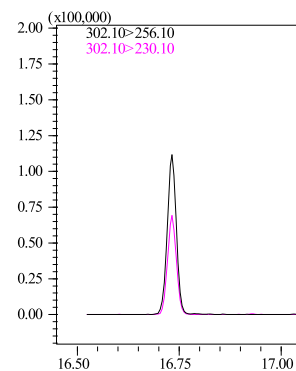
三硫磷



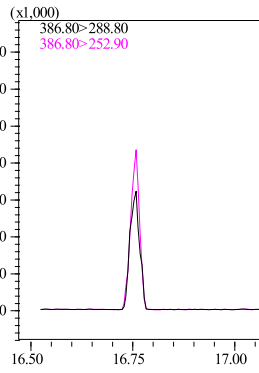
克温散(敌瘟磷)



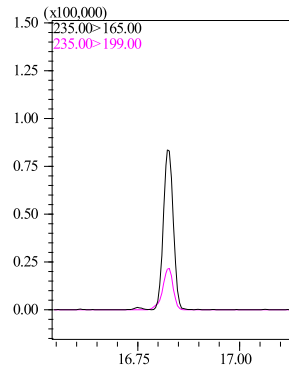
丙环唑-1,2



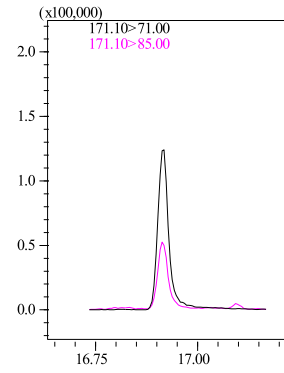
(Z,E)-甲基嘧草醚



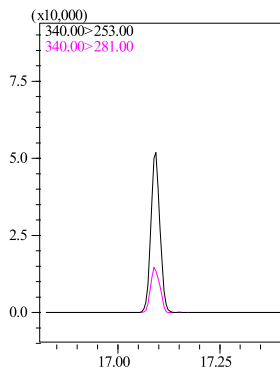
硫丹硫酸酯



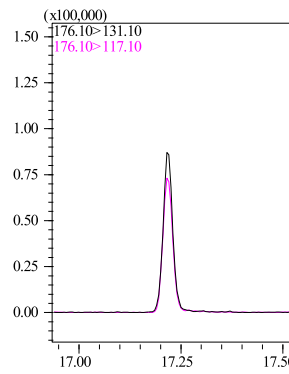
p,p'-DDT



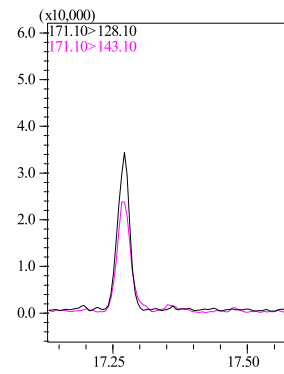
环磷酮



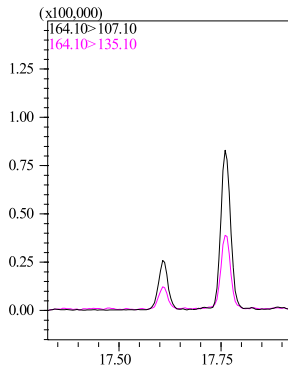
百草灵



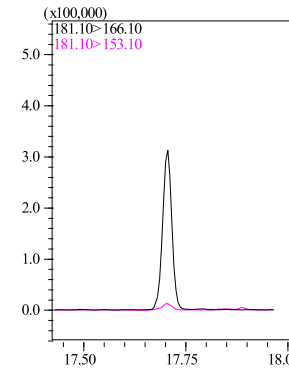
胡椒基丁醚 (增效醚)



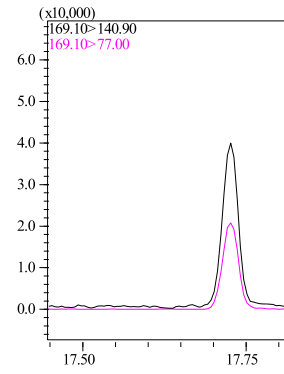
苯呋菊酯



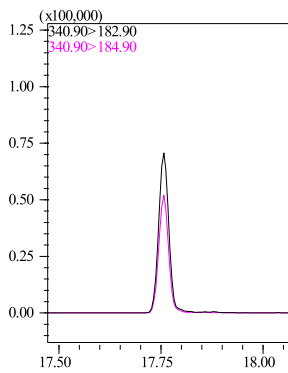
胺菊酯-1,2



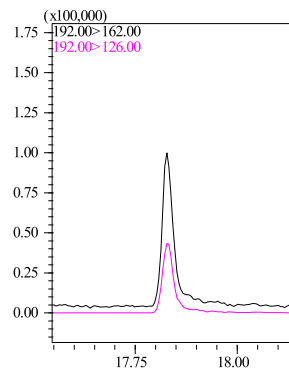
联苯菊酯



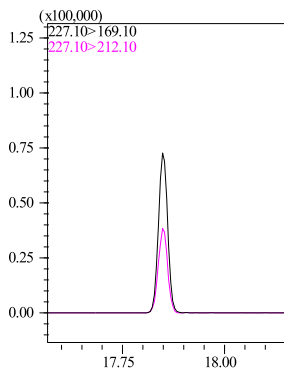
苯硫磷



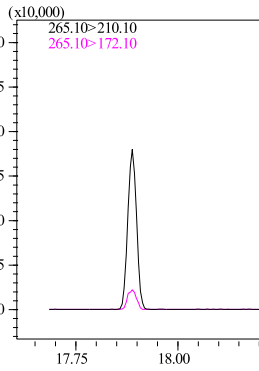
溴螨酯



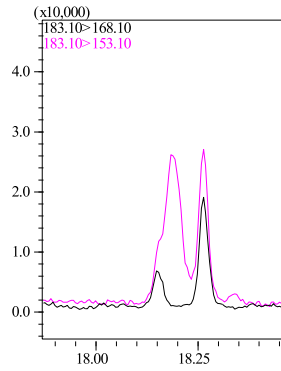
解毒啉



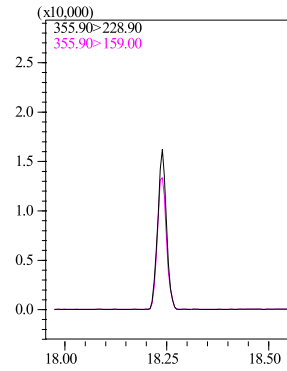
甲氧滴滴涕 (甲氧氯)



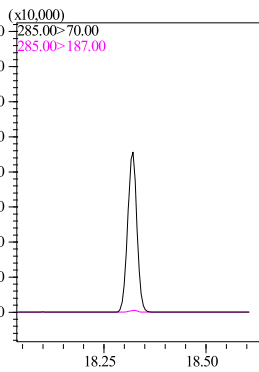
芬普宁 (甲氰菊酯)



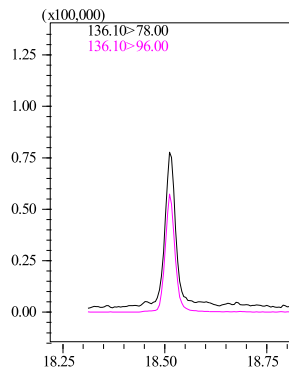
苯醚菊酯-1,2



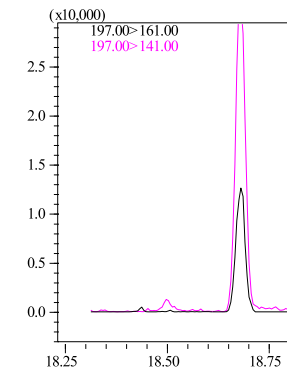
四氯杀螨砜 (三氯杀螨砜)



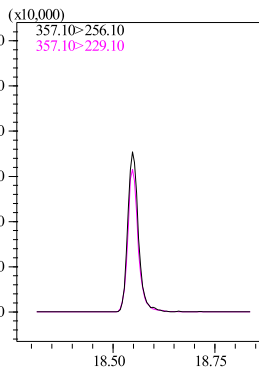
戊晴草酮 (戊基恶唑酮)



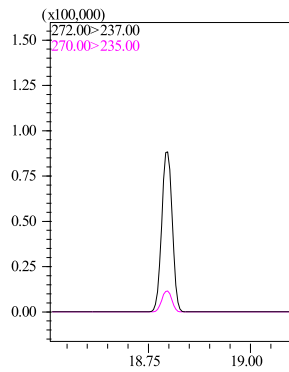
吡丙醚 (蚊蝇醚)



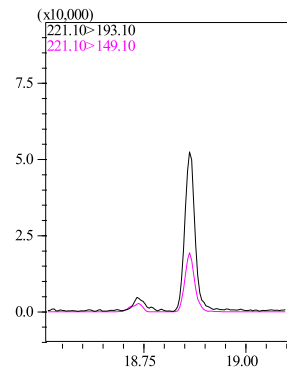
氯氟氰菊酯-1,2



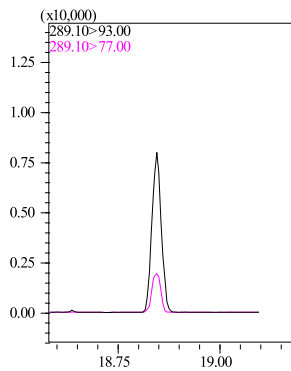
氰氟草酯



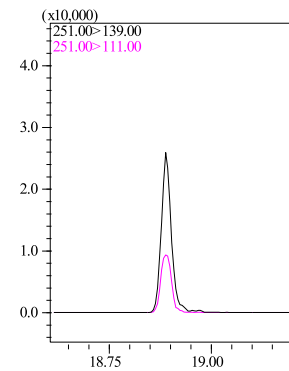
灭蚁灵



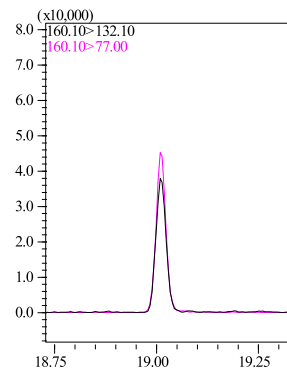
定菌磷 (吡菌磷)



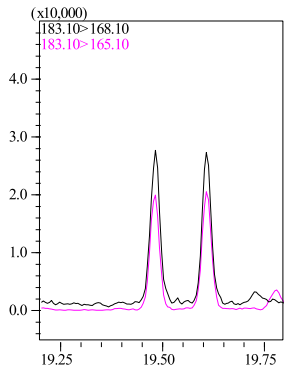
氟丙菊酯



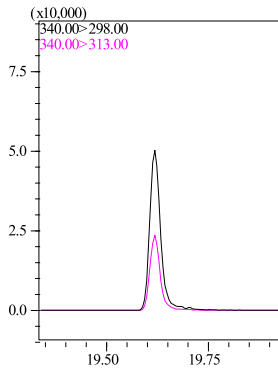
氯苯嘧啶醇



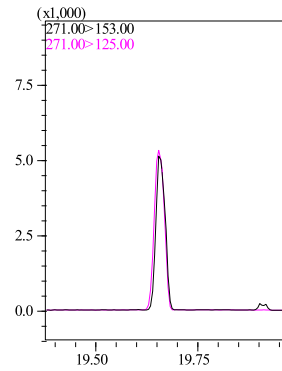
乙基谷硫磷



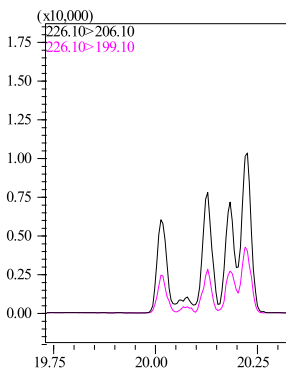
氯菊酯-1,2



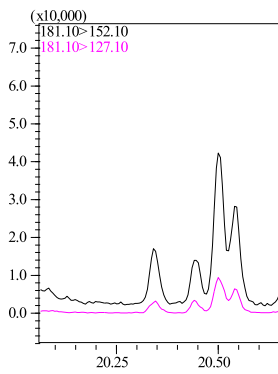
氯啶啉



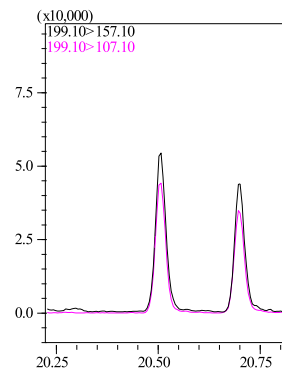
敌杀磷



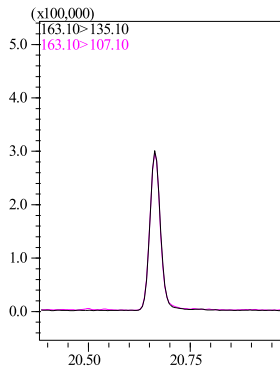
氟氯菊酯-1,2,3,4



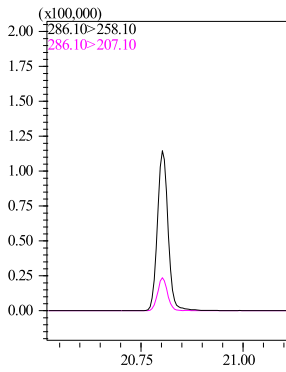
氯菊酯-1,2,3,4



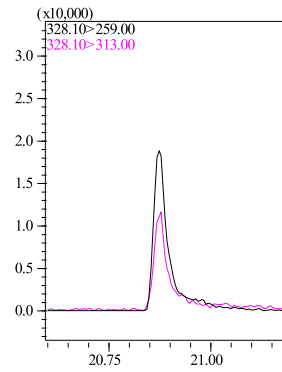
氟氯菊酯(氟氯戊菊酯)-1,2



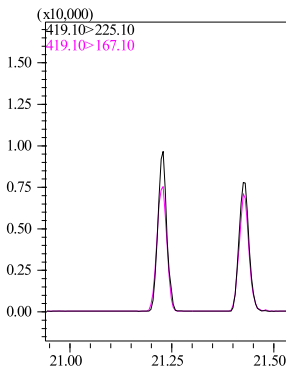
依芬宁(醚菊酯)



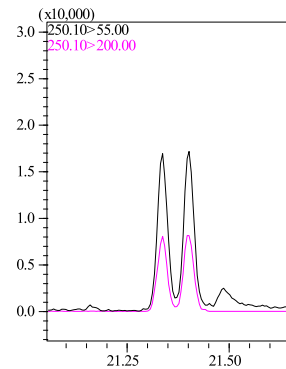
硅醚菊酯



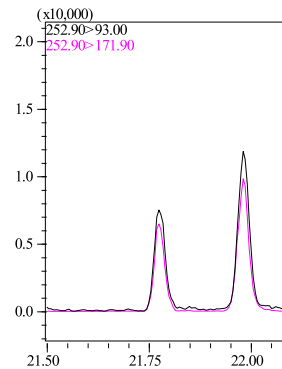
氟啶草酮



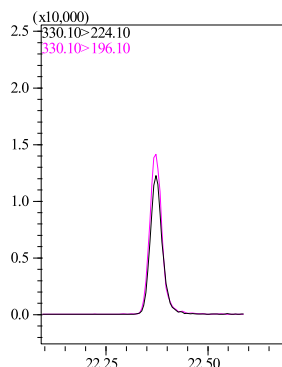
氟戊菊酯-1,2



氟胺菊酯-1,2



溴菊酯-1,2



恶唑菌酮(恶唑菌酮)

图1 葡萄中174种农药混标 (加标10 μg/L) 的质量色谱图

## 2.2 重复性测试

取葡萄空白基质配制的 10 μg/L 的混合标品, 重复进样 6 次, 重复性结果见表 2。

表 2 葡萄中 174 种农药残留 (加标 10 μg/L) 连续进样 6 针的峰面积

No.	中文名称	峰面积1	峰面积2	峰面积3	峰面积4	峰面积5	峰面积6	RSD%
1	二丙烯草胺	11068	11008	11073	10877	10999	11332	1.37
2	二氯丙烯胺	9974	10492	9557	9765	10430	10409	3.91
3	联苯	60905	60563	60136	59359	61427	61447	1.33
4	丁草特	46382	44093	45772	45258	47001	45131	2.24
5	依得利 (土菌灵)	61953	58994	59008	59589	63250	61012	2.87
6	苯胺灵	57280	56993	57444	56821	57952	58491	1.09
7	虫螨畏	24245	24129	24753	24372	24833	24472	1.14
8	地茂散	42922	41328	43021	42999	44021	42844	2.02
9	2-苯基苯酚 (邻苯基苯酚)	199887	198566	200375	198555	204269	203221	1.20
10	庚烯磷	151712	149790	148840	149742	153598	154740	1.56
11	四氯硝基苯	27629	28670	28786	28694	27381	29633	2.91
12	梨内二苯胺(二苯胺)	70214	71339	70525	68854	69317	70828	1.33
13	灭克磷 (灭线磷)	52432	50730	52581	53733	53967	52467	2.20
14	丁氟消草(乙丁烯氟灵)	14065	13326	14720	14359	13619	13631	3.76
15	氯苯胺灵	36823	34117	35265	37434	35937	33859	4.04
16	百治磷	112001	111795	119865	110334	105224	116951	4.56
17	氟乐灵	59308	57015	57364	60532	58129	60828	2.74
18	氟草胺 (乙丁氟灵)	47667	48391	49556	47680	47312	46949	1.94
19	蔬果磷	103719	104506	105135	104723	103706	103195	0.71
20	硫特普 (治螟磷)	40728	41125	42821	42199	43883	43951	3.20
21	硫线磷	95234	98532	95743	101985	97817	95009	2.74
22	甲拌磷	2108	2042	2288	1731	2114	1869	9.75
23	alpha-六六六	52819	51982	51623	50616	53717	52827	2.09
24	六氯苯	196697	188872	191189	199669	202403	198622	2.65
25	甲基乙拌磷 (二甲基硫吸磷)	20630	20662	20262	20622	20947	21062	1.36

26	五氯甲氧基苯(五氯茴香醚)	119723	117673	116528	118686	116837	119638	1.17
27	氯硝胺	41235	43530	41692	43025	42174	41775	2.07
28	绿谷隆	33522	34285	32019	31643	31845	35168	4.43
29	beta-六六六	39201	41893	40809	41185	42186	41448	2.58
30	噻节因	10534	10132	10792	10616	10065	10659	2.84
31	广灭灵(异恶草松)	100136	98047	94580	96317	98549	96280	2.03
32	五氯硝基苯	24325	25972	24004	24448	24377	24380	2.84
33	gamma-六六六	38600	39940	39007	40556	41782	40740	2.93
34	特丁硫磷	66767	67965	66755	64945	70072	68623	2.63
35	杀螟腈	97826	95625	97228	93001	96463	98577	2.05
36	大福松(地虫磷)(地虫硫磷)	80342	79666	79481	82302	81684	83004	1.80
37	炔敌稗	176176	178030	177378	171588	175313	178569	1.44
38	二嗪农(二嗪磷)	25865	26331	26277	25965	28264	26085	3.40
39	百菌清	140464	133219	136405	135208	133908	139560	2.18
40	乙拌磷	4911	4363	3926	4356	4381	4228	7.32
41	氯唑磷	71258	72905	72766	71158	69480	76011	3.08
42	特草定	68292	65084	63894	66309	64195	68235	2.94
43	七氟菊酯	167134	165501	163108	169326	165839	170885	1.68
44	益多松(乙噻硫磷)	20316	20920	23146	19783	22314	22849	6.52
45	delta-六六六	40526	40837	42249	40486	41655	42184	1.96
46	野麦畏	35712	37874	37411	36987	36903	35726	2.40
47	福木松(安硫磷)	11762	11355	11653	11364	10291	10948	4.81
48	呋草黄(呋草磺)	53264	51904	54916	54360	52710	53212	2.05
49	除线磷	154125	155677	154838	154810	154269	155105	0.37
50	汰草灭(二甲吩草胺)	116447	112856	111319	114796	113325	113485	1.54
51	敌稗	72270	70786	71735	67726	70190	73214	2.71
52	甲基毒死蜱	45053	45040	42643	42911	42173	42737	2.94
53	噻草酮	93396	85909	87921	85865	86388	88292	3.24
54	免克宁(乙烯菌核利)	25747	23820	28544	26682	25698	26705	5.94
55	甲基对硫磷	34515	34057	33944	33557	32476	34540	2.27
56	甲基立枯磷	123951	115337	120566	121878	121583	122312	2.45
57	七氯	75103	77142	72322	73179	74880	79835	3.63
58	莠灭净	35467	35691	32797	34415	34358	33404	3.28
59	皮蝇磷	105521	103315	105162	104964	98553	105408	2.60
60	扑草净	33595	30006	32126	29221	29188	31745	5.77
61	氟硫草定	84489	87485	84994	89067	90396	87521	2.61
62	八氯二丙醚	30548	31188	31720	31673	29922	33254	3.65
63	甲基嘧啶磷	20589	20250	21950	21637	20519	19754	4.05
64	杀螟硫磷	35714	32314	34813	31501	33112	35348	5.13
65	乙呋草黄	37919	35291	38120	35856	37898	37745	3.31

66	甲基五氯苯基硫醚	50685	50165	50453	50895	49663	49284	1.23
67	抑菌灵	117010	116867	117398	114747	119253	120663	1.75
68	甲拌磷亚砷	135751	137294	131747	132563	130684	135098	1.92
69	毒死蜱	56818	59236	59697	55111	56189	60014	3.57
70	甲拌磷砷	261927	256172	255156	248286	265133	254191	2.32
71	艾氏剂	18590	18491	19997	19150	20038	20074	3.83
72	倍硫磷	12436	12363	12387	11123	12322	12837	4.74
73	氯酞酸甲酯	92214	91790	88736	89952	92232	92921	1.76
74	对硫磷	18250	17539	19359	19341	17901	18763	4.08
75	三泰芬(三唑酮)	54766	53924	51493	52213	52937	54200	2.36
76	四克利(四氟醚唑)	21349	20655	20866	19832	19963	19315	3.71
77	水胺硫磷	16909	17722	16642	16181	16313	17795	4.09
78	三氯杀螨醇分解物(三氯杀螨醇)	42005	43096	44065	43659	44190	44990	2.35
79	酞菌酯	18852	19149	18620	21355	21445	23227	9.05
80	氟咯草酮	39849	39336	39320	38990	38352	38012	1.75
81	乙基虫螨磷密啶磷	43425	47243	46365	42621	43968	44986	3.97
82	溴硫磷	80103	75772	77401	77607	80552	78260	2.29
83	牧草谢双苯酰草胺	185616	183939	188976	188812	191096	189550	1.42
84	甲基异柳磷	103609	100142	96467	102453	102483	104261	2.82
85	二甲戊乐灵	20523	20719	19394	21524	21203	19600	4.15
86	异艾氏剂	32357	31418	29979	30968	30132	30921	2.82
87	啞菌环胺	108374	111392	109382	109370	107690	111277	1.37
88	氟虫腈	52443	49959	51315	49141	57038	55664	5.99
89	平克座(戊菌唑)	61714	62077	62243	65984	62298	67332	3.79
90	环氧七氯(exo)	24433	23759	25374	24899	23658	26632	4.50
91	乙菌利(克氯得)	16441	17172	17218	15609	18531	17286	5.71
92	亚芬松(异柳磷)	154569	163350	159415	159927	156400	158392	1.91
93	吲熟酯	86100	87534	82708	83664	80463	84743	2.98
94	灭蚜磷	8511	9313	8796	7622	7862	9166	8.04
95	稻丰散	54715	51528	53736	51437	51393	55305	3.37
96	喹硫磷	56091	57474	55225	61837	55779	59318	4.40
97	呋霜灵	92884	90846	92546	86608	90468	93941	2.85
98	克菌丹	6040	6201	5766	6047	5398	5295	6.45
99	腐霉利	161680	165879	164157	165328	168623	164256	1.39
100	乙基溴硫磷	184948	181717	181342	182488	182084	184047	0.78
101	氯杀螨	137498	134220	137527	136129	142261	144443	2.80
102	加护松(丙虫磷)	73118	69970	71684	70581	70370	72992	1.91
103	o,p'-DDE	249509	246282	251086	249589	259424	260218	2.28
104	杀虫威(杀虫畏)	60819	62487	62760	60336	60194	62472	1.93
105	多效唑	97516	99334	97228	96722	96403	102074	2.19

106	丁基拉草(丁草胺)	36985	39267	36309	36971	40610	36903	4.49
107	克线磷(苯线磷)	18714	16915	18230	18727	17398	16741	4.99
108	萘丙酰草胺(敌草胺)	73835	72513	72693	72700	72879	71114	1.21
109	福多宁(氟酰胺)	1779867	1783368	1744818	1785926	1785609	1798815	1.03
110	普硫松(丙硫磷)	76622	75666	76570	78920	77520	77473	1.44
111	丙溴磷	44626	43614	46914	44389	47024	44682	3.13
112	p,p'-DDE	153598	149215	151937	148129	155659	153287	1.87
113	脱叶磷	16033	17255	14543	15858	15440	17130	6.42
114	灭克落	143271	144520	141552	140731	135456	142430	2.24
115	狄氏剂(地特灵)	8117	8635	7778	8096	8286	7959	3.61
116	氟硅唑	82300	77904	80594	80411	79233	81007	1.89
117	o,p'-DDD	329562	329235	333765	326649	326425	330368	0.82
118	苄氯三唑醇	97121	92182	92525	93460	93697	95618	2.03
119	克凡派(虫螨脞)	4762	5463	5054	4365	4476	4975	8.33
120	异狄氏剂	15000	15075	14445	14568	15265	14714	2.15
121	杀螨酯(乙酯杀螨醇)	195508	191672	190389	193557	197756	197429	1.56
122	丰索磷	7942	7036	8647	7341	7069	8372	8.90
123	爱杀松(乙硫磷)	84817	83704	85797	86269	82463	84292	1.65
124	p,p'-DDD	349639	343266	336418	343880	338553	336426	1.52
125	o,p'-DDT	161263	159773	157023	155821	163350	170822	3.34
126	噁螨酯	13218	10641	10953	11740	11653	12091	7.77
127	灭普宁(灭锈胺)	116940	111585	122428	119189	122139	120471	3.43
128	三唑磷	28829	30850	30095	30883	30843	30594	2.64
129	本达乐(苯霜灵)	81556	81837	79261	82455	87084	85084	3.35
130	三硫磷	26464	26900	25656	25087	26718	26043	2.63
131	克温散(敌瘟磷)	63175	65626	63648	66274	62742	64475	2.18
132	硫丹硫酸酯	5535	4760	5327	4455	5249	5658	9.01
133	p,p'-DDT	137104	140261	132622	136232	141799	144244	3.03
134	环嗪酮	240592	237916	238952	239786	244523	247736	1.56
135	禾草灵	83147	79680	80423	81108	80619	78949	1.78
136	胡椒基丁醚(增效醚)	147250	145534	147399	142739	144882	147655	1.31
137	苄呋菊酯	48082	47631	49095	45348	53284	51596	5.82
138	联苯菊酯	494459	490281	492665	486284	494101	499365	0.89
139	苯硫磷	69590	73232	73985	73142	70327	70593	2.58
140	溴螨酯	117604	120644	122197	117753	122765	125555	2.54
141	解毒啞	224905	222421	206943	213437	202889	229810	4.92
142	甲氧滴滴涕(甲氧氯)	115532	112201	107644	106430	113934	114918	3.45
143	芬普宁(甲氧菊酯)	25730	26866	25616	26297	26773	27528	2.76
144	四氯杀螨砜(三氯杀螨砜)	23084	21699	22717	22007	23943	21967	3.76
145	戊唑草酮(戊基恶唑酮)	71298	68492	69653	69689	71279	71206	1.66

146	吡丙醚 (蚊蝇醚)	142786	150066	152518	148009	144281	149454	2.49
147	氰氟草酯	65310	65183	62323	65970	63755	64504	2.03
148	灭蚊灵	165951	159756	163993	165418	158725	165822	1.97
149	定菌磷 (吡菌磷)	87806	93452	91966	88200	92556	91660	2.59
150	氯苯嘧啶醇	43201	42079	41477	40585	43737	44581	3.51
151	乙基谷硫磷	71111	74211	71858	72938	66565	70481	3.69
152	氟啶唑	93004	89300	92039	92133	94105	93688	1.86
153	敌杀磷	8145	8174	8712	8194	8042	7811	3.63
154	依芬宁 (醚菊酯)	543064	534292	534872	541522	556696	551999	1.66
155	硅醚菊酯	201156	196137	204284	199857	206972	203865	1.89
156	氟啶草酮	43924	43787	44541	50298	49940	48328	6.54
157	恶唑酮菌恶唑菌酮	23626	23384	22868	24012	25334	25052	4.02
158	氯丹	8808	9070	9953	9489	8641	9841	5.86
159	硫丹	7158	7110	6329	6391	7052	7040	5.55
160	磷胺	29124	28612	28682	29488	28577	31631	3.99
161	毒虫畏	76862	78511	82123	71088	75558	81469	5.26
162	环唑醇	265242	278938	276076	285650	274820	280326	2.47
163	丙环唑	40664	41290	40727	41173	41292	40976	0.68
164	胺菊酯	184190	180319	185359	189560	180359	186587	1.96
165	苯醚菊酯	40359	41693	42613	38748	44271	42351	4.60
166	氯氟氰菊酯	19226	20142	18735	20385	20471	20574	3.81
167	氟丙菊酯	12146	11815	13140	12400	12652	12331	3.64
168	氯菊酯	86466	84236	85063	83957	89781	84987	2.52
169	氟氯氰菊酯	49556	49276	49545	50701	49824	51786	1.91
170	氯氰菊酯	157816	157366	163710	154952	160048	161178	1.95
171	氟氰菊酯 (氟氰戊菊酯)	169270	167773	166867	170352	176850	175760	2.45
172	氰戊菊酯	25194	24920	26168	25426	27672	27343	4.43
173	氟胺氰菊酯	59969	56806	56462	57688	59443	62177	3.72
174	溴氰菊酯	37219	37487	37275	37963	39214	38970	2.30

## 结论

采用岛津公司三重四极杆气质联用仪 GCMS-TQ8040 对葡萄基质中 174 种农药 (浓度为 10  $\mu\text{g/L}$ ) 的灵敏度和重复性进行考察。结果表明, 葡萄基质中 174 种农药色谱峰峰形好, 连续进 6 针进行重复性实验, 其峰面积的相对标准偏差 (RSD%) 均在 10% 以下, 岛津 GCMS-TQ8040 在分析葡萄中多农药残留时灵敏度高, 稳定性良好。