Table 1. Recovery of pesticides from green tea, oolong tea, black tea and matcha (powdered green tea). *(Continued)*

	Green tea		*Oolong tea*		*Black tea*		*Matcha (Powdered green tea)*	
Pesticide	*Recovery (%)*	*RSD%*	*Recovery (%)*	*RSD%*	*Recovery (%)*	*RSD%*	*Recovery (%)*	*RSD%*
Trifluralin	87	6	93	7	88	6	80	16
Uniconazole P	90	8	91	5	88	4	76	8
Vinclozolin	99	2	93	4	92	9	81	7

Initially, pesticide recoveries obtained from the silica gel cartridge were compared using four different elution solvent mixtures, namely, acetone/hexane mixtures in the ratios of 2:8, 3:7, 4:6 and 5:5. The majority of pesticides were eluted using either 15 mL of the 3:7 mixture, 10 mL of the 4:6 mixture or 10 mL of the 5:5 mixture. In contrast, using an acetone/hexane ratio of 2:8, relatively low recoveries were obtained for a number of pesticides, even when 20 mL of the eluting solvent was utilized. The triazole-based pesticides (bitertanol, cyproconazole, myclobutanil, penconazole, simeconazole and triadimenol) showed low recoveries with all solvents.

With the optimized solvent mixtures in hand, we investigated the efficiency of the silica gel cartridge cleanup using green tea extract. The quantity of matrix components present in the green tea extract was evaluated by comparing the TIC chromatograms using different elution solvent mixtures. Figure 3 shows TIC chromatograms of the green tea extract after cleanup using a silica gel cartridge and eluting with (a) acetone/hexane (3:7), (b) acetone/hexane (4:6) and (c) acetone/hexane (5:5). As can be seen, caffeine did not elute with the acetone/hexane solution (15 mL, 3:7). However, using acetone/hexane (4:6) or acetone/hexane (5:5), caffeine was eluted in the 10–15 mL fractions. The TIC chromatograms of acetone/hexane (15 mL, 3:7), acetone/hexane (10 mL, 4:6) and acetone/hexane (10 mL, 5:5) were then compared. The results showed that acetone/hexane (15 mL, 3:7) appeared to contain the lowest quantities of matrix components, thus demonstrating that the silica gel cartridge cleanup eluting with 15 mL of acetone/hexane (3:7) yielded a cleaner final test solution than elution with 10 mL acetone/hexane (4:6) or 10 mL acetone/hexane (5:5).

From these results, acetone/hexaen (15 mL, 3:7) was considered the optimal solvent mixture for silica gel cartridge cleanup, with the successful separation of pesticides and caffeine, elution of the majority of pesticides and retention of caffeine and other pigments on the cartridge. Out of all the pesticides tested, the triazole pesticides yielded the poorest recoveries, possibly due to low recoveries from the silica gel cartridge. However, quantification of the triazole pesticides is still possible, as they are LC-amenable and thus they can be quantified using a previously reported LC-MS/MS method[17] that did not require a silica gel cartridge cleanup step.

The overall schematic representation of the proposed modified method is shown in Figure 4. TIC chromatograms of green tea, oolong tea, black tea and matcha samples prepared by the Japanese official multiresidue method and the modified multiresidue method are shown in Figure 5 and the representative chromatograms of pesticides, where the retention times overlap with that of caffeine, can be seen in Figure A1. From the results presented in this study, we could conclude that the cleanup procedure for this method effectively removed coextracted matrix components such as pigments, caffeine and polyphenols, and gave a cleaner final test solution cleaner than that obtained by the original Japanese official multiresidue method. This final test solution was suitable for the subsequent GC-MS/MS analysis.

Recovery tests

The recovery tests were performed for green tea, oolong tea, black tea and matcha (powdered green tea) at a 0.01 mg kg^{-1} spike level, with each test being replicated five times for all matrices. A 0.01 mg kg^{-1} spike level was chosen for these tests, because a uniform limit of 0.01 mg kg^{-1} is applied in Japan to all pesticides for which maximum residue limits (MRLs) are not established. The results of the recovery tests are summarized in Table 1. Out of 162 pesticides tested, the recoveries of 157 pesticides for green tea (97% of the tested pesticides), 155 for oolong tea (96%), 158 for black tea (98%) and 154 for matcha (95%) were within the acceptable range according to the criteria set by the Japanese guidelines.[18] These guidelines state that the recoveries of 70–120% and relative standard deviations less than 25% at the 0.01 mg kg^{-1} spike level must be achieved. As mentioned previously, a possible reason for the low recoveries of triazole pesticides (i.e., bitertanol, cyproconazole, myclobutanil, penconazole, simeconazole and triadimenol) could be low recoveries from the silica gel cartridges. In the case of coumaphos, diflufenican, pyrazophos and tecnazene, despite poor recoveries in pure solvents using the tandem GCB/PSA cartridge, high recoveries from tea itself were achieved, indicating that coexisting matrix components facilitated their elution from the cartridge. In addition, no interfering peaks were observed in the chromatograms of the blank samples at retention times similar to those of the pesticides, thus confirming the high selectivity of the developed method and its suitability for the quantitative analysis of the GC-amenable pesticide residues in tea.

Conclusions

In this study, by modifying the Japanese official multiresidue method, we developed an efficient and reliable multiresidue method for the determination of 162 pesticides in tea using GC-MS/MS, which is an analytical method that can determine pesticide contents without the need for continual and time-consuming maintenance. A combination of ODS, tandem GCB/PSA and silica gel cartridge cleanups effectively removed coextracted matrix components such as pigments, caffeine and polyphenols. The final test solutions obtained by the proposed method were suitable for the subsequent GC-MS/MS analysis. Recoveries and precisions of the majority of the 162 tested pesticides from the samples of green tea, oolong tea, black tea and matcha at a spiking level of 0.01 mg kg^{-1} were within the acceptable range of the criteria of the Japanese guidelines. Therefore, the majority of the tested pesticides can be detected quantitatively by the modified method at 0.01 mg kg^{-1}, which is the uniform limit, established in Japan. Poor recoveries were obtained with triazole pesticides, possibly due to low recoveries from the silica gel cartridges. However, these triazole pesticides could be quantified using a previously reported LC-MS/MS method[17] that does not utilize the silica gel cartridge cleanup procedure. Overall, the results obtained suggest that the developed method is suitable for the quantitative analysis of the GC-amenable pesticide residues in tea.

Funding

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Appendix

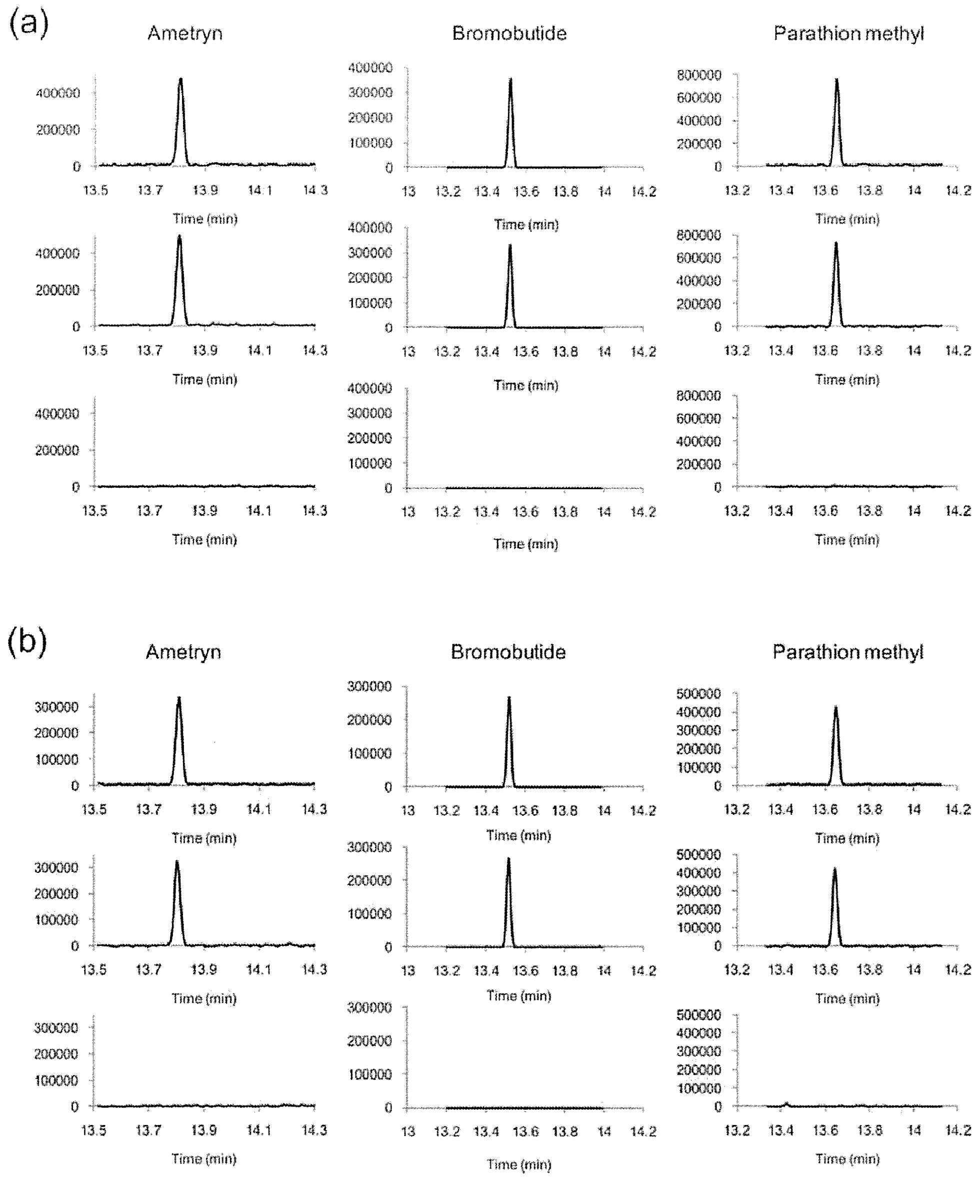

Fig. A1. Representative chromatograms of pesticides in (a) green tea, (b) oolong tea, (c) black tea and (d) matcha. Upper: matrix-matched standard. Middle: spiked sample. Lower: blank sample. (*Continued*)

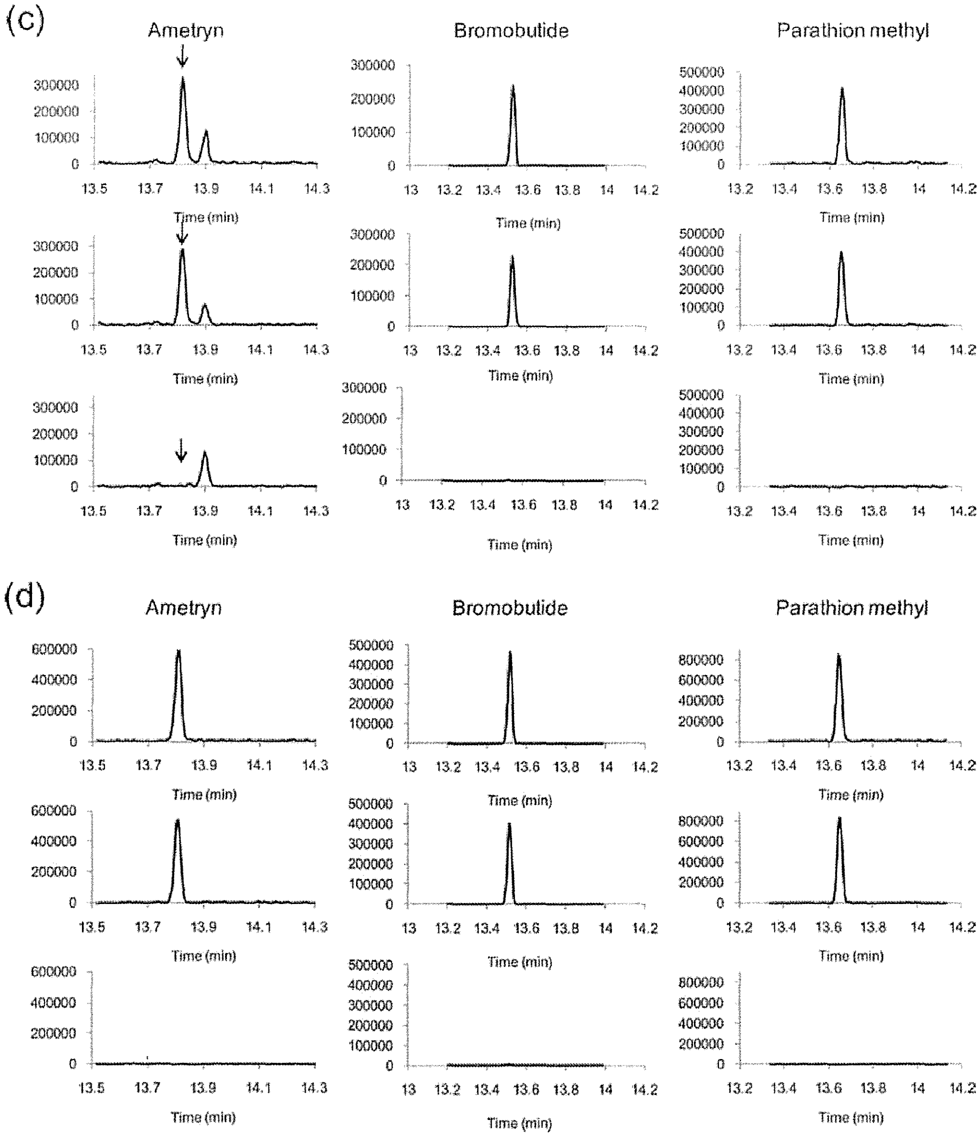

Fig. A1. Representative chromatograms of pesticides in (a) green tea, (b) oolong tea, (c) black tea and (d) matcha. Upper: matrix-matched standard. Middle: spiked sample. Lower: blank sample. (*Continued from previous page*)

Table A1. GC-MS/MS parameters for the tested pesticides.

		Quantification ion			*Confirmation ion*		
Pesticide	*Retention time (min)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*
Acetochlor	13.51	223.1	132.1	14	223.1	147.1	14
Acrinathrin	19.94	208.0	181.1	8	181.0	152.1	20
Alachlor	13.67	188.1	160.1	8	237.1	160.1	15
Aldrin	14.60	262.8	193.0	24	262.8	228.0	20
Ametryn	13.83	227.1	170.1	10	227.1	185.1	10
Anilofos	19.17	226.1	157.0	20	226.1	184.1	8
Aramite	16.48, 16.54, 16.63, 16.83	185.0	63.0	14	334.1	185.1	8
Atrazine	12.15	200.1	122.1	10	215.1	200.2	10
Azinphos methyl	19.63	160.1	77.0	15	160.1	132.0	5
Azoxystrobin	23.71	344.1	329.3	18	388.1	360.3	8
Benalaxyl	17.71	234.1	174.1	10	266.1	148.1	10
Benfluralin	11.22	292.1	264.2	8	292.1	206.2	14
Benfuresate	13.39	256.1	163.1	8	163.1	121.0	5
Benoxacor	13.19	259.0	120.0	14	261.0	120.0	14
α-BHC	11.70	181.0	145.0	14	218.9	183.0	8
β-BHC	12.19	181.0	145.0	14	218.9	183.0	8
γ-BHC	12.96	218.9	183.0	8	181.0	145.0	14
δ-BHC	12.39	181.0	145.0	14	218.9	183.0	8
Bifenox	18.92	341.0	185.0	20	341.0	183.0	20
Bifenthrin	18.82	181.1	165.1	20	181.1	166.2	10
Bitertanol	20.60, 20.71	170.1	141.1	20	170.1	115.1	20
Bromobutide	13.53	232.2	114.1	8	232.2	176.2	8
Bromophos	14.92	330.9	316.1	14	328.9	313.9	20
Bromophos ethyl	15.71	358.9	303.1	20	302.8	285.0	14
Bromopropylate	18.92	340.9	183.0	20	185.0	157.0	14
Bupirimate	16.54	273.2	193.2	14	316.2	208.2	8
Butachlor	15.88	237.1	160.1	10	176.1	147.1	10
Butafenacil	20.92	331.0	180.0	18	331.0	124.0	14
Butamifos	16.05	286.1	202.1	14	286.1	258.2	8
Cadusafos	11.48	159.0	96.9	14	159.0	130.9	8
Cafenstrole	21.11	100.1	72.0	8	188.2	119.1	20
Carfentrazone ethyl	17.64	312.1	151.0	18	330.0	269.1	18
Chlorbenside	15.81	268.0	125.0	14	125.0	89.0	20
Chlordane (*cis*)	16.07	372.8	266.1	20	374.8	266.0	20
Chlordane (*trans*)	15.82	372.8	266.1	20	374.8	266.0	20
Chlorfenson	16.27	175.0	111.0	14	302.0	175.0	8
Chlorfenvinphos	15.10, 15.31	323.0	267.1	14	267.0	159.0	14
Chlorobenzilate	17.08	251.0	139.0	14	139.0	111.0	14
Chlorpropham	11.15	213.1	171.0	8	213.1	127.0	14
Chlorpyrifos	14.46	314.0	258.0	14	196.9	169.0	14
Chlorpyrifos methyl	13.53	286.0	271.1	14	288.0	273.1	14
Chlorthal dimethyl	14.56	331.9	301.1	20	300.9	273.1	14
Clomazone	12.25	204.1	107.0	20	125.0	89.0	14
Clomeprop	19.28	288.1	169.1	18	290.1	171.0	18
Coumaphos	20.79	226.0	163.1	18	362.1	226.1	14
Cyanazine	14.54	225.1	189.2	14	212.1	123.0	20
Cyflufenamid	16.73	412.1	295.2	12	294.1	203.1	20
Cyfluthrin	21.18, 21.28, 21.34, 21.38	163.0	127.0	8	206.1	151.0	20
Cyhalothrin	19.63, 19.80	197.1	141.0	14	181.1	152.1	14
Cyproconazole	16.88	222.1	125.0	20	224.1	127.0	20

(*Continued on next page*)

Table A1. GC-MS/MS parameters for the tested pesticides. *(Continued)*

		Quantification ion			*Confirmation ion*		
Pesticide	*Retention time (min)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*
Cyprodinil	15.15	224.2	208.2	20	225.2	210.2	14
Deltamethrin	23.48	252.9	93.0	20	181.1	152.0	20
Di-allate	11.55, 11.75	234.1	150.0	20	234.1	192.1	14
Diazinon	12.54	179.1	137.1	20	199.1	135.1	14
Dichloran	11.94	206.0	176.0	14	176.0	148.0	20
Dieldrin	16.61	276.9	241.1	8	262.9	193.0	30
Diflufenican	18.23	394.1	266.2	18	266.1	246.2	14
Dimethametryn	15.24	212.1	122.1	12	212.1	94.1	20
Dimethenamid	13.42	230.1	154.1	8	203.1	126.0	20
Dimethoate	11.94	229.0	87.0	8	125.0	79.0	8
Dimethylvinphos (*E*)	14.23	295.0	109.0	16	297.0	109.0	16
Dimethylvinphos (*Z*)	14.51	295.0	109.0	16	297.0	109.0	16
Disulfoton	12.80	186.0	97.0	14	186.0	153.0	8
Dithiopyr	13.89	354.1	306.3	8	354.1	286.2	14
Edifenphos	17.84	310.1	109.0	20	173.0	109.0	14
α-Endosulfan	16.09	240.9	206.0	14	195.0	159.0	8
β-Endosulfan	17.22	240.9	206.0	14	195.0	159.0	8
Endosulfan sulfate	17.94	273.8	239.0	20	271.8	237.0	20
Endrin	17.02	262.9	228.0	18	262.9	193.0	30
EPN	18.89	157.0	110.0	14	169.1	141.0	8
Esprocarb	14.33	222.2	91.0	14	162.2	91.0	8
Ethion	17.24	231.0	128.9	20	231.0	175.0	14
Ethoprophos	10.92	158.0	96.9	16	200.0	158.0	8
Etofenprox	21.87	163.1	107.0	20	163.1	135.1	8
Etoxazole	18.99	300.1	270.3	20	330.1	300.3	20
Fenarimol	20.09	251.0	139.0	20	219.1	107.0	12
Fenchlorphos	13.87	285.0	270.1	20	287.0	272.1	20
Fenitrothion	14.16	277.1	260.2	8	260.0	125.0	14
Fenoxanil	16.89	293.1	155.0	20	189.0	125.0	14
Fenpropimorph	14.60	303.3	128.1	8	128.1	110.1	14
Fenvalerate	22.51, 22.75	167.1	125.0	14	225.1	119.0	14
Fipronil	15.15	367.0	213.0	24	369.0	215.0	24
Flamprop methyl	16.47	230.1	170.1	14	276.1	105.0	8
Flucythrinate	21.68, 21.88	199.1	107.0	20	199.1	157.1	8
Fludioxonil	16.25	248.1	127.0	20	248.1	154.0	16
Fluquinconazole	20.81	340.1	298.0	14	340.1	313.0	14
Flutolanil	16.20	323.1	173.1	20	173.0	145.1	14
Fosthiazate	14.96, 15.02	195.0	103.0	8	195.0	139.0	8
Fthalide	14.86	242.9	215.0	14	271.9	243.0	14
Indoxacarb	23.23	203.0	134.0	14	218.1	203.1	14
Iprobenfos	13.10	204.0	91.0	14	246.1	204.1	8
Isazophos	12.80	285.0	161.1	14	257.0	119.0	20
Isofenphos	15.28	213.1	121.0	20	255.1	213.1	8
Isofenphos oxon	14.64	229.1	201.1	8	201.0	121.0	14
Isoprocarb	9.81	136.1	121.1	10	121.1	103.0	10
Isoprothiolane	16.32	290.1	118.0	14	231.1	189.1	8
Isoxadifen ethyl	17.66	204.0	176.1	20	222.1	205.2	8
Isoxathion	16.81	177.1	130.1	14	313.1	177.1	8
Kresoxim methyl	16.57	206.2	116.0	8	206.2	131.1	14
Lenacil	17.90	153.1	136.1	14	153.1	110.0	14
Malathion	14.32	173.1	127.0	8	127.1	99.0	8
Mefenacet	19.78	192.0	136.0	14	192.0	109.0	20

(Continued on next page)

Table A1. GC-MS/MS parameters for the tested pesticides. *(Continued)*

		Quantification ion			*Confirmation ion*		
Pesticide	*Retention time (min)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*
Mefenpyr diethyl	18.49	253.0	189.1	20	255.0	189.1	20
Mepronil	17.49	269.2	119.1	14	269.2	210.2	8
Metalaxyl	13.82	234.2	146.1	14	206.2	132.1	14
Methidathion	15.74	145.1	85.0	8	145.1	58.0	14
Methoxychlor	19.00	227.1	212.2	14	227.1	169.1	20
Metolachlor	14.43	238.1	162.2	14	162.1	133.1	14
Myclobutanil	16.53	179.1	125.0	20	288.2	179.1	14
Oxadiazon	16.42	258.0	175.0	8	175.0	112.0	14
Oxadixyl	17.22	233.2	146.1	8	163.1	132.1	14
Paclobutrazol	15.91	236.1	125.0	14	236.1	167.1	20
Parathion	14.63	291.1	109.0	14	291.1	136.1	8
Parathion methyl	13.67	263.1	109.0	14	263.1	124.9	20
Penconazole	15.25	248.1	157.1	20	159.0	123.0	14
Pendimethalin	15.11	252.1	162.1	14	252.1	191.2	8
Permethrin	20.65, 20.78	163.0	127.0	8	183.1	153.1	14
Phenothrin	19.29, 19.41	183.1	153.1	14	183.1	165.2	8
Phenthoate	15.44	274.0	121.0	12	274.0	246.2	8
Phosalone	19.52	182.0	111.0	14	182.0	138.1	8
Phosmet	18.86	160.1	77.0	20	160.1	133.0	14
Piperonyl butoxide	18.34	176.1	131.1	14	176.1	103.0	20
Procymidone	15.51	283.1	96.0	14	283.1	255.2	14
Profenofos	16.38	337.0	267.0	20	339.0	269.0	14
Prometryn	13.88	241.1	184.2	14	226.1	184.2	8
Propiconazole	17.82, 17.94	259.1	173.0	14	261.1	175.0	14
Propoxur	10.61	152.1	110.0	8	110.1	82.0	20
Propyzamide	12.50	173.0	145.0	14	175.0	147.0	14
Prothiofos	16.29	309.0	239.1	14	267.0	239.0	8
Pyraflufen ethyl	17.87	412.0	349.3	14	349.0	307.2	14
Pyrazophos	20.01	221.1	193.2	12	232.1	204.2	14
Pyributicarb	18.56	165.1	108.0	12	181.1	108.0	14
Pyridaben	20.84	309.1	147.2	20	364.2	147.1	20
Pyridafenthion	18.68	340.1	199.0	12	340.1	203.1	20
Pyrifenox (*E*)	15.83	262.0	227.2	8	262.0	200.1	14
Pyrifenox (*Z*)	15.32	262.0	200.0	20	262.0	192.0	20
Pyrimethanil	12.67	198.1	183.2	16	199.1	158.1	25
Pyriminobac methyl (*E*)	17.84	302.1	256.2	14	302.1	230.2	14
Pyriminobac methyl (*Z*)	17.02	302.1	256.2	14	302.1	230.2	14
Pyriproxyfen	19.68	136.1	96.0	14	136.1	78.0	20
Quinoxyfen	17.86	237.1	208.2	20	272.0	237.2	8
Quintozene	12.26	236.9	142.9	20	294.9	237.0	20
Simeconazole	13.68	195.1	75.0	14	211.1	121.0	14
Tebufenpyrad	19.13	318.2	131.1	20	333.2	171.1	14
Tecnazene	10.47	260.9	203.0	14	202.9	142.9	20
Tefluthrin	12.80	177.1	127.0	20	197.1	141.1	8
Terbufos	12.45	231.0	128.9	20	231.0	175.0	14
Tetrachlorvinphos	15.83	328.9	109.0	20	330.9	109.0	20
Tetradifon	19.42	355.9	229.0	8	228.9	201.0	14
Thenylchlor	18.15	288.1	141.0	14	288.1	174.2	8
Thiobencarb	14.52	257.1	100.1	14	100.1	72.0	8
Tolclofos methyl	13.69	265.0	250.1	16	265.0	220.1	20
Tolfenpyrad	24.12	383.2	171.1	20	383.2	181.1	14
Triadimefon	14.68	208.1	181.0	8	208.1	127.0	14

(Continued on next page)

Table A1. GC-MS/MS parameters for the tested pesticides. *(Continued)*

		Quantification ion			*Confirmation ion*		
Pesticide	*Retention time (min)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*	*Precursor ion (m/z)*	*Product ion (m/z)*	*Collision energy (eV)*
Triadimenol	15.57, 15.67	168.2	70.0	10	168.2	112.0	5
Tri-allate	12.95	268.1	184.0	14	270.1	186.0	20
Triazophos	17.53	257.1	162.1	8	285.1	162.1	20
Tribuphos	16.50	202.0	146.9	8	258.1	146.9	14
Trifloxystrobin	17.72	222.1	190.2	8	190.1	130.0	8
Trifluralin	11.16	306.1	264.2	8	306.1	206.2	14
Uniconazole P	16.47	234.1	165.0	10	234.1	137.1	15
Vinclozolin	13.59	212.1	172.0	14	285.0	212.1	14