Multi-residue Method for Agricultural Chemicals by GC-MS (Animal and Fishery Products)

1. Analytes

For muscle, fat, liver, kidney and fish/shellfish, see Table 5.

For milk, egg and honey, see Table 6.

2. Instrument

Gas chromatograph/mass spectrometer (GC-MS)

3. Reagents

Use the reagents listed in Section 3 of the General Rules, except the following.

Reference standards of agricultural chemicals: Reference standards of known purities for each agricultural chemical.

4. Procedure

1) Extraction

i) Muscle, fat, liver, kidney and fish/shellfish

For muscle, liver, kidney and fish/shellfish, weigh 20.0 g of sample. For fat, weigh 5.0 g of sample.

Add 20 mL of water to the sample, homogenize, add 100 mL of acetone/*n*-hexane (1:2, v/v), homogenize again, centrifuge at 2,500 rpm for 5 minutes, and collect the organic layer.

Add 50 mL of *n*-hexane to the residue, homogenize, and centrifuge at 2,500 rpm for 5 minutes. Combine the obtained organic layers, dehydrate with anhydrous sodium sulfate, and filter out the anhydrous sodium sulfate. Concentrate the filtrate at below 40°C, and remove the solvent. Weigh the residue and record the weight as the extracted fat weight. Take all or aliquot of the residue, and dissolve in acetone/cyclohexane (1:4, v/v) so that the amount applying to a gel permeation chromatography column (styrene-divinylbenzene copolymer column) corresponds to 5.0 g of sample. (If the extracted fat weight in 5.0 g of sample is more than 0.5 g, the amount applying to the column should be corresponded to 0.50 g of extracted fat).

ii) Milk, egg and honey

For milk and egg, weigh 20.0 g of sample. For honey, weigh 20.0 g of sample and dissolve in 20 mL of water.

Add 100 mL of acetonitrile, homogenize, centrifuge at 2,500 rpm for 5 minutes, and take the organic layer. Add 50 mL of acetonitrile to the residue, homogenize, and centrifuge at 2,500 rpm for 5 minutes. Combine the obtained organic layers, add 10 g of sodium chloride, and shake. Let stand and discard the separated aqueous layer. Dehydrate the

acetonitrile layer with anhydrous sodium sulfate, and filter out the anhydrous sodium sulfate. Concentrate the filtrate at below 40°C and remove the solvent. For milk and egg, dissolve the residue in acetone/cyclohexane (1:4, v/v) so that the amount applying to a gel permeation chromatography column (styrene-divinylbenzene copolymer column) corresponds to 5.0 g of sample. For honey, dissolve the residue in acetone/*n*-hexane (1:1, v/v) to make exactly 10 mL.

2) Clean-up

i) Muscle, fat, fish/shellfish milk, and egg

a) Gel permeation chromatography

Centrifuge the solution obtained in 1) at 3,000 rpm for 5 minutes, transfer 5 mL of the supernatant to the gel permeation chromatography column (styrene-divinylbenzene copolymer column), and elute with acetone/cyclohexane (1:4, v/v). Collect the fraction eluted from the retention time of acrinathrin to the finish time of tricyclazole elution, concentrate at below 40°C, and remove the solvent. Dissolve the residue in 2 mL of acetone/*n*-hexane (1:1, v/v).

b) Ethylenediamine-*N*-propylsilanized silica gel column chromatography

Add 10 mL of acetone/*n*-hexane (1:1, v/v) to an ethylenediamine-*N*-propylsilanized silica gel cartridge (500 mg), and discard the effluent. Transfer the solution obtained in a) to the cartridge, elute with 20 mL of acetone/*n*-hexane (1:1, v/v), collect the total eluate, concentrate at below 40°C, and remove the solvent. Dissolve the residue in acetone/*n*-hexane (1:1, v/v) to make exactly 1 mL (0.5 mL for fat), and use this solution as the test solution.

ii) Liver and kidney

a) Gel permeation chromatography

Centrifuge the solution obtained in 1) at 3,000 rpm for 5 minutes, transfer 5 mL of the supernatant to the gel permeation chromatography column (styrene-divinylbenzene copolymer column), and elute with acetone/cyclohexane (1:4, v/v). Collect the fraction eluted from the retention time of acrinathrin to the finish time of acrinathrin elution (Fraction I), and the fraction eluted from the finish time of Fraction I collection to the finish time of tricyclazole elution (Fraction II).

b) Ethylenediamine-*N*-propylsilanized silica gel column chromatography

Add 10 mL of acetone/cyclohexane (1:4, v/v) to an ethylenediamine-*N*-propylsilanized silica gel cartridge (500 mg), and discard the effluent. Transfer the Fraction I to the cartridge, elute with 5 mL of acetone/cyclohexane (1:4, v/v), collect the total eluate, concentrate at below 40°C, and remove the solvent. Dissolve the residue in 1 mL of *n*-hexane.

c) Silica gel column chromatography

Add 10 mL of *n*-hexane to the silica gel cartridge (690 mg), and discard the effluent. Transfer the solution obtained in b) to the cartridge, add 10 mL of *n*-hexane, and discard the effluent. Elute with 15 mL of diethyl ether/*n*-hexane (1:19, v/v), combine the eluate with Fraction II obtained in a), concentrate at below 40°C, and remove the solvent. Dissolve the residue in acetone/*n*-hexane (1:1, v/v) to make exactly 1 mL, and use this solution as the test solution.

iii) Honey

Add 10 mL of acetone/*n*-hexane (1:1, v/v) to an ethylenediamine-*N*-propylsilanized silica gel cartridge (500 mg), and discard the effluent. Transfer 2.5 mL of acetone/*n*-hexane (1:1, v/v) solution obtained in 1) to the cartridge, elute with 20 mL of acetone/*n*-hexane (1:1, v/v), collect the total eluate, concentrate at below 40°C, and remove the solvent. Dissolve the residue in acetone/*n*-hexane (1:1, v/v) to make exactly 1 mL, and use this solution as the test solution.

5. Calibration curve

Prepare stock standard solutions (acetone) of each reference standard of agricultural chemical. Mix them, and prepare several solutions (acetone/*n*-hexane (1:1, v/v)) containing each agricultural chemical at appropriate concentration ranges. Inject 2 µL of each standard solution to GC-MS, and make calibration curves by peak-height or peak-area method.

6. Quantification

Inject 2 µL of the test solution to GC-MS, and calculate the concentration of each agricultural chemical from the calibration curves made in **5**.

7. Confirmation

Confirm using GC-MS.

8. Measurement conditions

GC-MS

Column: 5% phenyl-methyl silicone, 0.25 mm in inside diameter, 30 m in length and 0.25 µm in film thickness

Column temperature: 50°C (1 min) - 25°C/min heating - 125°C (0 min) - 10°C/min heating - 300°C (10 min)

Inlet temperature: 250°C

Carrier gas: Helium

Ionization mode (voltage): EI (70 eV)

Major monitoring ions (m/z): See Table 5 and 6.

Expected retention time: See Table 5 and 6.

9. Limit of quantification

See Table 5 and 6.

Note that these tables show examples of limits of measurement (ng), not limits of quantification.

10. Explanatory note

1) Outline of analytical method

The method consists of extraction of each agricultural chemical from sample with acetone/*n*-hexane (1:2, v/v) (acetonitrile for milk, egg and honey), clean-up with a gel permeation chromatography and an ethylenediamine-*N*-propylsilanized silica gel column chromatography (also clean-up with a silica gel column chromatography for liver and kidney, omit gel permeation chromatography for honey), and quantification and confirmation using GC-MS.

2) Notes

i) Table 5 and 6 list the analytes for which this method is applicable in the order they appear in the Japanese syllabary. Note that the maximum residue limits (MRLs) defined for some agricultural chemicals include not only the parent compounds, but also their metabolites or other transformation products, which are inapplicable to this method. Isomers with different retention times are listed as separate "Analytes". "Degradation product" in parentheses means that the analyte is a degraded product which is formed during analysis.

ii) This method does not ensure simultaneous analysis of all of the analytes listed in Table 5 and 6. In advance, confirm that degradation or interference does not occur as the result of interaction between the target analytes.

iii) Gas chromatograph/tandem mass spectrometer (GC-MS/MS) can also be used for analyses.

iv) If the quantity of sodium chloride (10 g) is too large to add to the acetonitrile extract, it may be reduced so long as saturation is achieved.

v) Concentration and complete removal of the solvent should be performed under a gentle stream of nitrogen.

vi) An example of the conditions for gel permeation chromatography is shown below.

Column: Styrene-divinylbenzene copolymer column (20 mm in inside diameter and 300 mm in length) connected with a styrene-divinylbenzene copolymer column (20 mm in inside diameter and 100 mm in length) as a guard column, or other column with equal characteristics.

Mobile phase: acetone/cyclohexane (1:4, v/v)

Flow rate: 5 mL/min

Column temperature: 40°C

Injection volume: 5 mL

Monitoring wavelength: 254 mm

Collection range: Determine in advance using the following method.

Prepare 5 mg/L mixed solution of acrinathrin and tricyclazole in mobile phase, transfer 5 mL of the solution to a gel permeation chromatography column, monitor the retention times at 254 nm, and confirm the elution positions. Alternative methods, such as, collecting fractions at appropriate intervals and analyzing by GC-MS(/MS) can also be used.

a. Collection range for muscle, fat, fish/shellfish, milk and egg (Figure 1)

From the retention time of acrinathrin to the finish time of tricyclazole elution

(Example) 58 to 165 mL (total volume: 107 mL)

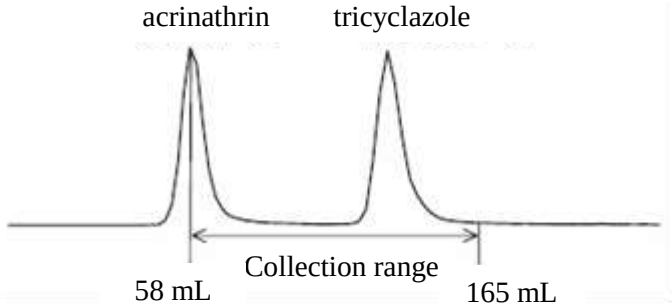


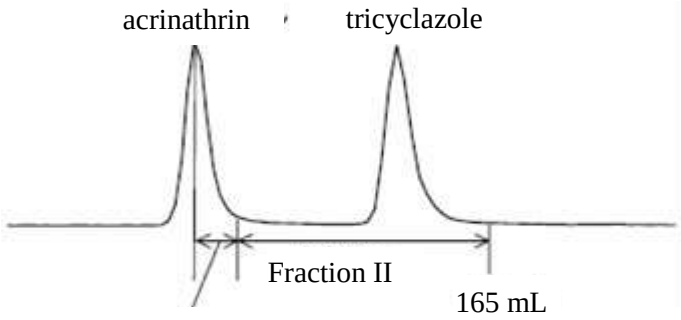
Figure 1. Collection range for muscle, fat, fish/shellfish, milk and egg

b. Collection range for liver and kidney (Figure 2)

Fraction I: From the retention time of acrinathrin to the finish time of its elution

Fraction II: From the finish time of Fraction I collection to the finish time of tricyclazole elution

(Example) Fraction I: 58 to 65 mL (total volume: 7 mL), Fraction II: 65 to 165 mL (total volume: 100 mL)



Fraction I (58 to 65 mL)

Contains high amounts of matrix components.

Figure 2. Collection range for liver and kidney

vii) Before using cartridges for clean-up, confirm the elution position of each agricultural chemical.

viii) For samples containing high quantities of fat, the concentration rates for the test solutions are low. If the targeted measurement sensitivity is not achievable, repeat the "gel permeation chromatography" procedure, and thereafter, using the extracted fat, combine the solutions and use the new mixture as the test solution.

ix) Matrix-matched calibration or standard addition may be required to obtain accurate measurement results.

x) Because the limit of quantification differs depending on the instrument used, the concentration rate of the test solution, and the injection volume, it may be necessary to optimize the conditions.

11. References

None

12. Type

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Table 5. Multi-residue Method for Agricultural Chemicals by GC-MS (Animal and Fishery Products : muscle, fat, liver, kidney and fish/shellfish)

Agricultural chemicals	Analytes	Retention index	Monitoring ions (m/z)					Limit of measurement (ng)
γ -BHC(Lindane)	γ -BHC(Lindane)	1775	***219***	183	181			0.005
DDT	o,p'-DDT	2289	237	***235***				0.001
	p,p'-DDD	2285	237	***235***				0.001
	p,p'-DDE	2192	***318***	246				0.0005
	p,p'-DDT	2367	237	***235***				0.001
EPTC	EPTC	1360	132	***128***	86			0.002
Azinphos-methyl	Azinphos-methyl	2570	***160***	132				0.006
Atrazine	Atrazine	1755	215	***200***				0.001
Ametryn	Ametryn	1912	***227***	212				0.0006
Alachlor	Alachlor	1899	237	***188***	160			0.001
Aramite	Aramite (isomer 1)	2190	***334***	197	***185***			0.046
	Aramite (isomer 2)	2196	***334***	197	***185***			0.046
	Aramite (isomer 3)	2208	334	***319***				0.004
	Aramite (isomer 4)	2230	334	***319***				0.009
Aldrin/Dieldrin	Aldrin	1993	***263***	261				0.003
Allethrin	Allethrin (isomer 1/isomer 2)	2066	***136***	***123***				0.002
	Allethrin (isomer 3/isomer 4)	2075	***136***	***123***				0.002
Isoprothiolane	Isoprothiolane	2175	***290***	231	***189***	***162***	118	0.002
Iprodione	Iprodione	2452	316	***314***				0.01
	Iprodione metabolite	2536	***329***	***187***				0.022
Imazalil	Imazalil	2171	***215***	173				0.003
Fenvalerate	Esfenvalerate (isomer 1)	2951	***419***	225	181	***167***		0.059
	Esfenvalerate (isomer 2)	2982	***419***	225	181	***167***		0.003
Ethion	Ethion	2279	384	***231***	153			0.0004
Etoxazole	Etoxazole	2487	359	***300***				0.003
Ethofumesate	Ethofumesate	1951	286	***207***				0.002
Ethoprophos	Ethoprophos	1640	***200***	***158***				0.006
Etridiazole	Etridiazole	1456	213	***211***	183			0.001
Epoxiconazole	Epoxiconazole	2424	194	***192***				0.006
Endosulfan	α-Endosulfan	2150	243	***241***	170			0.012
	β-Endosulfan	2277	***241***	195				0.014
	Endosulfan sulfate	2362	274	***272***				0.004
Endrin	Endrin	2255	317	***263***	245			0.005
Oxadiazon	Oxadiazon	2187	344	***258***	***175***			0.001
Oxabetrinil	Oxabetrinil	1841	103	77	***73***			0.003
Oxyfluorfen	Oxyfluorfen	2197	***361***	***252***				0.004
Carfentrazone-ethyl	Carfentrazone-ethyl	2325	340	330	***312***			0.002

Carboxin	Carboxin	2211	235	***143***	87			0.002
Carbosulfan	Carbosulfan	2451	***160***	118				0.002
Quinoxyfen	Quinoxyfen	2353	307	***237***				0.001
Quintozene	Quintozene	1764	249	***237***				0.003
Kresoxim-methyl	Kresoxim-methyl	2203	***206***	132	***116***			0.002
Chlorthal-dimethyl	Chlorthal-dimethyl	1988	***301***	299				0.0003
Chlordane	*cis*-Chlordane	2148	375	***373***				0.001
	trans-Chlordane	2121	375	***373***				0.001
	Oxychlordane	2071	389	***387***				0.006
Chlorpyrifos	Chlorpyrifos	1980	316	***314***				0.004
Chlorpyrifos-methyl	Chlorpyrifos-methyl	1885	288	***286***				0.0003
Chlorfenapyr	Chlorfenapyr	2221	406	247	***59***			0.002
Chlorfenson	Chlorfenson	2166	304	***302***	175			0.01
Chlorfenvinphos	(*E*)-Chlorfenvinphos	2046	***323***	***267***				0.009
	(*Z*)-Chlorfenvinphos	2069	***323***	***267***				0.003
Chlorbufam	Chlorbufam	1751	225	***223***	164	***153***		0.016
Chlorbenside	Chlorbenside	2117	270	***268***	125			0.003
Chloroneb	Chloroneb	1509	208	206	***193***	***191***		0.001
Chlorobenzilate	Chlorobenzilate	2262	253	***251***	139			0.003
Diclofop-methyl	Diclofop-methyl	2392	342	***340***	253			0.003
1,1-Dichloro-2,2-bis(4-ethylphenyl) ethane	1,1-Dichloro-2,2-bis (4-ethylphenyl) ethane	2243	224	***223***				0.0005
Dicofol	Degradation product of dicofol (4,4'-dichlorobenzofenone)	2014	250	***139***				0.003
Disulfoton	Disulfoton	1814	274	186	89	***88***		0.001
	Disulfoton sulfone	2130	***213***	153				0.003
Cyhalothrin	Cyhalothrin (isomer 1)	2572	***197***	181				0.009
	Cyhalothrin (isomer 2)	2596	***197***	181				0.009
Diphenylamine	Diphenylamine	1634	***169***	168	167			0.0004
Difenoconazole	Difenoconazole (isomer 1)	3019	***323***	265				0.009
	Difenoconazole (isomer 2)	3027	***323***	265				0.007
Cyfluthrin	Cyfluthrin (isomer 1)	2777	226	***206***				0.034
	Cyfluthrin (isomer 2)	2791	226	***206***				0.029
	Cyfluthrin (isomer 3)	2799	226	***206***				0.042
	Cyfluthrin (isomer 4)	2805	226	***206***				0.05
Diflufenican	Diflufenican	2396	394	***266***				0.0002
Cyproconazole	Cyproconazole (isomer 1)	2238	224	***222***				0.008
	Cyproconazole (isomer 2)	2240	224	***222***				0.006
Cypermethrin	Cypermethrin (isomer 1)	2823	165	***163***	127			0.039
	Cypermethrin (isomer 2)	2837	165	***163***	127			0.025
	Cypermethrin (isomer 3)	2845	165	***163***	127			0.041

	Cypermethrin (isomer 4)	2850	165	***163***	127			0.034
Simazine	Simazine	1748	***201***	186				0.003
Spiroxamine	Spiroxamine (isomer 1)	1896	198	101	***100***			0.002
	Spiroxamine (isomer 2)	1948	198	101	***100***			0.001
Diazinon	Diazinon	1791	304	***179***				0.004
Di-Allate	Di-Allate (isomer 1)	1696	236	***234***				0.001
	Di-Allate (isomer 2)	1714	236	***234***				0.003
Thiobencarb	Thiobencarb	1985	257	***100***				0.001
Thiometon	Thiometon	1724	125	***88***				0.002
Aldrin/Dieldrin	Dieldrin	2208	277	***263***				0.01
Tecnazene	Tecnazene	1597	***261***	259				0.002
Tetrachlorvinphos	(Z)-Tetrachlorvinphos	2121	331	***329***	109			0.002
Tebuconazole	Tebuconazole	2398	***250***	125				0.005
Tefluthrin	Tefluthrin	1816	197	***177***				0.0004
Deltamethrin/Tralomethrin	Deltamethrin (isomer 1)	3029	***253***	***181***				0.417
	Deltamethrin (isomer 2)	3059	***253***	***181***				0.008
Terbutryn	Terbutryn	1944	241	***226***				0.001
Terbufos	Terbufos	1781	***231***	153				0.002
Deltamethrin/Tralomethrin	Degradation product of tralomethrin 1 [=Deltamethrin (isomer 1)]	3028	***253***	***181***				0.587
	Degradation product of tralomethrin 2 [=Deltamethrin (isomer 2)]	3057	***253***	***181***				0.02
Triadimenol	Triadimenol	2095	***168***	112				0.01
Triadimefon	Triadimefon	1999	210	***208***	181			0.01
Triazophos	Triazophos	2310	177	***172***	***161***			0.014
Tri-allate	Tri-allate	1827	270	***268***	143			0.003
Triticonazole	Triticonazole	2556	299	237	***235***			0.008
Tribuphos	Tribuphos	2194	***202***	169				0.005
Triflumizole	Triflumizole	2087	***278***	206				0.002
Trifluralin	Trifluralin	1661	***306***	264				0.001
Trifloxystrobin	Trifloxystrobin	2333	222	186	***116***			0.003
Nitrapyrin	Nitrapyrin	1452	***196***	***194***				0.0005
Barban	Barban	2190	***222***	***153***				0.021
Parathion	Parathion	1996	***291***	139	87			0.004
Parathion-methyl	Parathion-methyl	1899	***263***	109				0.002
Allethrin	Bioallethrin (isomer 1)	2073	136	***123***				0.003
	Bioallethrin (isomer 2)	2075	136	***123***				0.004
Bioresmethrin	Bioresmethrin (isomer 1)	2401	***171***	***123***				0.223
	Bioresmethrin (isomer 2)	2413	***171***	***123***				0.005
Picolinafen	Picolinafen	2477	***376***	238				0.001
Bitertanol	Bitertanol (isomer 1)	2700	171	***170***	168			0.0004
	Bitertanol (isomer 2)	2714	171	***170***	168			0.002

Bifenthrin	Bifenthrin	2471	***181***	166	165			0.001
Piperonyl butoxide	Piperonyl butoxide	2407	177	***176***	149			0.001
Pyraclostrobin	Degradation product of pyraclostrobin	2964	164	***132***				0.032
Pyraclofos	Pyraclofos	2664	362	***360***				0.004
Pyrazophos	Pyrazophos	2619	373	232	***221***			0.013
Pyridaben	Pyridaben	2732	309	***147***				0.004
Pyriproxyfen	Pyriproxyfen	2578	226	***136***	78			0.002
Pirimicarb	Pirimicarb	1839	238	***166***	72			0.001
Pirimiphos-methyl	Pirimiphos-methyl	1941	305	***290***				0.001
Pyrimethanil	Pyrimethanil	1799	199	***198***				0.0002
Pyrethrins	Pyrethrins I	2297	***162***	133	***123***			0.154
	Pyrethrins II	2629	167	***161***	***160***	107		0.258
Vinclozolin	Vinclozolin	1890	287	***285***	212			0.002
Famphur	Famphur	2334	***218***	217				0.005
Famoxadone	Famoxadone	3106	***330***	197	196			0.007
Fipronil	Fipronil	2049	369	***367***	351	213		0.002
Fenamiphos	Fenamiphos	2152	***303***	288	154			0.009
Fenarimol	Fenarimol	2631	251	***219***				0.007
Fenitrothion	Fenitrothion	1949	***277***	260				0.003
Fenoxaprop-ethyl	Fenoxaprop-ethyl	2667	***361***	288				0.003
Phenothrin	Phenothrin (isomer 1)	2526	***183***	123				0.007
	Phenothrin (isomer 2)	2540	***183***	123				0.003
Fenobucarb	Fenobucarb	1609	150	***121***				0.001
Fenamidone	Fenamidone	2496	***268***	***238***				0.003
Fenthion	Fenthion	1990	279	***278***	169			0.001
Fenvalerate	Fenvalerate (isomer 1)	2953	225	***167***				0.006
	Fenvalerate (isomer 2)	2982	225	***167***				0.022
Fenbuconazole	Fenbuconazole	2776	***198***	129				0.004
Fenpropathrin	Fenpropathrin	2495	***181***	125				0.006
Fenpropimorph	Fenpropimorph	1991	303	129	***128***			0.001
Buprofezin	Buprofezin	2204	305	175	***172***	106		0.004
Furathiocarb	Furathiocarb	2526	***194***	***163***				0.003
Flamprop-methyl	Flamprop-methyl	2190	335	***276***	231	***105***	77	0.003
Fluquinconazole	Fluquinconazole	2723	375	342	***340***			0.001
Fludioxonil	Fludioxonil	2169	***248***	154				0.004
Flucythrinate	Flucythrinate (isomer 1)	2847	***199***	157				0.011
	Flucythrinate (isomer 2)	2874	***199***	157				0.017
Flusilazole	Flusilazole	2202	234	***233***	206			0.001
Flutolanil	Flutolanil	2162	***323***	281	***173***			0.003
Flufenacet	Flufenacet	1991	***211***	151				0.011
Fluridone	Fluridone	2908	329	***328***				0.003
Prochloraz	Prochloraz	2738	310	***180***				0.014
Procymidone	Procymidone	2088	285	***283***				0.003
Propaquizafop	Propaquizafop	3277	***443***	299				0.015

Propanil	Propanil	1879	217	***163***	***161***			0.013
Propargite	Propargite (isomer 1/isomer 2)	2402	***350***	173	***135***			0.014
Propiconazole	Propiconazole (isomer 1)	2348	261	***259***				0.007
	Propiconazole (isomer 2)	2362	261	***259***				0.006
Propyzamide	Propyzamide	1789	175	***173***				0.003
Profenofos	Profenofos	2186	339	***337***				0.004
Propetamphos	Propetamphos	1777	***194***	***138***				0.004
Prometryn	Prometryn	1918	***241***	226	184			0.002
Bromopropylate	Bromopropylate	2487	343	***341***	339			0.005
Hexachlorobenzene	Hexachlorobenzene	1717	286	***284***				0.001
Benalaxyl	Benalaxyl	2331	***206***	***148***				0.002
Heptachlor	Heptachlor	1920	337	274	***272***			0.001
	Heptachlor epoxide	2072	***353***	351				0.001
Permethrin	Permethrin (isomer 1)	2706	184	***183***				0.003
	Permethrin (isomer 2)	2723	184	***183***				0.003
Penconazole	Penconazole	2064	***248***	159				0.003
Pendimethalin	Pendimethalin	2047	253	***252***				0.005
Benfuracarb	Benfuracarb	2624	***190***	164	163			0.002
Boscalid	Boscalid	2832	344	***342***	***140***			0.016
Phosmet	Phosmet	2480	161	***160***				0.008
Phorate	Phorate	1700	***260***	231	75			0.01
Malathion	Malathion	1965	***173***	127	125			0.006
Myclobutanil	Myclobutanil	2198	***179***	150				0.006
Methacrifos	Methacrifos	1496	***240***	208	180			0.003
Methidathion	Methidathion	2113	***145***	85				0.003
Methoxychlor	Methoxychlor	2491	228	***227***				0.002
Methoprene	Methoprene	2097	***191***	153	111	***73***		0.009
Metolachlor	Metolachlor	1977	238	***162***				0.002
	S-Metolachlor	1975	***238***	162				0.0007
Mefenpyr-diethyl	Mefenpyr-diethyl	2424	255	***253***				0.002
Resmethrin	Resmethrin (isomer 1)	2399	***171***	123				0.037
	Resmethrin (isomer 2)	2414	***171***	123				0.004

・The compounds are listed in the order of the Japanese syllabary, and the isomers are listed by their retention times.

・Retention indices are obtained based on the retention times of the *n*-alkanes and show the average values obtained from 2-4 laboratories.

・Monitoring ions in bold italic font are for quantification; the others are for confirmation.

・The limit of measurement is the value at S/N=10 when 2 μL of a standard solution is injected into an GC-MS. The limit is the lowest of the values obtained from laboratories.

・When 2 μL of a test solution prepared by the described method is injected into an GC-MS(/MS), 0.1 ng[*1] (0.025 ng[*2] for fat sample) corresponds to 0.01 ppm.

*1 For test solutions (final volume: 1 mL) prepared using an amount corresponding to 5 g of sample.

*2 For test solutions (final volume: 0.5 mL) prepared using an amount corresponding to 0.625 g of sample (and corresponding to 0.5 g of fat when the sample contains 80% fat).

Table 6. Multi-residue Method for Agricultural Chemicals by GC-MS (Animal and Fishery Products : milk, egg and honey**)**

Agricultural chemicals	Analytes	Retention index	Monitoring ions (m/z)					Limit of measurement (ng)
γ -BHC(Lindane)	γ -BHC(Lindane)	1775	***219***	183	181			0.005
DDT	o,p'-DDT	2289	237	***235***				0.001
	p,p'-DDD	2285	237	***235***				0.001
	p,p'-DDE	2192	***318***	246				0.0005
	p,p'-DDT	2367	237	***235***				0.001
Azamethiphos	Azamethiphos	2323	324	217	***215***			0.024
Azinphos-methyl	Azinphos-methyl	2570	***160***	132				0.006
Acetamiprid	Acetamiprid	2458	***152***	***126***	90			0.022
Acephate	Acephate	1436	***136***	94				0.003
Azoxystrobin	Azoxystrobin	3083	388	345	***344***			0.002
Atrazine	Atrazine	1755	215	***200***				0.001
Ametryn	Ametryn	1912	***227***	212				0.0006
Alachlor	Alachlor	1899	237	***188***	160			0.001
Aramite	Aramite (isomer 1)	2190	***334***	197	***185***			0.046
	Aramite (isomer 2)	2196	***334***	197	***185***			0.046
	Aramite (isomer 3)	2208	334	***319***				0.004
	Aramite (isomer 4)	2230	334	***319***				0.009
Aldicarb	Degradation product of aldicarb	897	***115***	100				0.012
Aldoxycarb	Degradation product of aldoxycarb	1131	80	***68***				0.003
Aldrin/Dieldrin	Aldrin	1993	***263***	261				0.003
Allethrin	Allethrin (isomer 1/isomer 2)	2066	***136***	***123***				0.002
	Allethrin (isomer 3/isomer 4)	2075	***136***	***123***				0.002
Isofenphos	Isofenphos	2066	255	***213***	121			0.004
	Isofenphos oxon	1998	***229***	201				0.003
Isoprothiolane	Isoprothiolane	2175	***290***	231	***189***	***162***	118	0.002
Iprodione	Iprodione	2452	316	***314***				0.01
Imazalil	Imazalil	2171	***215***	173				0.003
Fenvalerate	Esfenvalerate (isomer 1)	2951	***419***	225	181	***167***		0.059
	Esfenvalerate (isomer 2)	2982	***419***	225	181	***167***		0.003
Ethion	Ethion	2279	384	***231***	153			0.0004
Etoxazole	Etoxazole	2487	359	***300***				0.003
Ethofumesate	Ethofumesate	1951	286	***207***				0.002
Ethoprophos	Ethoprophos	1640	***200***	***158***				0.006
Epoxiconazole	Epoxiconazole	2424	194	***192***				0.006
Endosulfan	α-Endosulfan	2150	243	***241***	170			0.012
	β-Endosulfan	2277	***241***	195				0.014
	Endosulfan sulfate	2362	274	***272***				0.004

Endrin	Endrin	2255	317	***263***	245			0.005
Oxadiazon	Oxadiazon	2187	344	***258***	***175***			0.001
Oxabetrinil	Oxabetrinil	1841	103	77	***73***			0.003
Oxyfluorfen	Oxyfluorfen	2197	***361***	***252***				0.004
Omethoate	Omethoate	1596	110	***156***				0.005
Carbaryl	Carbaryl	1912	***144***	115				0.001
Carfentrazone-ethyl	Carfentrazone-ethyl	2325	340	330	***312***			0.002
Carboxin	Carboxin	2211	235	***143***	87			0.002
Carbofuran	Carbofuran	1742	221	***164***	149			0.001
Quinoxyfen	Quinoxyfen	2353	307	***237***				0.001
Quintozene	Quintozene	1764	249	***237***				0.003
Kresoxim-methyl	Kresoxim-methyl	2203	***206***	132	***116***			0.002
Chlorthal-dimethyl	Chlorthal-dimethyl	1988	***301***	299				0.0003
Chlordane	*cis*-Chlordane	2148	375	***373***				0.001
	trans-Chlordane	2121	375	***373***				0.001
	Oxychlordane	2071	389	***387***				0.006
Chlorpyrifos	Chlorpyrifos	1980	316	***314***				0.004
Chlorpyrifos-methyl	Chlorpyrifos-methyl	1885	288	***286***				0.0003
Chlorfenapyr	Chlorfenapyr	2221	406	247	***59***			0.002
Chlorfenson	Chlorfenson	2166	304	***302***	175			0.01
Chlorfenvinphos	(*E*)- Chlorfenvinphos	2046	***323***	***267***				0.009
	(*Z*)- Chlorfenvinphos	2069	***323***	***267***				0.003
Chlorbufam	Chlorbufam	1751	225	***223***	164	***153***		0.016
Chlorbenside	Chlorbenside	2117	270	***268***	125			0.003
Chloroneb	Chloroneb	1509	208	206	***193***	***191***		0.001
Chlorobenzilate	Chlorobenzilate	2262	253	***251***	139			0.003
Diclofop-methyl	Diclofop-methyl	2392	342	***340***	253			0.003
1,1-Dichloro-2,2-bis(4-ethylphenyl) ethane	1,1-Dichloro-2,2-bis (4-ethylphenyl) ethane	2243	224	***223***				0.0005
Dicofol	Degradation product of dicofol (4,4'-Dichlorobenzofenone)	2014	250	***139***				0.003
Disulfoton	Disulfoton	1814	274	186	89	***88***		0.001
	Disulfoton sulfone	2130	***213***	153				0.003
Cyhalothrin	Cyhalothrin (isomer 1)	2572	***197***	181				0.009
	Cyhalothrin (isomer 2)	2596	***197***	181				0.009
Diphenylamine	Diphenylamine	1634	***169***	168	167			0.0004
Difenoconazole	Difenoconazole (isomer 1)	3019	***323***	265				0.009
	Difenoconazole (isomer 2)	3027	***323***	265				0.007
Cyfluthrin	Cyfluthrin (isomer 1)	2777	226	***206***				0.034
	Cyfluthrin (isomer 2)	2791	226	***206***				0.029
	Cyfluthrin (isomer 3)	2799	226	***206***				0.042
	Cyfluthrin (isomer 4)	2805	226	***206***				0.05
Diflufenican	Diflufenican	2396	394	***266***				0.0002

Cyproconazole	Cyproconazole (isomer 1)	2238	224	***222***				0.008
	Cyproconazole (isomer 2)	2240	224	***222***				0.006
Cypermethrin	Cypermethrin (isomer 1)	2823	165	***163***	127			0.039
	Cypermethrin (isomer 2)	2837	165	***163***	127			0.025
	Cypermethrin (isomer 3)	2845	165	***163***	127			0.041
	Cypermethrin (isomer 4)	2850	165	***163***	127			0.034
Simazine	Simazine	1748	***201***	186				0.003
Dimethoate	Dimethoate	1733	125	93	***87***			0.005
Dimethomorph	Dimethomorph (isomer 1)	3099	387	***303***	***301***			0.01
	Dimethomorph (isomer 2)	3141	387	***303***	***301***			0.012
Spiroxamine	Spiroxamine (isomer 1)	1896	198	101	***100***			0.002
	Spiroxamine (isomer 2)	1948	198	101	***100***			0.001
Diazinon	Diazinon	1791	304	***179***				0.004
Di-Allate	Di-Allate (isomer 1)	1696	236	***234***				0.001
	Di-Allate (isomer 2)	1714	236	***234***				0.003
Thiacloprid	Thiacloprid	2922	***251***	101				0.4
Thiabendazole	Thiabendazole	2091	***201***	174				0.002
Thiobencarb	Thiobencarb	1985	257	***100***				0.001
Thiometon	Thiometon	1724	125	***88***				0.002
Aldrin/Dieldrin	Dieldrin	2208	277	***263***				0.01
Tecnazene	Tecnazene	1597	***261***	259				0.002
Tetrachlorvinphos	(Z)-Tetrachlorvinphos	2121	331	***329***	109			0.002
Tebuconazole	Tebuconazole	2398	***250***	125				0.005
Tebuthiuron	Degradation product of tebuthiuron	1524	171	***156***				0.01
Tefluthrin	Tefluthrin	1816	197	***177***				0.0004
Deltamethrin/Tralomethrin	Deltamethrin (isomer 1)	3029	***253***	***181***				0.417
	Deltamethrin (isomer 2)	3059	***253***	***181***				0.008
Terbutryn	Terbutryn	1944	241	***226***				0.001
Terbufos	Terbufos	1781	***231***	153				0.002
Deltamethrin/Tralomethrin	Degradation product of tralomethrin 1 [=Deltamethrin (isomer 1)]	3028	***253***	***181***				0.587
	Degradation product of tralomethrin 2 [=Deltamethrin (isomer 2)]	3057	***253***	***181***				0.02
Triadimenol	Triadimenol	2095	***168***	112				0.01
Triadimefon	Triadimefon	1999	210	***208***	181			0.01
Triazophos	Triazophos	2310	177	***172***	***161***			0.014
Tri-allate	Tri-allate	1827	270	***268***	143			0.003
Triticonazole	Triticonazole	2556	299	237	***235***			0.008
Tribuphos	Tribuphos	2194	***202***	169				0.005

Triflumizole	Triflumizole	2087	***278***	206				0.002
Trifluralin	Trifluralin	1661	***306***	264				0.001
Trifloxystrobin	Trifloxystrobin	2333	222	186	***116***			0.003
Norflurazon	Norflurazon	2339	305	***303***	145			0.005
Barban	Barban	2190	***222***	***153***				0.021
Parathion	Parathion	1996	***291***	139	87			0.004
Parathion-methyl	Parathion-methyl	1899	***263***	109				0.002
Allethrin	Bioallethrin (isomer 1)	2073	136	***123***				0.003
	Bioallethrin (isomer 2)	2075	136	***123***				0.004
Bioresmethrin	Bioresmethrin (isomer 1)	2401	***171***	***123***				0.223
	Bioresmethrin (isomer 2)	2413	***171***	***123***				0.005
Picolinafen	Picolinafen	2477	***376***	238				0.001
Bitertanol	Bitertanol (isomer 1)	2700	171	***170***	168			0.0004
	Bitertanol (isomer 2)	2714	171	***170***	168			0.002
Bifenthrin	Bifenthrin	2471	***181***	166	165			0.001
Piperonyl butoxide	Piperonyl butoxide	2407	177	***176***	149			0.001
Pyraclostrobin	Degradation product of pyraclostrobin	2964	164	***132***				0.032
Pyrazophos	Pyrazophos	2619	373	232	***221***			0.013
Pyridaben	Pyridaben	2732	309	***147***				0.004
Pyriproxyfen	Pyriproxyfen	2578	226	***136***	78			0.002
Pirimicarb	Pirimicarb	1839	238	***166***	72			0.001
Pirimiphos-methyl	Pirimiphos-methyl	1941	305	***290***				0.001
Pyrimethanil	Pyrimethanil	1799	199	***198***				0.0002
Pyrethrins	Pyrethrins I	2297	***162***	133	***123***			0.154
	Pyrethrins II	2629	167	***161***	***160***	107		0.258
Vinclozolin	Vinclozolin	1890	287	***285***	212			0.002
Famphur	Famphur	2334	***218***	217				0.005
Famoxadone	Famoxadone	3106	***330***	197	196			0.007
Fipronil	Fipronil	2049	369	***367***	351	213		0.002
Fenamiphos	Fenamiphos	2152	***303***	288	154			0.009
Fenarimol	Fenarimol	2631	251	***219***				0.007
Fenitrothion	Fenitrothion	1949	***277***	260				0.003
Fenoxaprop-ethyl	Fenoxaprop-ethyl	2667	***361***	288				0.003
Phenothrin	Phenothrin (isomer 1)	2526	***183***	123				0.007
	Phenothrin (isomer 2)	2540	***183***	123				0.003
Fenobucarb	Fenobucarb	1609	150	***121***				0.001
Fenamidone	Fenamidone	2496	***268***	***238***				0.003
Fenthion	Fenthion	1990	279	***278***	169			0.001
Fenvalerate	Fenvalerate (isomer 1)	2953	225	***167***				0.006
	Fenvalerate (isomer 2)	2982	225	***167***				0.022
Fenbuconazole	Fenbuconazole	2776	***198***	129				0.004
Fenpropathrin	Fenpropathrin	2495	***181***	125				0.006
Fenpropimorph	Fenpropimorph	1991	303	129	***128***			0.001

Buprofezin	Buprofezin	2204	305	175	***172***	106		0.004
Furathiocarb	Furathiocarb	2526	***194***	***163***				0.003
Flamprop-methyl	Flamprop-methyl	2190	335	***276***	231	***105***	77	0.003
Fluquinconazole	Fluquinconazole	2723	375	342	***340***			0.001
Fludioxonil	Fludioxonil	2169	***248***	154				0.004
Flucythrinate	Flucythrinate (isomer 1)	2847	***199***	157				0.011
	Flucythrinate (isomer 2)	2874	***199***	157				0.017
Flusilazole	Flusilazole	2202	234	***233***	206			0.001
Flutolanil	Flutolanil	2162	***323***	281	***173***			0.003
Flutriafol	Flutriafol	2152	***219***	164				0.01
Fluvalinate	Fluvalinate (isomer 1)	2966	252	***250***				0.004
	Fluvalinate (isomer 2)	2976	252	***250***				0.004
Flumioxazin	Flumioxazin	2943	***354***	287				0.03
Flumiclorac pentyl	Flumiclorac pentyl	3077	***423***	308				0.006
Fluridone	Fluridone	2908	329	***328***				0.003
Prochloraz	Prochloraz	2738	310	***180***				0.014
Procymidone	Procymidone	2088	285	***283***				0.003
Propaquizafop	Propaquizafop	3277	***443***	299				0.015
Propanil	Propanil	1879	217	***163***	***161***			0.013
Propargite	Propargite (isomer 1/isomer 2)	2402	***350***	173	***135***			0.014
Propiconazole	Propiconazole (isomer 1)	2348	261	***259***				0.007
	Propiconazole (isomer 2)	2362	261	***259***				0.006
Propyzamide	Propyzamide	1789	175	***173***				0.003
Profenofos	Profenofos	2186	339	***337***				0.004
Propetamphos	Propetamphos	1777	***194***	***138***				0.004
Propoxur	Propoxur	1612	152	***110***				0.002
Bromacil	Bromacil	1952	231	***207***	205			0.028
Prometryn	Prometryn	1918	***241***	226	184			0.002
Bromopropylate	Bromopropylate	2487	343	***341***	339			0.005
Hexazinone	Hexazinone	2381	172	***171***				0.005
Benalaxyl	Benalaxyl	2331	***206***	***148***				0.002
Heptachlor	Heptachlor	1920	337	274	***272***			0.001
	Heptachlor epoxide	2072	***353***	351				0.001
Permethrin	Permethrin (isomer 1)	2706	184	***183***				0.003
	Permethrin (isomer 2)	2723	184	***183***				0.003
Penconazole	Penconazole	2064	***248***	159				0.003
Bendiocarb	Bendiocarb	1674	***166***	***151***				0.003
Pendimethalin	Pendimethalin	2047	253	***252***				0.005
Benfuracarb	Benfuracarb	2624	***190***	164	163			0.002
Boscalid	Boscalid	2832	344	***342***	***140***			0.016
Phosmet	Phosmet	2480	161	***160***				0.008
Phorate	Phorate	1700	***260***	231	75			0.01
Malathion	Malathion	1965	***173***	127	125			0.006

Myclobutanil	Myclobutanil	2198	***179***	150				0.006
Methamidophos	Methamidophos	1230	141	***94***				0.004
Metalaxyl/Mefenoxam	Metalaxyl	1916	***249***	234	***206***	132		0.006
Methidathion	Methidathion	2113	***145***	85				0.003
Methoxychlor	Methoxychlor	2491	228	***227***				0.002
Methoprene	Methoprene	2097	***191***	153	111	***73***		0.009
Metolachlor	Metolachlor	1977	238	***162***				0.002
	S-Metolachlor	1975	***238***	162				0.0007
Metribuzin	Metribuzin	1888	199	***198***	144			0.003
Mevinphos	Mevinphos (isomer 1)	1420	***192***	127				0.007
	Mevinphos (isomer 2)	1424	***192***	127				
Metalaxyl/Mefenoxam	Mefenoxam	1912	249	***206***	160			0.002
Mefenpyr-diethyl	Mefenpyr-diethyl	2424	255	***253***				0.002
Resmethrin	Resmethrin (isomer 1)	2399	***171***	123				0.037
	Resmethrin (isomer 2)	2414	***171***	123				0.004

・The compounds are listed in the order of the Japanese syllabary, and the isomers are listed by their retention times.

・Retention indices are obtained based on the retention times of the *n*-alkanes and show the average values obtained from 2-4 laboratories.

・Monitoring ions in bold italic font are for quantification; the others are for confirmation.

・The limit of measurement is the value at S/N=10 when 2 μL of a standard solution is injected into an GC-MS. The limit is the lowest of the values obtained from laboratories.

・When 2 μL of a test solution prepared by the described method is injected into an GC-MS(/MS), 0.1 ng[*1] corresponds to 0.01 ppm.

*1 For test solutions (final volume: 1 mL) prepared using an amount corresponding to 5 g of sample.