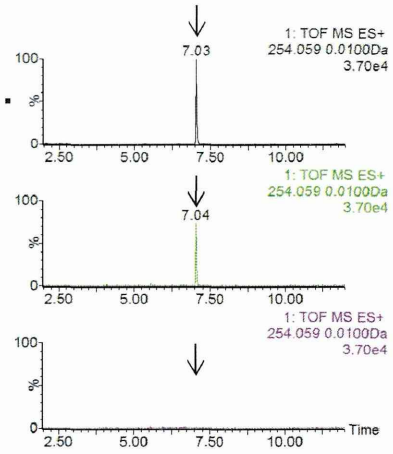
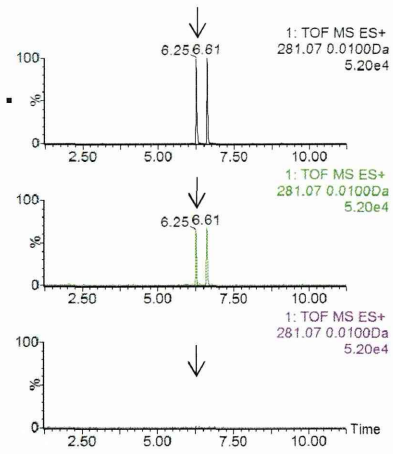
図 4-2 （つづき）

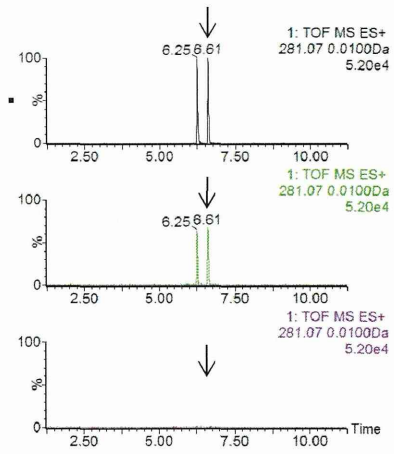
Sulfamethoxazole



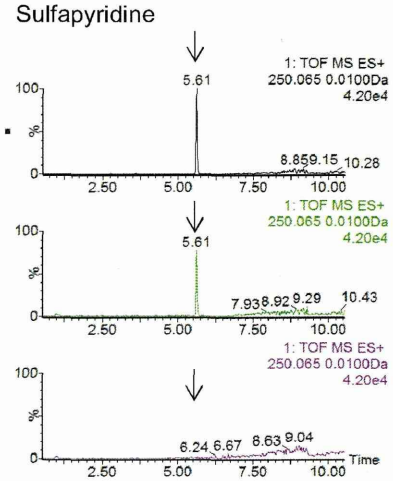
Sulfamethoxypyridazine



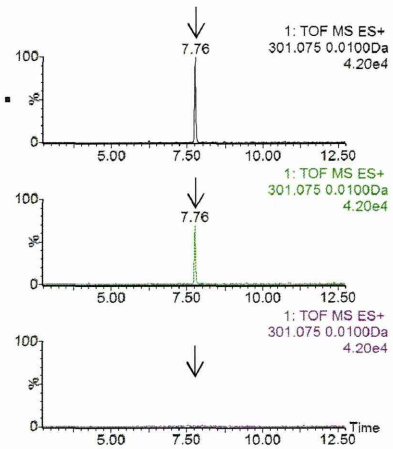
Sulfamonomethoxine



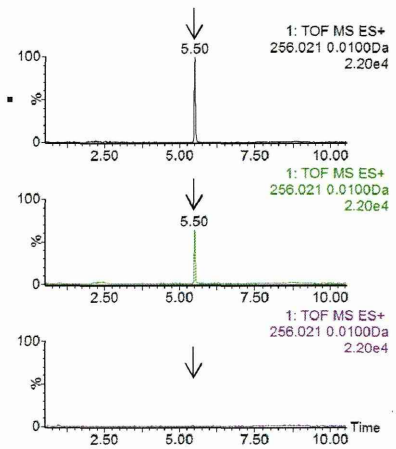
Sulfapyridine



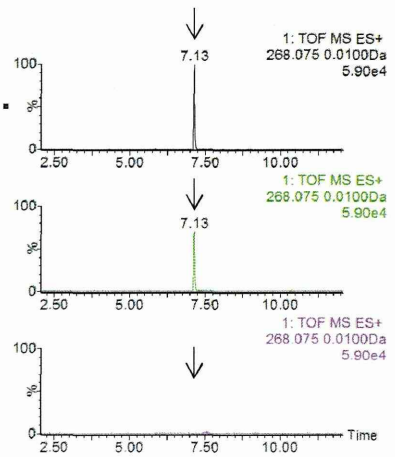
Sulfaquinoxaline



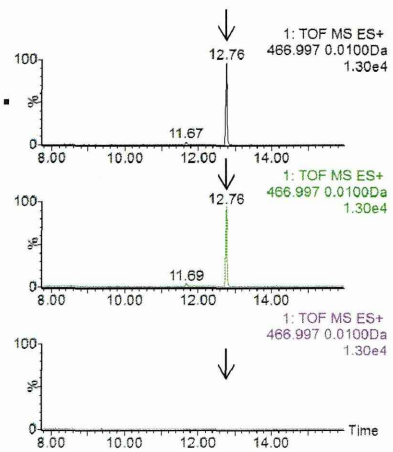
Sulfathiazole



Sulfatroxazole



Temephos



Thiabendazole

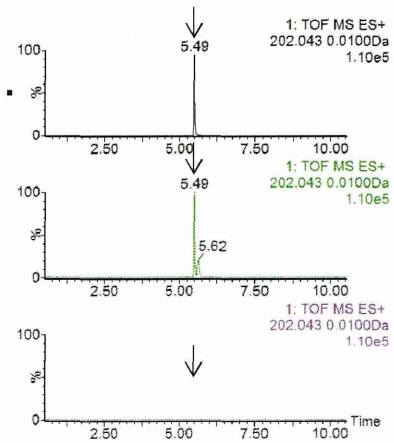
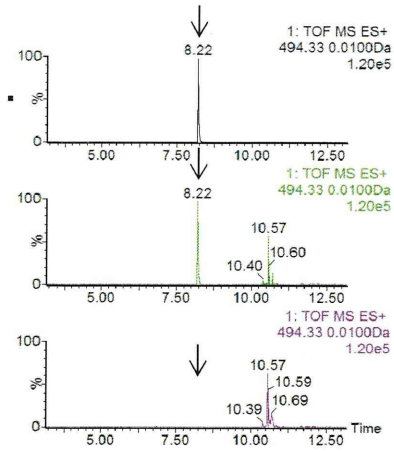
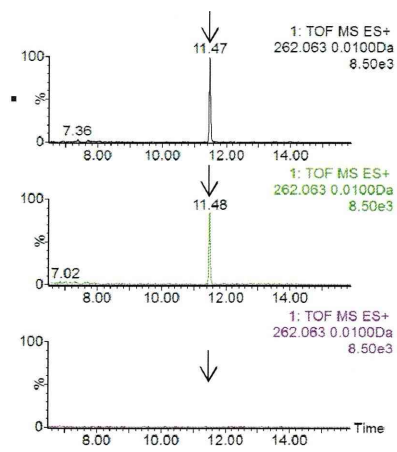


図 4-2 （つづき）

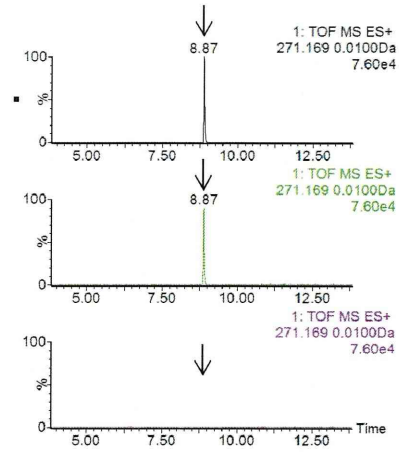
Tiamulin



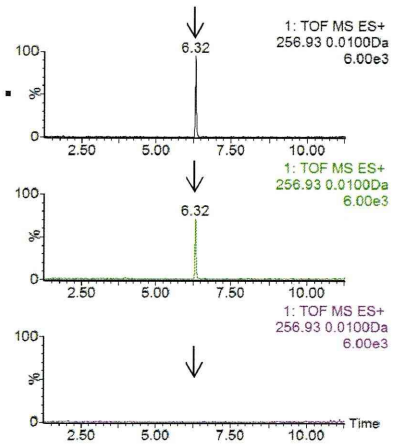
Tolfenamic acid



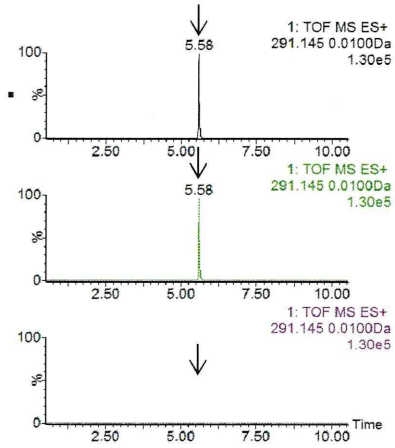
β-Trenbolone



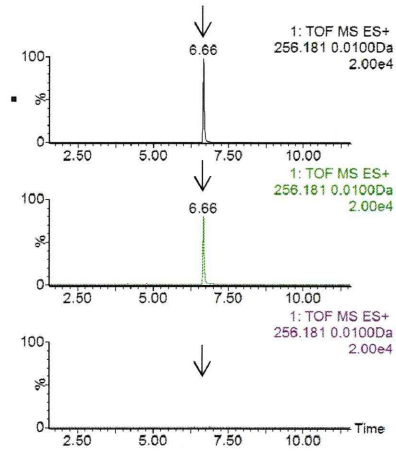
Trichlorfon



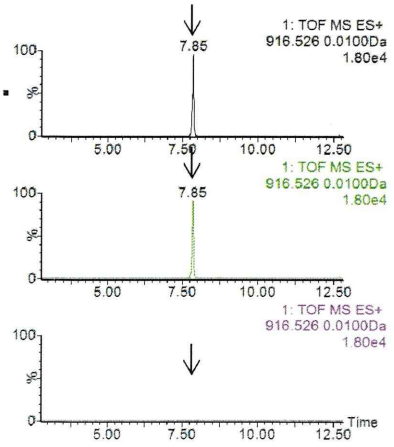
Trimethoprim



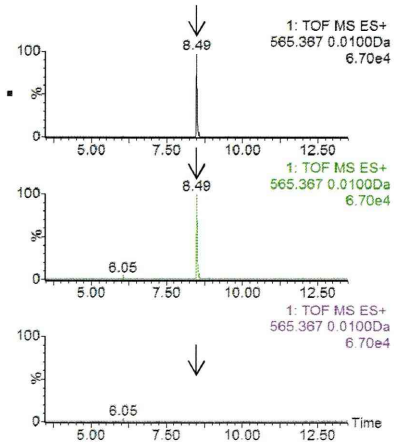
Tripelennamine



Tylosin



Valnemulin



Warfarin

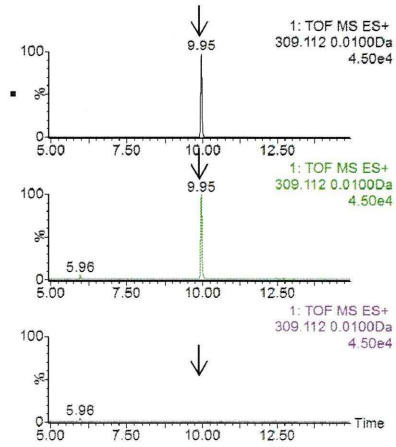
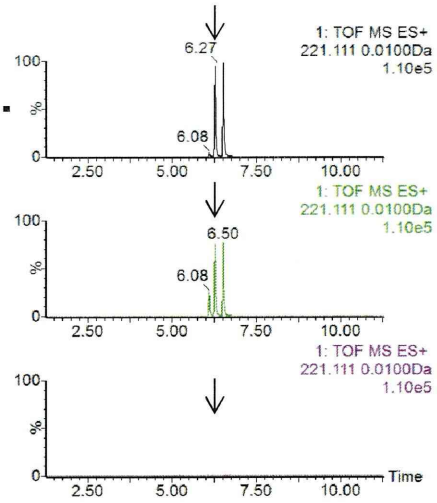


図 4-2 （つづき）

Xylazine



別添

表 検討に用いた標準品

	標準品 （英名）	標準品 （和名）	純度	メーカー
1	2-Acetylamino-5-nitrothiazole	2-アセチルアミノ-5-ニトロチアゾール	99.9	関東化学
2	Albendazole	アルベンダゾール	99	Dr.E
3	Altrenogest	アルトレノゲスト	99.9	Sigma
4	Azaperone	アザペロン	98.3	林純薬
5	Benzocaine	ベンゾカイン	98	和光純薬
6	Bromacil	ブロマシル	98.5	Sigma
7	Brotizolam	ブロチゾラム	98	和光純薬
8	Cefoperazone dihydrate	セフォペラゾン二水和物	99.8	Sigma
9	Chlormadinone	クロルマジノン	99.4	関東化学
10	Clostebol	クロステボル	98	和光純薬
11	Danofloxacin mesylate	メシル酸ダノフロキサシン	99.9	関東化学
12	Dexamethasone	デキサメタゾン	99.5	Sigma
13	Diaveridine	ジアベリジン	99.6	Sigma
14	Dicyclanil	ジシクラニル	99.9	Sigma
15	Difloxacin hydrochloride	ジフロキサシン塩酸塩	98	Dr.E
16	Diflubenzuron	ジフルベンズロン	98.1	Sigma
17	Emamectin benzoate	エマメクチン安息香酸塩	B1a:B1b (90.7% : 5.2%)	林純薬
18	Enrofloxacin	エンロフロキサシン	99.9	関東化学
19	Ethopabate	エトパベート	99.7	Sigma
20	Famphur	ファムフール	98.9	Sigma
21	Fenobucarb	フェノブカルブ	97	Sigma
22	Flubendazole	フルベンダゾール	99.9	林純薬
23	Flumequine	フルメキン	99.3	Sigma
24	Flunixin meglumine	フルニキシンメグルミン	99	Dr.E
25	Halofuginone hydrobromide	ハロフジノン臭化水素酸塩	99	Sigma
26	Hydrocortisone	ヒドロコルチゾン	98	和光純薬
27	5-Hydroxythiabendazole	5-ヒドロキシチアベンダゾール	99.9	林純薬
28	Ketoprofen	ケトプロフェン	99.1	Dr.E
29	Levamisole hydrochloride	レバミゾール塩酸塩	99	和光純薬
30	Lincomycin hydrochloride monohydrate	リンコマイシン塩酸塩一水和物	100.3	Sigma
31	Mafoprazine mesilate	メシル酸マフォプラジン	99.9	林純薬
32	Marbofloxacin	マルボフロキサシン	98.7	Sigma
33	Mebendazole	メベンダゾール	98	和光純薬
34	Meloxicam	メロキシカム	98	和光純薬
35	Menbutone	メンブトン	98	Dr.E
36	Methylprednisolone	メチルプレドニゾロン	98.6	Sigma
37	Miloxacin	ミロキサシン	97.5	林純薬
38	Morantel Citrate Monohydrate	クエン酸モランテル一水和物	99	関東化学
39	Nalidixic acid	ナリジクス酸	99	和光純薬
40	Ofloxacin	オフロキサシン	99.8	Sigma
41	Olaquindox	オラキンドックス	99	和光純薬
42	Orbifloxacin	オルビフロキサシン	99.9	林純薬
43	Ormetoprim	オルメトプリム	99	Dr.E
44	Oxibendazole	オキシベンダゾール	98	和光純薬
45	Oxolinic acid	オキソリニック酸	99.2	林純薬
46	Phenoxymethyl penicillin potassium salt	フェノキシメチルペニシリンカリウム塩	99.2	関東化学
47	Praziquantel	プラジクアンテル	99.9	Sigma
48	Prednisolone	プレドニゾロン	99	Sigma
49	Prifinium bromide	臭化プリフィニウム	—[a)]	Toronto
50	Pyrantel pamoate	ピランテルパモ酸塩	99	Dr.E

表（つづき）

	標準品 （英名）	標準品 （和名）	純度	メーカー
51	Pyrimethamine	ピリメタミン	99.8	Sigma
52	Robenidine hydrochloride	ロベニジン塩酸塩	98	和光純薬
53	Sarafloxacin hydrochloride hydrate	サラフロキサシン塩酸塩水和物	97.2	Sigma
54	Sulfabenzamide	スルファベンズアミド	99.8	Sigma
55	Sulfabromomethazine	スルファブロモメタジン	98.9	林純薬
56	Sulfacetamide	スルファセタミド	99.5	Dr.E
57	Sulfachlorpyridazine	スルファクロルピリダジン	98.9	関東化学
58	Sulfadiazine	スルファジアジン	99.3	Sigma
59	Sulfadimethoxine	スルファジメトキシン	99.9	Sigma
60	Sulfadimidine	スルファジミジン	99	和光純薬
61	Sulfadoxine	スルファドキシン	99.8	Sigma
62	Sulfaethoxypyridazine	スルファエトキシピリダジン	99.8	林純薬
63	Sulfamerazine	スルファメラジン	98.8	Sigma
64	Sulfamethoxazole	スルファメトキサゾール	99.9	Sigma
65	Sulfamethoxypyridazine	スルファメトキシピリダジン	99.7	関東化学
66	Sulfamonomethoxine	スルファモノメトキシン	99.9	林純薬
67	Sulfapyridine	スルファピリジン	99.5	Sigma
68	Sulfaquinoxaline	スルファキノキサリン	98	Dr.E
69	Sulfathiazole	スルファチアゾール	100	関東化学
70	Sulfatroxazole	スルファトロキサゾール	98.8	林純薬
71	Temephos	テメホス	97	Dr.E
72	Thiabendazole	チアベンダゾール	99.9	Sigma
73	Tiamulin	チアムリン	98.8	Sigma
74	Tolfenamic acid	トルフェナム酸	99.9	Sigma
75	β-Trenbolone	β-トレンボロン	99.3	林純薬
76	Trichlorfon	トリクロルホン	99.6	和光純薬
77	Trimethoprim	トリメトプリム	99.7	Sigma
78	Tripelennamine hydrochloride	塩酸トリペレナミン	99.9	林純薬
79	Tylosin tartrate	タイロシン酒石酸塩	96	Dr.E
80	Valnemulin	バルネムリン	96.2	Sigma
81	Warfarin	ワルファリン	98	Dr.E
82	Xylazine	キシラジン	99.9	Sigma

a) 記載なし

表 1　GC-TOF-MS 法の検討農薬の保持時間、定量イオン及び確認イオン

	Compound	Retention time (min)	Quatification (*m/z*)	Confirmation (*m/z*)
1	Acetochlor	13.65	146.0970	223.0764
2	Acrinathrin	20.05	181.0653	208.0762
3	Alachlor	13.83	160.1126	188.1075
4	Aldrin	14.76	262.8564	293.9346
5	Ametryn	13.98	227.1205	212.0970
6	Anilofos	19.28	226.0457	124.9826
7	Aramite	16.76, 16.95	185.0039	334.1006
8	Atrazine	12.31	200.0703	215.0938
9	Azaconazole	16.80	216.9823	172.9561
10	Azinphos methyl	19.72	160.0511	132.0449
11	Azoxystrobin	23.79	344.1035	388.0934
12	Benfluralin	11.40	292.0545	264.0232
13	Benfuresate	13.54	163.0759	256.0769
14	Benoxacor	13.35	120.0449	259.0167
15	α-BHC	11.87	182.9349	218.9116
16	β-BHC	12.36	182.9349	218.9116
17	γ-BHC	13.10	182.9349	218.9116
18	δ-BHC	12.55	182.9349	218.9116
19	Bifenox	19.29	340.9858	342.9831
20	Bifenthrin	18.94	181.1017	166.0783
21	Bitertanol	20.69	170.0732	171.0766
22	Bromobutide	13.70	232.1701	119.0861
23	Bromofos	15.07	330.8781	328.8804
24	Bromophos ethyl	15.86	358.9094	302.8468
25	Bromopropylate	19.03	340.9000	182.9446
26	Bupirimate	16.67	273.1021	208.1450
27	Buprofezin	16.72	172.1034	105.0579
28	Butachlor	16.03	176.1075	160.1126
29	Butafenacil	21.00	331.0097	179.9852
30	Butamifos	16.19	286.1031	200.0113
31	Cadusafos	11.64	158.9703	157.9625
32	Cafenstrole	21.19	100.0762	188.1188
33	Cafentrazone ethy	17.77	312.0596	340.0909
34	Chlorbenside	15.94	125.0158	127.0129
35	Chlordane (cis)	16.22	372.8254	374.8225
36	Chlordane (trans)	15.96	372.8254	374.8225
37	Chlorfenapyr	16.85	247.0483	59.0497
38	Chlorfenson	16.39	301.9571	176.9777
39	Chlorfenvinphos (E)	15.25	266.9381	323.0007
40	Chlorfenvinphos (Z)	15.46	266.9381	323.0007
41	Chlorobenzilate	17.21	251.0031	138.9951
42	Chlorpropham	11.31	127.0189	213.0557
43	Chlorpyrifos	14.62	313.9574	196.9202
44	Chlorpyrifos methyl	13.69	285.9261	287.9232
45	Chlorthal dimethyl	14.72	300.8629	298.8836
46	Chlozolinate	15.39	258.9803	331.0014
47	Clomazone	12.41	204.1025	125.0158
48	Clomeprop	19.39	288.0791	120.0813
49	Coumaphos	20.87	362.0145	210.0084
50	Cyanazine	14.67	212.0703	225.0656

表 1 （つづき）

	Compound	Retention time (min)	Quatification (*m/z*)	Confirmation (*m/z*)
51	Cyanophos	12.60	243.0119	109.0081
52	Cyflufenamid	16.87	412.1210	294.0780
53	Cyfluthrin	21.25, 21.35, 21.44, 21.46	163.0081	206.0606
54	Cyhalothrin	19.73,19.91	181.0653	197.0345
55	Cypermethrin	21.59, 21.69, 21.76, 21.79	181.0653	163.0081
56	Cyproconazole	17.02	222.0434	138.9951
57	Cyprodinil	15.29	224.1188	225.1266
58	pp'-DDD	17.40	235.0081	237.0048
59	pp'-DDE	16.59	246.0003	247.9970
60	op'-DDT	17.45	235.0081	237.0048
61	pp'-DDT	18.11	235.0081	237.0048
62	Deltamethrin	23.56	252.9051	250.9071
63	Di-allate	11.73, 11.92	234.0719	86.0606
64	Diazinon	12.70	304.1011	179.1184
65	Dichloran	12.11	205.9650	123.9954
66	Dieldrin	16.75	262.8564	264.8535
67	Diethofencarb	14.62	267.1471	225.1001
68	Diflufenican	18.34	266.0429	394.0741
69	Dimethametryn	15.38	212.0970	255.1518
70	Dimethenamid	13.59	230.0406	154.0690
71	Dimethoate	12.09	124.9826	87.0143
72	Dimethylvinphos (E)	14.38	294.9694	296.9666
73	Dimethylvinphos (Z)	14.65	294.9694	296.9666
74	Disulfoton	12.96	88.0347	274.0285
75	Dithiopyr	14.06	354.0587	286.0473
76	Edifenphos	17.96	310.0251	172.9826
77	Endosulfan sulfate	18.06	271.8102	386.8400
78	α-Endosulfan	16.23	240.9030	194.9480
79	β-Endosulfan	17.35	240.9070	194.9480
80	Endrin	17.16	262.8564	264.8535
81	EPN	19.00	156.9877	185.0190
82	Epoxiconazole	18.60	192.0329	165.0220
83	Esprocarb	14.49	222.0953	162.1283
84	Ethion	17.37	230.9737	153.0139
85	Ethoprophos	11.09	157.9625	200.0095
86	Etofenprox	21.94	163.1123	183.0810
87	Etoxazole	19.10	141.0152	300.1200
88	Fenarimol	20.18	138.9951	219.0325
89	Fenchlorphos	14.04	284.9309	286.9280
90	Fenitrothion	14.31	277.0174	260.0146
91	Fenoxanil	17.02	188.9874	293.1057
92	Fenpropathrin	19.13	181.0653	265.0739
93	Fenpropimoph	14.76	128.1075	129.1107
94	Fenvalerate	22.6, 22.85	125.0158	167.0628
95	Fipronil	15.31	366.9435	368.9406
96	Flamprop methyl	16.60	105.0340	77.0391
97	Flucythrinate	21.76, 21.96	199.0935	157.0465
98	Fludioxonil	16.37	248.0397	154.0531
99	Fluquinconazole	20.89	340.0401	342.0377
100	Flutolanil	16.31	173.0214	145.0265

表 1 （つづき）

	Compound	Retention time (min)	Quatification (*m/z*)	Confirmation (*m/z*)
101	Fluvalinate	22.71, 22.79	250.0610	209.0841
102	Fosthiazate	15.09	195.0119	283.0466
103	Fthalide	15.01	242.8752	240.8782
104	Indoxacarb	23.32	203.0219	150.0111
105	Iprobenfos	13.27	204.0010	91.0548
106	Isazophos	12.96	161.0356	256.9791
107	Isofenphos	15.43	213.0317	255.0786
108	Isofenphos oxon	14.79	229.0266	200.9953
109	Isoprocarb	9.97	121.0653	136.0888
110	Isoprothiolane	16.44	290.0647	117.9911
111	Isoxadifen ethyl	17.78	294.1130	222.0919
112	Isoxathion	16.94	105.0340	313.0538
113	Kresoxim methyl	16.69	116.0500	131.0735
114	Lenacil	18.01	153.0664	136.0399
115	Malathion	14.46	173.0814	127.0395
116	Mecarbam	15.50	131.0041	159.0354
117	Mefenacet	19.87	192.0119	120.0813
118	Mefenpyr diethyl	18.60	252.9935	254.9907
119	Mepronil	17.61	119.0497	269.1416
120	Metalaxyl	13.97	206.1181	249.1365
121	Methidathion	15.88	145.0072	85.0402
122	Methoxychlor	19.11	227.1072	228.1106
123	Metolachlor	14.59	238.0999	162.1283
124	Myclobutanil	16.65	179.0310	150.0111
125	Oxadiazon	16.55	174.9592	258.0327
126	Oxadixyl	17.34	163.0997	233.0926
127	Paclobutrazol	16.04	236.0591	125.0158
128	Parathion	14.77	291.0330	109.0055
129	Parathion methyl	13.81	263.0017	247.0068
130	Penconazole	15.39	248.0955	158.9768
131	Pendimethalin	15.27	252.0984	281.1376
132	Permethrin	20.74, 20.87	183.0810	163.0081
133	Phenothrin	19.4, 19.51	183.0810	123.1174
134	Phenthoate	15.57	273.9887	245.9938
135	Phosalone	19.63	182.0009	366.9869
136	Phosmet	18.96	160.0399	161.0477
137	Phosphamidon	13.50	264.1001	127.0160
138	Piperonyl butoxide	18.46	176.0837	177.0916
139	Pirimiphos methyl	14.24	290.0728	276.0572
140	Pretilachlor	16.43	238.0999	176.1075
141	Procymidone	15.66	283.0167	96.0575
142	Profenofos	16.51	338.9643	336.9663
143	Prometryn	14.02	241.1361	184.0657
144	Propaphos	15.90	219.9959	304.0898
145	Propiconazole	17.94, 18.05	259.0293	172.9561
146	Propoxur	10.77	110.0368	152.0837
147	Propyzamide	12.67	172.9561	174.9532
148	Prothiofos	16.43	308.9940	266.9470
149	Pyraflufen ethyl	17.99	412.0205	414.0178
150	Pyrazophos	20.11	221.0800	232.1086

表 1 （つづき）

	Compound	Retention time (min)	Quatification (*m/z*)	Confirmation (*m/z*)
151	Pyributicarb	18.68	108.0449	165.0664
152	Pyridaben	20.93	147.1174	309.0828
153	Pyridafenthion	18.78	340.0647	199.0871
154	Pyrifenox (E)	15.96	262.0065	264.0037
155	Pyrifenox (Z)	15.46	262.0065	264.0037
156	Pyrimethanil	12.82	198.1031	199.1110
157	Pyriminobac methyl (E)	17.95	302.1141	256.0722
158	Pyriminobac methyl (Z)	17.15	302.1141	256.0722
159	Pyriproxyfen	19.77	136.0762	226.0994
160	Quinalphos	15.60	146.0480	157.0766
161	Quinoxyfen	17.99	237.0590	272.0278
162	Quintozene	12.44	236.8413	248.8413
163	Silafluofen	22.09	179.0892	286.1189
164	Simeconazole	13.83	121.0454	195.0641
165	Tebuconazole	18.35	250.0747	125.0158
166	Tebufenpyrad	19.24	318.1373	333.1608
167	Tecnazene	10.64	202.8803	214.8803
168	Tefluthrin	12.97	177.0327	197.0345
169	Terbufos	12.61	230.9737	153.0139
170	Tetrachlorvinphos	15.98	328.9304	330.9276
171	Tetraconazole	14.81	336.0527	338.0501
172	Tetradifon	19.52	355.8814	158.9671
173	Thenylchlor	18.27	288.1058	127.0218
174	Thiobencarb	14.66	100.0762	125.0158
175	Tolclofos methyl	13.85	264.9855	266.9827
176	Tolfenpyrad	24.21	383.1401	171.0325
177	Triadimefon	14.83	208.0278	57.0704
178	Triallate	13.12	268.0330	270.0300
179	Triazophos	17.64	257.0024	161.0589
180	Tribuphos	16.55	258.0336	314.0962
181	Trifloxystrobin	17.84	116.0500	145.0265
182	Trifluralin	11.34	306.0702	264.0232
183	Uniconazole P	16.61	234.0434	236.0407
184	Vinclozolin	13.75	284.9960	212.0034

表 2　マトリックス標準溶液のピーク面積の再現性(試料中 0.005 ppm 相当)、検出限界及び定量限界

	Compound	RSD%				LOD[c] (ppb)	LOQ[c] (ppb)
		10mDa	20mDa	50mDa	100mDa		
1	Acetochlor	5.2	6.3	4.0	3.7	1	2
2	Acrinathrin	6.9	6.9	6.9	9.7	1	3
3	Alachlor	6.4	5.5	6.5	5.8	1	3
4	Aldrin	0.6	0.6	0.6	0.6	<1	<1
5	Ametryn	3.8	1.2	1.2	1.2	<1	1
6	Anilofos	6.3	6.3	6.4	8.0	1	3
7	Aramite	3.2	3.2	3.2	3.2	<1	2
8	Atrazine	0.6	0.4	0.4	0.4	<1	<1
9	Azaconazole	2.7	4.3	2.9	1.7	<1	1
10	Azinphos methyl	2.8	2.8	2.8	6.8	<1	1
11	Azoxystrobin	142.4	8.3	8.4	8.3	1	4
12	Benfluralin	2.9	2.9	2.9	2.9	<1	1
13	Benfuresate	2.4	2.7	2.8	2.3	<1	1
14	Benoxacor	3.6	1.6	2.3	9.7	<1	1
15	α-BHC	1.0	1.0	1.0	1.0	<1	1
16	β-BHC	1.5	1.5	1.5	1.5	<1	1
17	γ-BHC	2.4	2.4	2.4	2.4	<1	1
18	δ-BHC	0.7	0.7	0.7	0.7	<1	<1
19	Bifenox[a]	22.4	4.1	12.5	5.0	19	63
20	Bifenthrin	1.8	1.9	2.5	2.5	<1	1
21	Bitertanol	6.5	6.5	6.6	8.3	1	3
22	Bromobutide	2.8	2.8	2.3	3.6	<1	1
23	Bromofos	1.4	1.4	1.4	1.4	<1	1
24	Bromophos ethyl	1.9	1.9	1.9	1.9	<1	1
25	Bromopropylate	4.3	4.3	4.3	4.3	1	2
26	Bupirimate	1.4	1.4	1.4	1.4	<1	1
27	Buprofezin	2.6	3.4	2.5	2.3	<1	1
28	Butachlor	1.1	1.1	1.1	2.3	<1	1
29	Butafenacil	9.4	9.4	9.4	9.4	1	5
30	Butamifos	1.0	1.0	1.0	1.0	<1	<1
31	Cadusafos	3.2	3.2	3.2	3.2	<1	2
32	Cafenstrole	6.8	6.8	4.5	7.6	1	2
33	Cafentrazone ethy	49.9	2.8	2.8	2.8	<1	1
34	Chlorbenside	2.9	2.5	2.5	5.6	<1	1
35	Chlordane (cis)	0.9	0.9	0.9	0.9	<1	<1
36	Chlordane (trans)	0.3	0.3	0.3	0.3	<1	<1
37	Chlorfenapyr	3.1	3.1	2.8	2.8	<1	1
38	Chlorfenson	1.4	1.8	1.8	1.5	<1	1
39	Chlorfenvinphos (E)	2.8	2.8	2.8	2.8	<1	1
40	Chlorfenvinphos (Z)	4.5	4.5	4.5	4.5	1	2
41	Chlorobenzilate	0.9	0.9	2.2	1.3	<1	1
42	Chlorpropham	2.8	2.9	2.9	3.2	<1	1
43	Chlorpyrifos	4.0	4.0	4.0	4.0	1	2
44	Chlorpyrifos methyl	0.9	0.9	0.9	0.9	<1	<1
45	Chlorthal dimethyl	—[b]	—[b]	0.4	0.4	<1	<1
46	Chlozolinate	2.5	2.5	2.5	1.4	<1	1
47	Clomazone	1.7	1.5	1.6	2.6	<1	1
48	Clomeprop	5.6	5.9	6.2	6.2	1	3
49	Coumaphos	7.7	7.7	7.7	7.7	1	4
50	Cyanazine	4.7	4.6	4.6	4.6	1	2

表 2 （つづき）

	Compound	RSD%				LOD[c] (ppb)	LOQ[c] (ppb)
		10mDa	20mDa	50mDa	100mDa		
51	Cyanophos	1.0	0.6	0.6	0.6	<1	<1
52	Cyflufenamid	8.0	4.9	4.9	4.9	1	2
53	Cyfluthrin[a]	5.8	5.3	11.3	8.4	17	56
54	Cyhalothrin	6.2	6.2	6.2	8.8	1	3
55	Cypermethrin	2.0	5.2	5.8	8.7	1	3
56	Cyproconazole	3.7	3.7	3.7	3.6	1	2
57	Cyprodinil	0.7	1.3	1.9	1.1	<1	1
58	pp'-DDD	1.6	1.6	1.6	1.6	<1	1
59	pp'-DDE	0.4	0.4	0.4	0.4	<1	<1
60	op'-DDT	2.0	2.0	2.0	2.0	<1	1
61	pp'-DDT	3.1	3.1	3.1	3.1	<1	2
62	Deltamethrin	7.1	9.6	9.6	9.6	1	5
63	Di-allate	2.4	2.4	2.4	2.4	<1	1
64	Diazinon	1.2	1.2	1.2	1.2	<1	1
65	Dichloran	2.8	2.8	2.8	2.8	<1	1
66	Dieldrin	2.7	2.7	2.7	2.7	<1	1
67	Diethofencarb	3.6	3.6	3.6	3.6	1	2
68	Diflufenican	1.5	1.7	2.0	2.1	<1	1
69	Dimethametryn	1.1	1.1	1.1	1.1	<1	1
70	Dimethenamid	3.3	2.2	1.5	1.6	<1	1
71	Dimethoate	2.8	3.4	2.3	2.3	<1	1
72	Dimethylvinphos (E)	0.5	0.5	0.5	0.5	<1	<1
73	Dimethylvinphos (Z)	1.6	1.6	1.8	1.9	<1	1
74	Disulfoton	4.3	4.3	3.6	4.7	1	2
75	Dithiopyr	1.5	1.5	1.5	1.5	<1	1
76	Edifenphos	7.6	5.2	5.1	3.1	1	3
77	Endosulfan sulfate	6.0	6.0	6.0	6.0	1	3
78	α-Endosulfan	0.7	1.1	1.1	1.1	<1	1
79	β-Endosulfan	6.7	4.4	4.4	4.4	1	2
80	Endrin	1.6	1.6	1.6	1.6	<1	1
81	EPN	5.2	5.2	5.2	3.0	1	3
82	Epoxiconazole	4.2	4.2	4.2	4.7	1	2
83	Esprocarb	2.8	8.5	2.6	2.6	<1	1
84	Ethion	2.0	2.0	2.0	2.0	<1	1
85	Ethoprophos	2.7	2.7	2.7	2.7	<1	1
86	Etofenprox	5.9	5.9	5.9	6.7	1	3
87	Etoxazole	2.2	2.2	2.2	2.2	<1	1
88	Fenarimol	6.8	6.8	6.8	7.0	1	3
89	Fenchlorphos	0.4	0.4	0.4	0.4	<1	<1
90	Fenitrothion	0.7	0.7	0.7	0.7	<1	<1
91	Fenoxanil	1.8	1.8	1.8	1.8	<1	1
92	Fenpropathrin	4.8	4.8	4.8	8.0	1	2
93	Fenpropimoph	3.4	3.5	3.5	3.2	1	2
94	Fenvalerate	9.6	6.8	7.7	8.5	1	4
95	Fipronil	2.9	2.9	2.9	2.9	<1	1
96	Flamprop methyl	2.7	2.7	2.7	5.4	<1	1
97	Flucythrinate	8.8	8.3	8.5	8.5	1	4
98	Fludioxonil	5.5	5.5	5.9	5.8	1	3
99	Fluquinconazole	7.8	9.0	9.0	9.0	1	5
100	Flutolanil	2.1	2.0	2.3	2.3	<1	1

表 2（つづき）

	Compound	RSD%				LOD[c] (ppb)	LOQ[c] (ppb)
		10mDa	20mDa	50mDa	100mDa		
101	Fluvalinate	5.4	4.5	4.5	4.5	1	2
102	Fosthiazate	6.0	3.0	3.0	9.3	<1	2
103	Fthalide	1.4	1.7	1.4	1.4	<1	1
104	Indoxacarb	46.5	4.2	9.3	6.8	1	5
105	Iprobenfos	1.9	1.9	1.9	1.9	<1	1
106	Isazophos	6.9	0.9	1.0	1.0	<1	<1
107	Isofenphos	2.7	1.2	1.4	1.0	<1	1
108	Isofenphos oxon	0.2	0.2	0.2	0.2	<1	<1
109	Isoprocarb	4.3	4.3	4.0	7.4	1	2
110	Isoprothiolane	2.0	2.0	2.0	2.0	<1	1
111	Isoxadifen ethyl	2.9	2.9	2.9	2.5	<1	1
112	Isoxathion	2.6	2.6	2.6	18.7	<1	1
113	Kresoxim methyl	2.3	3.5	2.7	2.7	<1	1
114	Lenacil	1.6	4.3	4.3	4.3	1	2
115	Malathion	3.4	2.2	2.6	2.6	<1	1
116	Mecarbam	3.4	3.4	3.4	—[b]	1	2
117	Mefenacet	4.2	7.0	5.7	5.7	1	3
118	Mefenpyr diethyl	4.2	2.2	3.6	5.4	1	2
119	Mepronil	2.2	2.2	2.2	—[b]	<1	1
120	Metalaxyl	0.5	1.2	6.2	—[b]	1	3
121	Methidathion	2.4	2.4	2.4	2.4	<1	1
122	Methoxychlor	3.7	3.3	3.6	3.6	1	2
123	Metolachlor	3.7	2.5	2.5	2.5	<1	1
124	Myclobutanil	97.9	3.8	5.3	3.8	1	3
125	Oxadiazon	22.2	1.1	3.8	3.4	1	2
126	Oxadixyl	2.8	7.5	2.6	10.1	<1	1
127	Paclobutrazol	1.9	1.6	1.6	1.6	<1	1
128	Parathion	0.9	0.9	0.9	0.9	<1	<1
129	Parathion methyl	3.2	3.2	3.2	3.2	<1	2
130	Penconazole	1.8	1.8	1.8	1.8	<1	1
131	Pendimethalin	0.3	0.4	0.3	0.3	<1	<1
132	Permethrin	6.7	7.4	7.0	9.3	1	4
133	Phenothrin	5.6	5.5	5.6	6.4	1	3
134	Phenthoate	5.5	5.5	5.5	5.5	1	3
135	Phosalone	4.6	4.6	4.6	4.6	1	2
136	Phosmet	4.2	4.2	4.2	5.5	1	2
137	Phosphamidon	0.8	0.8	0.8	0.8	<1	<1
138	Piperonyl butoxide	0.8	1.1	0.6	0.3	<1	<1
139	Pirimiphos methyl	2.7	2.7	2.7	2.7	<1	1
140	Pretilachlor	2.4	2.4	2.4	2.4	<1	1
141	Procymidone	7.1	5.8	1.6	1.7	<1	1
142	Profenofos	4.3	4.6	4.6	4.6	1	2
143	Prometryn	0.5	0.3	0.3	0.3	<1	<1
144	Propaphos	2.5	2.5	2.5	3.6	<1	1
145	Propiconazole	3.9	3.9	3.9	3.9	1	2
146	Propoxur	3.0	3.0	3.0	2.9	<1	2
147	Propyzamide	1.6	2.7	2.7	2.7	<1	1
148	Prothiofos	0.9	0.9	2.0	3.2	<1	1
149	Pyraflufen ethyl	83.6	4.8	4.8	4.8	1	2
150	Pyrazophos	3.6	3.6	3.6	3.6	1	2

表 2 （つづき）

	Compound	RSD%				LOD[c] (ppb)	LOQ[c] (ppb)
		10mDa	20mDa	50mDa	100mDa		
151	Pyributicarb	4.7	3.8	3.0	2.6	<1	2
152	Pyridaben	6.6	6.6	6.6	6.6	1	3
153	Pyridafenthion	2.4	2.4	4.5	4.5	1	2
154	Pyrifenox (E)	2.0	2.0	2.0	2.0	<1	1
155	Pyrifenox (Z)	0.7	0.7	0.7	0.7	<1	<1
156	Pyrimethanil	1.6	1.6	1.6	1.4	<1	1
157	Pyriminobac methyl (E)	3.2	3.2	3.2	3.2	<1	2
158	Pyriminobac methyl (Z)	1.5	1.5	1.5	1.5	<1	1
159	Pyriproxyfen	5.0	7.9	4.1	5.3	1	2
160	Quinalphos	2.8	2.8	2.8	—[b]	<1	1
161	Quinoxyfen	2.5	3.8	4.0	3.4	1	2
162	Quintozene	1.1	1.1	1.1	1.1	<1	1
163	Silafluofen	5.4	8.9	9.1	9.1	1	5
164	Simeconazole	4.5	4.5	6.3	6.3	1	3
165	Tebuconazole	4.6	4.7	4.7	4.7	1	2
166	Tebufenpyrad	3.3	4.0	4.0	4.0	1	2
167	Tecnazene	1.7	1.7	1.7	1.7	<1	1
168	Tefluthrin	1.7	1.7	1.7	1.4	<1	1
169	Terbufos	2.1	2.1	2.1	2.1	<1	1
170	Tetrachlorvinphos	2.8	2.2	3.1	2.3	<1	2
171	Tetraconazole	0.3	0.1	0.1	0.1	<1	<1
172	Tetradifon	5.9	6.7	6.7	6.7	1	3
173	Thenylchlor	1.6	1.6	1.6	1.6	<1	1
174	Thiobencarb	3.6	3.5	3.4	3.2	1	2
175	Tolclofos methyl	2.2	2.2	1.9	1.8	<1	1
176	Tolfenpyrad	107.2	9.2	9.4	9.4	1	5
177	Triadimefon	20.9	2.9	1.6	3.5	<1	1
178	Triallate	2.1	2.1	2.1	1.5	<1	1
179	Triazophos	4.3	3.7	3.7	3.7	1	2
180	Tribuphos	1.5	1.5	1.5	1.5	<1	1
181	Trifloxystrobin	5.1	3.5	5.5	7.6	1	3
182	Trifluralin	2.1	2.1	2.1	2.1	<1	1
183	Uniconazole P	2.6	2.6	2.6	2.6	<1	1
184	Vinclozolin	1.3	0.8	0.8	1.8	<1	<1

a: 試料中 0.05 ppm 相当
b: 検出せず
c: 抽出質量幅 50 mDa での結果を用いて算出

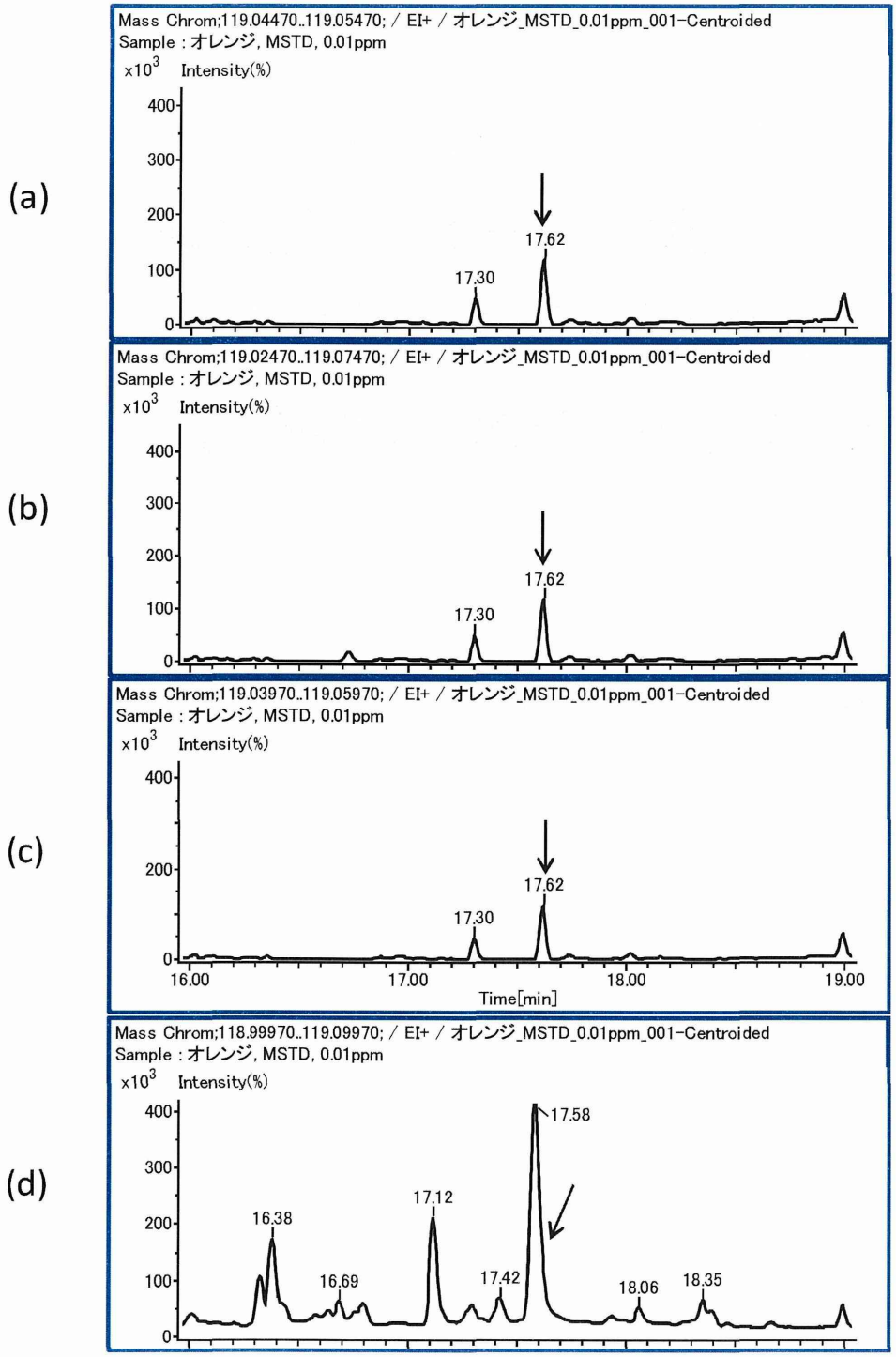


図 1　オレンジのマトリックス標準溶液の mepronil (*m/z* 119.0497) の抽出イオンクロマトグラム
(a) 10 mDa、(b) 20 mDa、(c) 50 mDa、(d) 100 mDa

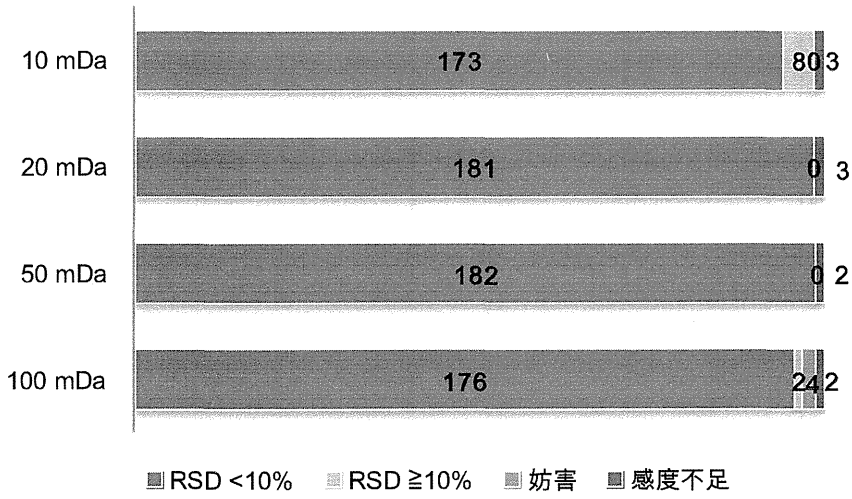


図 2　オレンジのマトリックス標準溶液（試料中 0.005 ppm 相当）のピーク面積の変動
（図内の数字は農薬数を示した。）

Ⅲ. 研究成果の刊行に関する一覧表

Ⅲ. 研究成果の刊行に関する一覧表

雑誌

発表者氏名	論文タイトル名	発表誌名	巻号	ページ	出版年
Shida, S., Nemoto, S., and Matsuda, R.	Simultaneous determination of acidic pesticides in vegetables and fruits by liquid chromatography–tandem mass spectrometry.	*Journal of Environmental Science and Health, Part B*	50	151-162	2015
Saito-Shida, S., Nemoto, S., and Teshima, R.	Multiresidue determination of pesticides in tea by gas chromatography-tandem mass spectrometry.	*Journal of Environmental Science and Health, Part B*	50	760-776	2015

Ⅳ. 研究成果の刊行物・別刷

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Simultaneous determination of acidic pesticides in vegetables and fruits by liquid chromatography—tandem mass spectrometry

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A sensitive and efficient method has been developed for the simultaneous determination of 73 multi-class acidic pesticides, such as phenoxy acid and sulfonylurea herbicides, in vegetables and fruits. The sample preparation procedure was carefully optimized for the efficient removal of co-extracted matrix components. The method involves extraction of acidic pesticides with acetonitrile containing hydrochloric acid, removal of water from crude extract by salting out, and sequential cleanup by octadecylsilyl silica gel and silica gel columns. For samples containing high amounts of pigments, such as spinach, additional cleanup using a graphitized carbon column was performed prior to liquid chromatography–mass spectrometry (LC–MS/MS) analysis. Recovery tests were performed for five times for each sample of cabbage, spinach, potato, eggplant, orange, and apple fortified at 0.01 mg kg−1. Out of the 73 tested pesticides, 70 for cabbage, 67 for spinach, 69 for potato, 67 for eggplant, 64 for orange, and 70 for apple were within the range of 70–120%, with relative standard deviations below 25%. Nitenpyram and pyrasulfotole showed low recoveries for all the samples tested, probably due to low recoveries from silica gel column. The developed method effectively removed co-extracted matrix components and was highly selective, with no interfering peaks found in the chromatograms of blank samples. The overall results indicate that the developed method is suitable for the quantitative analysis of acidic pesticide residues in vegetables and fruits.

Keywords: Acidic pesticides, LC–MS/MS, Multi-residue method, vegetables and fruits.

Introduction

Pesticides are used extensively throughout the world to protect agricultural products from pests such as insects, bacteria, fungi, and viruses. However, since pesticides are harmful to humans as well as animals and the environment,[1,2] pesticide residues must be controlled. Therefore, regulatory agencies of many countries have established maximum residue limits (MRLs) in foods, with the aim of minimizing the health risks associated with their consumption. For this reason, it is important to develop sensitive and reliable Multi-residue methods for monitoring pesticides in various foods. To date, numerous Multi-residue methods have been developed for monitoring pesticides in foods. Anastassiades et al. reported the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method for the analyses of a wide range of pesticides;[3] many modified versions of this method applied to various foods have been subsequently reported.[4–7] Fillion et al. demonstrated a Multi-residue method in vegetables and fruits by employing gas chromatography–mass spectrometry (GC–MS) and liquid chromatography (LC) with fluorescence detection.[8] In Japan, an official "Multi-residue method I for agricultural chemicals by LC–MS" has been established (Fig. 1a),[9] which is a modification of the method developed by Fillion et al.[8] These methods use anion exchange sorbents – i.e., primary secondary amine (PSA) or aminopropyl-silanized silica gel (NH_2) sorbents – for cleanup and can effectively remove acidic co-extracted matrix components such as organic and fatty acids. However, PSA and NH_2 sorbents also retain acidic pesticides, leading to poor recoveries.

Several methods have been published for the analysis of phenoxy acid herbicides in vegetables and fruits,[10,11] rice,[12] and kidney tissues.[13] In addition, methods have been reported for analyzing sulfonylurea herbicides in crops,[14–16] grapes,[17] and milk.[18] However, the simultaneous determination of multi-class acidic pesticides in complicated food matrices is a challenging task because of the wide range of pK_a values and polarities of pesticides; consequently, there are very few reported methods for such analyses. Pareja et al. have evaluated various

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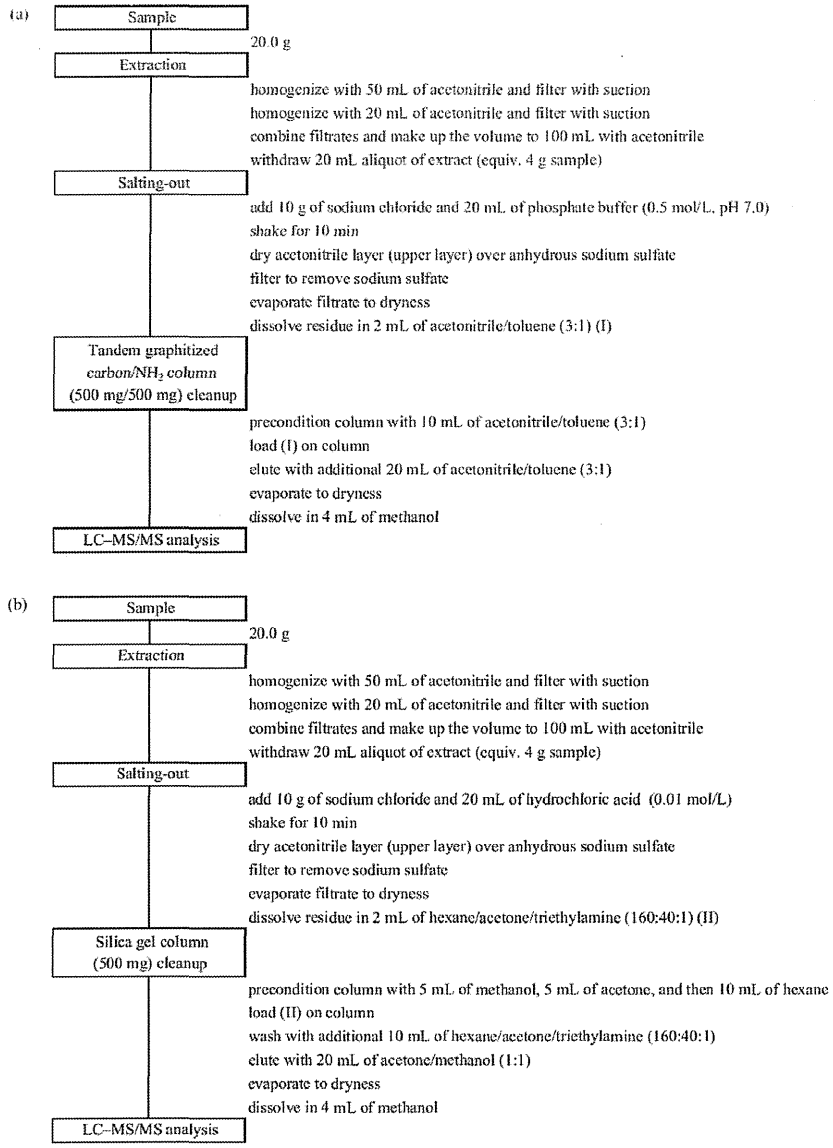

Fig. 1. Flow chart showing the sequence of steps in (a) the Japanese official Multi-residue method I, and (b) the Japanese official Multi-residue method II in vegetables and fruits.

modified QuEChERS methods and described a method with no cleanup step for analyzing acidic herbicides, including phenoxy acid and sulfonylurea herbicides, in polished rice.[19] Akiyama et al. demonstrated the simultaneous determination of multi-class acidic pesticides in vegetables and fruits without a cleanup step and determined by liquid chromatography–time-of-flight mass spectrometry (LC–TOFMS).[20] In Japan, an official "Multi-residue method II for agricultural chemicals by LC–MS" has been established (Fig. 1b)[9] for acidic pesticides that cannot be determined by the Japanese official Multi-residue method I (Fig. 1a). However, the removal of co-extracted matrix components without using PSA or NH_2 sorbent is insufficient, often causing significant matrix effects.

The aim of this study was to develop a sensitive and reliable Multi-residue method for acidic pesticides in