Multi-residue Method I for Agricultural Chemicals by LC-MS (Agricultural Products)

1. Analytes

See Table 2 or 3.

2. Instruments

Liquid chromatograph-mass spectrometer (LC-MS)

Liquid chromatograph-tandem mass spectrometer (LC-MS/MS)

3. Reagents

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

0.5 mol/L Phosphate buffer (pH 7.0): Weigh 52.7 g of dipotassium hydrogenphosphate (K_2HPO_4) and 30.2 g of potassium dihydrogenphosphate (KH_2PO_4), dissolve in about 500 mL of water, adjust the pH to 7.0 with 1 mol/L sodium hydroxide or 1 mol/L hydrochloric acid, and add water to make a 1 L solution.

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

4. Procedure

1) Extraction

i) Grains, beans, nuts and seeds

Add 20 mL of water to 10.0 g of sample and let stand for 15 minutes.

Add 50 mL of acetonitrile, homogenize, and filter with suction. Add 20 mL of acetonitrile to the residue on the filter paper, homogenize, and filter with suction. Combine the resulting filtrates, and add acetonitrile to make exactly 100 mL.

Take a 20 mL aliquot of the extract, add 10 g of sodium chloride and 20 mL of 0.5 mol/L phosphate buffer (pH 7.0), and shake for 10 minutes. Let stand, and discard the separated aqueous layer.

Add 10 mL of acetonitrile to an octadecylsilanized silica gel cartridge (1,000 mg) and discard the effluent. Transfer the acetonitrile layer to the cartridge, elute with 2 mL of acetonitrile, collect the total eluates, dehydrate with anhydrous sodium sulfate, and filter out the anhydrous sodium sulfate. Concentrate the filtrate at below 40°C and remove the solvent. Dissolve the residue in 2 mL of acetonitrile/toluene (3:1, v/v).

ii) Fruits, vegetables, herbs, tea and hops

For fruits, vegetables and herbs, weigh 20.0 g of sample. For tea and hops, add 20 mL of water to 5.00 g of sample and let stand for 15 minutes.

Add 50 mL of acetonitrile, homogenize, and filter with suction. Add 20 mL of acetonitrile to the residue on the filter paper, homogenize, and filter with suction.

Combine the resulting filtrates, and add acetonitrile to make exactly 100 mL.

Take a 20 mL aliquot of the extract, add 10 g of sodium chloride and 20 mL of 0.5 mol/L phosphate buffer (pH 7.0), 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. Dissolve the residue in 2 mL of acetonitrile/toluene (3:1, v/v).

2) Clean-up

Add 10 mL of acetonitrile/toluene (3:1, v/v) to a graphite carbon/aminopropylsilanized silica gel layered cartridge (500 mg/500 mg) and discard the effluent. Transfer the solution obtained in 1) to the cartridge, elute with 20 mL of acetonitrile/toluene (3:1, v/v), collect the total eluate, and concentrate to below 1 mL at below 40°C. Add 10 mL of acetone and concentrate to below 1 mL at below 40°C, add 5 mL of acetone, and remove the solvent. Dissolve the residue in methanol to make exactly 4 mL, and use this solution as the test solution.

5. Calibration curve

Prepare standard solutions (acetonitrile) of each agricultural chemical. Mix them, prepare solutions (methanol) of several concentrations. Inject 5 μL of each standard solution to LC-MS or LC-MS/MS, and make calibration curves by peak-height or peak-area method.

6. Quantification

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

7. Confirmation

Confirm using LC-MS or LC-MS/MS.

8. Measurement conditions

Column: Octadecylsilanized silica gel, 2-2.1 mm in inside diameter. 150 mm in length and 3-3.5 μm in particle diameter

Column temperature: 40°C

Mobile phase: Control the gradient by mixing the mobile phases A and B as directed in the following table.

Flow rate: 0.2 mL/min

Mobile phase A: 5 mmol/L ammonium acetate solution

Mobile phase B: 5 mmol/L ammonium acetate-methanol solution

Time (min)	Mobile phase A (%)	Mobile phase B (%)
0	85	15
1	60	40
3.5	60	40

6	50	50
8	45	55
17.5	5	95
30	5	95
30	85	15

Ionization mode: ESI

Major monitoring ions (*m/z*): See Table 2 or 3.

Expected retention time: See Table 2 or 3.

9. Limit of quantification

See Table 2 or 3.

10. Explanatory note

1) Outline of analytical method

The method consists of extraction of each agricultural chemical from sample with acetonitrile, dehydration by salting out, clean-up with an octadecylsilanized silica gel cartridge for grains, beans, nuts and seeds, (omit for fruits, vegetables, herbs, tea and hops), clean-up with a graphite carbon/aminopropylsilanized silica gel layered cartridge, and quantification and confirmation using LC-MS or LC-MS/MS.

2) Notes

i) Table 2 and 3 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”.

ii) This method does not ensure simultaneous analysis of all of the analytes listed in the Table 2 and 3. In advance, confirm that degradation or interference does not occur as the result of interaction between the target analytes.

iii) Sodium phosphate can be used for the preparation of a phosphate buffer.

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) Depending on the sensitivity of the LC-MS or LC-MS/MS, it may be necessary to dilute the test solution with methanol.

vii) Because some agricultural chemicals are particularly unstable in methanol, LC-MS/MS analysis should be performed immediately after preparation of a test solution. The standard solutions used to determine the calibration curves should be prepared just prior to

use. Do not leave the test solutions in the autosampler rack at room temperature for a long time.

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

ix) 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. Reference

Fillion, J. et. al., J. AOAC Int, 83: 698-713, 2000

12. Type

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Table 2. Multi-residue Method I for Agricultural Chemicals by LC/MS (Grains, beans, nut, seeds fruits and vegetables)

Agricultural chemicals	Analytes	RRT	Monitoring ions (*m/z*)						Limit of quantification (mg/kg)
XMC	XMC	0.91	+180→123	+180→108					0.01
Azafenidin	Azafenidin	1.00	+338→299	+338→264					0.01
Acibenzolar-*S*-methyl	Acibenzolar-*S*-methyl	1.10	+211→136	+211→91					0.01
Azinphos-methyl	Azinphos-methyl	1.04	+318→160	+318→132	+318→77				0.01
Acetamiprid	Acetamiprid	0.41	+223→126	+223→90	+223→56				0.01
Azoxystrobin	Azoxystrobin	1.08	+404→372	+404→344	+404→329				0.01*
Anilofos	Anilofos	1.22	+368→199	+368→125					0.01
Amisulbrom	Amisulbrom	1.35	+468→229	+468→108	+466→227	+466→108			0.01
Aramite	Aramite	1.45	+352→255	+352→191	+352→91	+352→57			0.01
Aldicarb/Aldoxycarb	Aldicarb	0.64	+208→116	+208→115	+208→89				0.01*
Isouron	Isouron	0.76	+212→167	+212→72					0.01*
Isoxathion	Isoxathion	1.34	+341→105	+341→97					0.01*
Iprodione	*N*-(3,5-dichlorophenyl)-3-isopropyl-2,4-dioxoimidazolidine-1-carboxamide (Iprodione metabolite)	1.31	+330→143	+330→101	-330→141	-328→141	-328→99		0.01*
Iprovalicarb	Iprovalicarb	1.20	+321→203	+321→119					0.01
Imazalil	Imazalil	1.27	+299→161	+297→255	+297→159				0.01*
Imicyafos	Imicyafos	0.76	+305→235	+305→201					0.01
Imidacloprid	Imidacloprid	0.40	+256→209	+256→175					0.01*
Indanofan	Indanofan	1.23	+341→187	+341→175					0.01
Indoxacarb	Indoxacarb	1.38	+528→203	+528→150					0.01
Ethiprole	Ethiprole	1.13	+397→351	+397→255					0.01
Etoxazole	Etoxazole	1.46	+360→304	+360→177	+360→141				0.01
Oxadiargyl	Oxadiargyl	1.26	+358→341	+358→223	+358→151	+341→258	+341→223		0.01
Oxaziclomefone	Oxaziclomefone	1.42	+376→190	+376→161					0.01
Oxamyl	Oxamyl	0.32	+237→90	+237→72					0.01
Oxycarboxin	Oxycarboxin	0.54	+268→175	+268→147					0.01
Carbaryl	Carbaryl	0.88	+202→145	+202→127					0.01*
Carfentrazone-ethyl	Carfentrazone-ethyl	1.21	+412→366	+412→346					0.01*
Carpropamid	Carpropamid	1.26	+336→139	+336→103	+334→139	+334→103			0.01
Carbofuran	Carbofuran	0.82	+222→165	+222→123					0.01*
	3-hydroxycarbofuran	0.48	+255→220	+255→163	+238→220	+238→181	+238→163		0.01*
Quizalofop	Quizalofop-ethyl	1.34	+373→299	+373→271	+373→91				0.01
	Quizalofop-*P*-tefuryl	1.36	+429→299	+429→85					0.01
Quinoxyfen	Quinoxyfen	1.49	+308→197	+308→162					0.01
Cumyluron	Cumyluron	1.16	+303→185	+303→125					0.01
Kresoxim-methyl	Kresoxim-methyl	1.29	+331→314	+331→116	+314→267	+314→222	+314→131	+314→116	0.01*

Chromafenozide	Chromafenozide	1.21	+395→339	+395→175	+395→147	+395→91			0.01
Clomeprop	Clomeprop	1.44	+324→203	+324→148	+324→120				0.01
Chlorpyrifos	Chlorpyrifos	1.48	+350→198	+350→97					0.01
Chlorfenvinphos	Chlorfenvinphos (*E*)	1.35	+361→155	+361→99	+359→170	+359→155	+359→127		0.01*
Chlorbufam	Chlorbufam	1.10	+224→172	+224→154					0.01
Chloroxuron	Chloroxuron	1.19	+291→218	+291→164	+291→72				0.01
Cyazofamid	Cyazofamid	1.20	+327→108	+325→261	+325→108				0.01
Diuron	Diuron	1.01	+233→160	+233→72					0.01*
Diethofencarb	Diethofencarb	1.10	+268→226	+268→124					0.01
Cyenopyrafen	Cyenopyrafen	1.44	+394→310	+394→254					0.01
Cycloate	Cycloate	1.34	+216→154	+216→83					0.01
Difenoconazole	Difenoconazole (isomer 1/isomer 2)	1.36	+406→251	+406→111					0.01
Diflufenican	Diflufenican	1.31	+395→266	+395→246	+395→238	-393→329	-393→272		0.002
Diflubenzuron	Diflubenzuron	1.18	+311→158	+311→141					0.01*
Cyprodinil	Cyprodinil	1.28	+226→108	+226→93	+226→92				0.01
Simeconazole	Simeconazole	1.19	+294→135	+294→73	+294→70				0.01
Dimethametryn	Dimethametryn	1.26	+256→186	+256→91	+256→68				0.01
Dimethirimol	Dimethirimol	0.94	+210→140	+210→71					0.01
Dimethoate	Dimethoate	0.42	+230→199	+230→125					0.01*
Dimethomorph	Dimethomorph (*E*)	1.14	+388→301	+388→165					0.01
	Dimethomorph (*Z*)	1.18	+388→301	+388→165					0.01
Cymoxanil	Cymoxanil	0.56	+199→128	+199→111					0.01*
Silafluofen	Silafluofen	1.67	+426→287	+426→168					0.01
Spinosad	Spinosyn A	1.55	+733→142	+733→98	+732→142	+732→98			0.01*
Spirodiclofen	Spirodiclofen	1.53	+411→313	+411→71					0.01
Terbacil	Terbacil	0.82	-215→159	-215→73					0.01
Daimuron	Daimuron	1.14	+269→151	+269→119	+269→91				0.01
Thiacloprid	Thiacloprid	0.58	+255→128	+253→126	+253→90	+253→73			0.01
Tiadinil	Tiadinil	1.19	+268→101	-266→238	-266→71	-266→56			0.01
Thiabendazole	Thiabendazole	0.63	+202→175	+202→131					0.01*
Thiamethoxam	Thiamethoxam	0.36	+292→211	+292→181					0.01
Methomyl/Thiodicarb	Methomyl	0.40	+163→106	+163→88					0.01*
Tetrachlorvinphos	Tetrachlorvinphos (z)	1.24	+367→206	+367→127					0.01
Tetraconazole	Tetraconazole	1.17	+372→159	+372→70					0.01
Tebuconazole	Tebuconazole	1.29	+308→125	+308→70					0.01
Tebufenozide	Tebufenozide	1.27	+353→297	+353→133	+353→105				0.01
Teflubenzuron	Teflubenzuron	1.38	+381→158	+381→141					0.01*
Triadimenol	Triadimenol	1.21	+296→99	+296→70					0.01*
Triadimefon	Triadimefon	1.18	+294→197	+294→69					0.01*
Trichlamide	Trichlamide	1.29	+340→266	+340→121	-340→304	-340→119	-338→146	-338→117	0.01*
Triticonazole	Triticonazole	1.18	+318→125	+318→70					0.01

Tridemorph	Tridemorph (isomer 1/isomer 2)	1.69	+299→130	+299→57	+298→130	+298→98			0.01*
Triflumizole	Triflumizole	1.33	+346→278	+346→73					0.01*
	4-Chloro-α,α,α-trifluoro-*N*-（1-amino-2-propoxyethylidene）-*o*-toluidine (Triflumizole metabolite)	1.18	+295→278	+295→215	+295→73	+295→72	+295→55		0.01*
Triflumuron	Triflumuron	1.34	+359→156	+359→139					0.01*
Trifloxystrobin	Trifloxystrobin	1.31	+409→186	+409→145					0.01
Triforine	Triforine (isomer 1)	1.03	+437→392	+435→390	+435→215	+435→98			0.01*
	Triforine (isomer 2)	1.06	+437→392	+435→390	+435→215	+435→98			0.01*
Tolfenpyrad	Tolfenpyrad	1.37	+384→197	+384→154	+384→145	+384→91			0.01
Naproanilide	Naproanilide	1.23	+292→171	+292→120					0.01
Novaluron	Novaluron	1.36	+493→158	+493→141	-491→471				0.01
Barban	Barban	1.14	+275→178	+258→178	+258→143	+258→87			0.01
Paclobutrazol	Paclobutrazol	1.15	+294→125	+294→70					0.01
Bitertanol	Bitertanol	1.26	+338→269	+338→99	+338→70				0.01
Piperonyl butoxide	Piperonyl butoxide	1.46	+356→177	+356→119					0.01*
Pyraclostrobin	Pyraclostrobin	1.29	+390→163	+388→194	+388→164	+388→163	+388→105		0.01
Pyraclonil	Pyraclonil	0.87	+315→276	+315→241	+315→169				0.01
Pyraclofos	Pyraclofos	1.34	+361→257	+361→138					0.01
Pyrazoxyfen	Pyrazoxyfen	1.31	+403→105	+403→91					0.01
Pyrazophos	Pyrazophos	1.27	+374→222	+374→194					0.01*
Pyrazolynate	Pyrazolynate	1.35	+439→173	+439→91					0.01*
Pyridaben	Pyridaben	1.50	+366→309	+366→147	+365→309	+365→147			0.01
Pyriftalid	Pyriftalid	1.07	+319→179	+319→139	+319→83				0.01
Pyributicarb	Pyributicarb	1.39	+331→190	+331→181	+331→133	+331→108			0.01
Pirimicarb	Pirimicarb	0.94	+239→182	+239→72					0.01
Pyriminobac-methyl	Pyriminobac-methyl (*E*)	1.14	+362→330	+362→284					0.01
Pirimiphos-methyl	Pirimiphos-methyl	1.35	+306→164	+306→108					0.01*
Famoxadone	Famoxadone	1.24	+392→331	+392→238					0.01
Fenoxaprop-ethyl	Fenoxaprop-ethyl	1.41	+362→288	+362→91					0.01*
Fenoxycarb	Fenoxycarb	1.27	+302→116	+302→115	+302→88				0.01*
Fenobucarb	Fenobucarb	1.02	+208→152	+208→95					0.01
Ferimzone	Ferimzone (*E*)	1.13	+255→132	+255→91					0.01
	Ferimzone (*Z*)	1.06	+255→132	+255→124	+255→91				0.01
Fenamidone	Fenamidone	1.12	+312→236	+312→92					0.01
Fensulfothion	Fensulfothion	0.93	+309→281	+309→280	+309→173	+309→157			0.01
Fenpyroximate	Fenpyroximate (*E*)	1.48	+422→366	+422→214	+422→135				0.01*
	Fenpyroximate (*Z*)	1.42	+422→366	+422→214	+422→135				0.01*
Fenpropimorph	Fenpropimorph	1.62	+305→147	+305→98	+304→147	+304→130			0.01*
Phenmedipham	Phenmedipham	1.06	+318→168	+318→136					0.01

Butachlor	Butachlor	1.40	+313→238	+313→162	+312→238	+312→162	+312→57		0.01
Butafenacil	Butafenacil	1.13	+492→331	+492→180					0.01
Buprofezin	Buprofezin	1.45	+306→201	+306→106	+306→57				0.01
Furathiocarb	Furathiocarb	1.37	+383→252	+383→195	+383→167				0.01*
Flamprop-methyl	Flamprop-methyl	1.18	+336→105	+336→77					0.01
Furametpyr	Furametpyr	0.96	+335→289	+335→157	+334→290	+334→157			0.01*
Fluopicolide	Fluopicolide	1.09	+385→175	+385→173	+383→173	+383→109			0.01
Fluometuron	Fluometuron	0.84	+233→160	+233→72	+233→46				0.01*
Fludioxonil	Fludioxonil	1.14	-247→180	-247→126					0.01*
Flusilazole	Flusilazole	1.26	+316→247	+316→165					0.01
Flutriafol	Flutriafol (isomer 1)	0.86	+302→123	+302→109	+302→70				0.01
	Flutriafol (isomer 2)	0.96	+302→123	+302→109	+302→70				0.01
Flufenacet	Flufenacet	1.19	+364→194	+364→152					0.01
Flufenoxuron	Flufenoxuron	1.45	+489→158	+489→141					0.01
Flubendiamide	Flubendiamide	1.20	-681→272	-681→254					0.01
Flumioxazin	Flumioxazin	0.98	+372→355	+372→327	+355→327	+355→299	+355→79		0.01
Fluridone	Fluridone	1.08	+330→310	+330→259					0.01
Prochloraz	Prochloraz	1.34	+378→310	+378→70	+376→308	+376→266	+376→70		0.01*
Propaquizafop	Propaquizafop	1.44	+444→371	+444→163	+444→100	+444→70			0.01
Profenofos	Profenofos	1.42	+375→347	+375→305	+373→303	+373→128			0.01*
Propoxur	Propoxur	0.71	+210→168	+210→111					0.01*
Bromacil	Bromacil	0.78	+261→205	+261→188					0.01
Prometryn	Prometryn	1.22	+242→200	+242→158					0.01
Bromobutide	Bromobutide	1.22	+312→194	+312→119					0.01
	N-(α, α-dimethylbenzyl)-3, 3-dimethyl butyramide (deBr-bromobutide)	1.15	+234→119	+234→116	+234→91				0.01
Hexaflumuron	Hexaflumuron	1.32	-459→439	-459→175					0.01*
Hexythiazox	Hexythiazox	1.43	+353→228	+353→168	+353→116				0.01
Benalaxyl	Benalaxyl	1.27	+326→294	+326→208	+326→148	+326→91			0.01*
Pencycuron	Pencycuron	1.36	+329→218	+329→125	+329→89				0.01
Bensulide	Bensulide	1.22	+398→356	+398→314	+398→158				0.01*
Benzofenap	Benzofenap	1.36	+433→105	+431→119	+431→105				0.01
Bendiocarb	Bendiocarb	0.82	+224→167	+224→109					0.01
Benthiavalicarb-isopropyl	Benthiavalicarb-isopropyl	1.12	+382→180	+382→116	+382→72				0.01
Penthiopyrad	Penthiopyrad	1.22	+360→276	+360→256	+360→177				0.01
Pentoxazone	Pentoxazone	1.35	+371→286	+371→186	+354→286	+354→186			0.01
Phoxim	Phoxim	1.34	+299→129	+299→77					0.01*
Boscalid	Boscalid	1.11	+345→307	+343→307	+343→140				0.01
Phosphamidon	Phosphamidon	0.71	+300→174	+300→127					0.01
Malathion	Malathion	1.21	+331→285	+331→127	+331→99				0.01*
Mandipropamid	Mandipropamid	1.12	+412→356	+412→328	+412→204	+412→125			0.01

Milbemectin	Milbemectin A3	1.49	+551→337	+551→240	+546→511	+546→493			0.01
Methabenzthiazuron	Methabenzthiazuron	0.96	+222→165	+222→150					0.01
Metalaxyl/Mefenoxam	Metalaxyl	0.92	+280→220	+280→192	+280→160				0.01*
	Mefenoxam	0.98	+281→192	+281→160	+280→220	+280→192			0.01*
Methiocarb	Methiocarb	1.12	+226→169	+226→121					0.01*
	Methiocarb sulfoxide	0.50	+242→185	+242→170	+242→122				0.01*
	Methiocarb sulfone	0.43	+258→201	+258→122	+258→107				0.01
Methidathion	Methidathion	1.04	+320→145	+320→85	+303→145	+303→85			0.01*
Methoxyfenozide	Methoxyfenozide	1.09	+369→149	+369→91					0.01
Metconazole	Metconazole (*Z*)	1.33	+320→125	+320→70					0.01
Mepanipyrim	Mepanipyrim	1.14	+224→106	+224→77					0.01
Monolinuron	Monolinuron	0.90	+215→148	+215→126					0.01*
Lactofen	Lactofen	1.39	+479→344	+479→223					0.01
Linuron	Linuron	1.08	+251→162	+249→182	+249→160				0.01*
Lufenuron	Lufenuron	1.40	+511→158	+511→141	-509→339	-509→326	-509→175		0.01

1) The analytes are listed in the order of the Japanese syllabary, and the isomers are listed by their retention times. 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. All values are determined by measurement using LC-MS/MS.

2) Relative retention time (RRT) is the relative value when isoxaflutole is 1. The RRT above shows the average values obtained from laboratories.

3) The figures in “Monitoring ions” show [precursor ion → product ion] from LC-MS/MS measurement, and the code (+ or -) before the figures represents the ionization mode used (ESI (+) or ESI (-)). Each ion is listed in order of descending m/z.

4) Limit of quantification was regarded as 0.01 mg/kg (or the lowest spiked level) when the *S/N* of analyte peak obtained from a recovery test at a spiked level of 0.01 ppm (or the lowest spiked level) was ≥ 10 in at least one sample. For analyte which was not performed a recovery test at a spiked level of 0.01 ppm, the limit of quantification was estimated to be 0.01 mg/kg, when the *S/N* of the analyte peak of matrix-matched standard corresponding to 0.01 mg/kg in the sample was ≥ 10 in at least one sample, and indicated this in the table with “*”.

Table 3. Multi-residue Method I for Agricultural Chemicals by LC/MS (Tea and hops)

Agricultural chemicals	Analytes	RRT	Monitoring ions (*m/z*)						Limit of quantification (mg/kg)
XMC	XMC	0.94	+180→123	+180→108	+180→107				0.01*
Acetamiprid	Acetamiprid	0.57	+223→126	+223→90	+223→56				0.01*
Azoxystrobin	Azoxystrobin	1.09	+404→372	+404→344	+404→329				0.01*
Atrazine	Atrazine	1.01	+216→174	+216→96					0.01*
Isoxathion	Isoxathion	1.28	+314→170	+314→105	+314→97				0.01*
Iprovalicarb	Iprovalicarb	1.15	+321→203	+321→119	+321→91				0.01
Imidacloprid	Imidacloprid	0.49	+256→209	+256→175					0.01*
Imibenconazole	Imibenconazole	1.33	+413→171	+413→125	+411→342	+411→171	+411→125		0.01*
Indoxacarb	Indoxacarb	1.28	+528→203	+528→150					0.01
Ethion	Ethion	1.36	+385→199	+385→143	+385→97				0.01*
Ethiprole	Ethiprole	1.07	+397→351	+397→255					0.01*
Etoxazole	Etoxazole	1.40	+360→304	+360→177	+360→141	+360→113			0.01*
Etofenrpox	Etofenprox	1.52	+394→177	+394→135	+394→107				0.01+
Oxaziclomefone	Oxaziclomefone	1.32	+376→190	+376→91					0.01
Carfentrazone-ethyl	Carfentrazone-ethyl	1.19	+412→366	+412→346					0.01*
Cabofuran	Carbofuran	0.85	+222→165	+222→123					0.01*
Quizalofop	Quizalofop-ethyl	1.31	+373→299	+373→91					0.01
Quinalphos	Quinalphos	1.25	+299→163	+299→146	+299→97				0.01*
Cumyluron	Cumyluron	1.14	+303→185	+303→125					0.01
Kresoxim-methyl	Kresoxim-methyl	1.23	+314→131	+314→116	+267→235	+267→207			0.01*
Cloquintocet-mexyl	Cloquintocet-mexyl	1.33	+336→238	+336→192	+336→179				0.01
Clodinafop-propargyl	Clodinafop-propargyl	1.18	+350→266	+350→91					0.01*
Clothianidin	Clothianidin	0.50	+250→169	+250→132					0.01*
Clofentezine	Clofentezine	1.31	+303→138	+303→102					0.01*
Clomazone	Clomazone	1.03	+240→125	+240→89					0.01*
Chromafenozide	Chromafenozide	1.17	+395→339	+395→175	+395→147				0.01*
Chlorpyrifos	Chlorpyrifos	1.38	+350→200	+350→198	+350→97				0.01*
Chlorpyrifos-methyl	Chlorpyrifos-methyl	1.28	+322→290	+322→125					0.01*
Chloroxuron	Chloroxuron	1.11	+291→218	+291→164	+291→72	+291→46			0.01*
Cyazofamid	Cyazofamid	1.18	+325→261	+325→108	+325→44				0.01
Dioxation	Dioxation	1.32	+474→271	+474→97					0.01*
Cycloprothirn	Cycloprothirn	1.40	+499→499	+499→257	+499→229	+499→181			0.5
Difenoconazole	Difenoconazole	1.27	+406→251	+406→111					0.01*
Difenzoquat	Difenzoquat	0.59	+249→130	+249→77					0.01*
Diflubenzuron	Diflubenzuron	1.19	+311→158	+311→141					0.01*
Simeconazole	Simeconazole	1.15	+294→135	+294→73	+294→70				0.01*
Dimethoate	Dimethoate	0.56	+230→199	+230→125					0.01*
Dimethomorph	Dimethomorph (*E*)	1.10	+388→301	+388→165					0.01

	Dimethomorph (*Z*)	1.12	+388→301	+388→165					0.01
Spinosad	Spinosyn A	1.52	+733→142	+733→98					0.01*
	Spinosyn D	1.57	+744→142	+744→98					0.01*
Spiromesifen	Spiromesifen	1.38	+388→273	+388→255	+371→273	+371→255	+273→255	+273→187	0.01*
Diazinon	Diazinon	1.24	+305→169	+305→153	+305→97				0.01*
Daimuron	Daimuron	1.09	+269→151	+269→91					0.01
Thiacloprid	Thiacloprid	0.65	+253→126	+253→90					0.01*
Thiamethoxam	Thiamethoxam	0.39	+292→211	+292→181	+292→132				0.01*
Tetrachlorvinphos	Tetrachlorvinphos	1.20	+367→206	+367→127					0.01
Tetraconazole	Tetraconazole	1.15	+372→159	+372→70					0.01*
Tebuconazole	Tebuconazole	1.21	+308→125	+308→70					0.01*
Tebthiuron	Tebthiuron	0.87	+229→172	+229→116					0.01*
Teflubenzuron	Teflubenzuron	1.35	+381→158	+381→141	-379→339	-379→196			0.01*
Triadimenol	Triadimenol	1.13	+296→99	+296→70	+296→43				0.01*
Triadimefon	Triadimefon	1.09	+294→197	+294→69					0.01*
Triflumizole	Triflumizole	1.30	+346→278	+346→73	+346→42				0.01*
Trifloxystrobin	Trifloxystrobin	1.30	+409→186	+409→206	+409→145				0.01*
Tolfenpyrad	Tolfenpyrad	1.35	+384→197	+384→154	+384→117	+384→91			0.01*
Parathion	Parathion	1.19	+292→264	+292→236	+292→140				0.01*
Bitertanol	Bitertanol	1.23	+338→148	+338→99	+338→70				0.01*
Pyrazophos	Pyrazophos	1.27	+374→238	+374→222	+374→194				0.01*
Pyraflufen-ethyl	Pyraflufen-ethyl	1.21	+415→341	+415→339	+415→261	+415→253			0.01*
Pyridaben	Pyridaben	1.45	+365→309	+365→147					0.01*
Pyriftalid	Pyriftalid	1.09	+319→179	+319→139	+319→83	+319→82			0.01
Pyriproxyfen	Pyriproxyfen	1.39	+322→227	+322→185	+322→96	+322→77			0.01*
Pirimicarb	Pirimicarb	0.97	+239→182	+239→72					0.01
Ptrimidifen	Pyrimidifen	1.38	+378→184	+378→150					0.01
Pirimiphos-methyl	Pirimiphos-methyl	1.29	+306→164	+306→108					0.01*
Febamiphos	Fenamiphos	1.16	+304→234	+304→217	+304→202				0.01*
Fenoxaprop-ethyl	Fenoxaprop-ethyl	1.30	+362→288	+362→119	+362→91	+362→77			0.01
Fenobucarb	Fenobucarb	1.02	+208→152	+208→95					0.01*
Ferimzone	Ferimzone (*Z*)	1.10	+255→132	+255→91					0.01
Fenamidone	Fenamidone	1.05	+312→236	+312→92					0.01
Phenthoate	Phenthoate	1.20	+321→247	+321→163	+321→135	+321→79			0.01*
Fenpyroximate	Fenpyroximate (*E*)	1.43	+422→366	+422→138	+422→135				0.01*
	Fenpyroximate (*Z*)	1.37	+422→366	+422→138	+422→135				0.01*
Fenbuconazole	Fenbuconazole	1.17	+337→366	+337→70					0.01*
Fenpropathrin	Fenpropathrin	1.40	+367→125	+350→125	+350→97				0.01*
Fenpropimorph	Fenpropimorph	1.50	+304→117	+304→98					0.01*
Phenmedipham	Phenmedipham	1.04	+318→168	+318→136	+318→168	+168→136	+168→93		0.01
Butafenacil	Butafenacil	1.11	+492→349	+492→331	+492→180				0.01
Buprofezin	Buprofezin	1.34	+306→201	+306→106	+306→57				0.01*

Fluometuron	Fluometuron	0.90	+233→160	+233→72	+233→46				0.01*
Flufenacet	Flufenacet	1.16	+364→194	+364→152					0.01
Flufenoxuron	Flufenoxuron	1.37	+489→158	+489→141					0.01*
Flubendiamide	Flubendiamide	1.19	-681→254	-681→274					0.01*
Fluridone	Fluridone	1.04	+330→310	+330→309	+330→259				0.01
Prochloraz	Prochloraz	1.23	+378→310	+378→308	+376→70				0.01*
Prothiofos	Prothiofos	1.46	+347→243	+345→269	+345→241	+345→133			0.01*
Propaquizafop	Propaquizafop	1.34	+444→371	+444→163	+444→100	+444→50			0.01
Propargite	Propargite	1.38	+368→231	+368→175	+231→175	+231→57			0.01*
Propiconazole	Propiconazole	1.23	+342→159	+342→69					0.01*
Propizamide	Propizamide	1.09	+256→190	+256→173					0.01*
Profenpfos	Profenofos	1.31	+375→305	+375→96	+373→345	+373→303	+373→128		0.01*
Propoxur	Propoxur	0.80	+210→168	+210→111					0.01*
Hexaconazole	Hexaconazole	1.21	+316→70	+314→159	+314→70				0.01*
Hexythiazox	Hexythiazox	1.37	+353→228	+353→168					0.01*
Benalaxyl	Benalaxyl	1.21	+326→148	+326→91					0.01*
Pencycuron	Pencycuron	1.24	+329→218	+329→125	+329→89				0.01
Benzofenap	Benzofenap	1.31	+433→119	+431→105					0.01
Bendiocarb	Bendiocarb	0.81	+224→167	+224→109					0.01
Phosalone	Phosalone	1.26	+368→322	+368→182	+368→111				0.01*
Boscalid	Boscalid	1.10	+343→307	+343→139					0.01
Phosphamidon	Phosphamidon	0.73	+300→174	+300→127					0.01*
Malathion	Malathion	1.13	+331→127	+331→99					0.01*
Mycrobutanil	Myclobutanil	1.12	+289→125	+289→70					0.01*
Methiocarb	Methiocarb	1.09	+226→169	+226→121					0.01*
Methidathion	Methidathion	1.02	+303→145	+303→85	+303→84				0.01*
Methoxyfenozide	Methoxyfenozide	1.14	+369→313	+369→149					0.01*
Monolinuron	Monolinuron	0.95	+215→148	+215→126	+215→99				0.01*
Lactofen	Lactofen	1.32	+479→344	+479→223	+462→344	+462→233			0.01
Linuron	Linuron	1.06	+249→182	+249→160	+249→133				0.01*
Lufenuron	Lufenuron	1.35	+511→158	+511→141	509→326	509→175			0.01*

1) The analytes are listed in the order of the Japanese syllabary, and the isomers are listed by their retention times. 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. All values are determined by measurement using LC-MS/MS.
2) Relative retention time (RRT) is the relative value when isoxaflutole is 1. The RRT above shows the average values obtained from laboratories.
3) The figures in "Monitoring ions" show [precursor ion → product ion] from LC-MS/MS measurement, and the code (+ or -) before the figures represents the ionization mode used (ESI (+) or ESI (-)). Each ion is listed in order of descending m/z.
4) Limit of quantification was regarded as 0.01 mg/kg (or the lowest spiked level) when the *S/N* of analyte peak obtained from a recovery test at a spiked level of 0.01 ppm (or the lowest spiked level) was ≥ 10 in at least one sample. For analyte which was not performed a recovery test at a spiked level of 0.01 ppm, the limit of quantification was estimated to be 0.01 mg/kg, when the *S/N* of the analyte peak of matrix-matched standard corresponding to 0.01 mg/kg in the sample was ≥ 10 in at least one sample, and indicated this in the table with "*".