QuEChERS Combined with Agilent 7000 Series Triple Quadrupole GC/MS System for the Analysis of Over 200 Pesticide Residues in Cereals

Application Note

Food

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Abstract

This application note describes a simple and high-throughput method for the analysis of 218 pesticides in cereals (corn, wheat flour, and rice) using an Agilent QuEChERS kit combined with an Agilent 7000 Triple Quadrupole GC/MS System. Matrix-matched standard calibration method was used to avoid quantitation bias resulting from matrix interference. It showed that the method has a linearity with two orders of magnitude (2–200 µg/L), with the linear regression coefficients (R^2) at 0.99 or above for the majority of the pesticides. The limits of quantification (LOQs) ranged between 5 and 50 µg/kg, and for the majority of the pesticides the LOQ was 5 µg/kg, which is below the regulatory maximum residue limits. A spiking test showed that most recoveries at 5, 10, 20, 50, 100, and 200 µg/kg were in the range of 70–120 % (n = 6) with associated RSDs below 20 %. This procedure can be applied for the routine analysis of these pesticide residues in cereals.

Introduction

Rice, wheat, and corn are the three most important cereal crops worldwide. To ensure high production, the extensive use of agrochemicals (fertilizers and pesticides) is common practice. However, unregulated pesticide use can result in pesticide residues in the products. A number of international organizations and the legislation of different countries (for example, USA, China, and Japan) have set maximum residue limits (MRLs) for pesticides in foodstuffs including cereals. The latest MRLs established by China set pesticide residue levels generally between 50 and 500 µg/kg in cereals [1]. In this study, the monitoring of pesticide residues in cereals is important to ensure not only food safety, but also compliance with good manufacturing practices.

The most used approach for the extraction and cleanup of pesticides from food samples is QuEChERS. Since it was firstly introduced by Anastassiades *et al*. [2] in 2003, the QuEChERS approach has been widely accepted by the scientific community. The QuEChERS multiresidue procedure omits or replaces many complicated analytical steps in traditional methods with easier ones.

Due to the high complexity and diversity of the matrices, the analysis of pesticides in dried samples such as cereals is considered to be a difficult task. Compared to vegetables, cereals, such as corns, have high fat content that makes them even more difficult to extract and clean. The QuEChERS procedure was developed to determine pesticide residues in samples with more than 75 % moisture and nonfatty matrices. Thus, the QuEChERS procedure is rarely used in pesticide residue analysis of cereals compared to its use in vegetables and fruits.

Previously, a number of studies have reported multiresidue pesticide analysis based on GC-MS/MS, GC-TOFMS, and UHPLC-MSMS detection [3-5]. However, these reports do not analyze more than 200 pesticides. This application note describes a recently published study of QuEChERS combined with GC-MS/MS for the analysis of over 200 pesticide residues in cereals [6]. It is a rapid multiresidue method based on modified QuEChERS sample preparation combined with GC-MS/MS detection, aiming to determine more than 200 pesticide targets in corn, rice, and wheat flour.

Materials and Methods

Acetonitrile, ethyl acetate, and acetone were HPLC grade. Agilent QuEChERS extraction salt packets with ceramic homogenizer (p/n 5982-5755CH), QuEChERS dispersive SPE kit (p/n 5982-5158).

The standard pesticides were bought from Chemservice (West Chester, PA, USA) and Dr. Ehrenstorfer (Ausberg, Germany). Stock standard solution of 5 µg/mL (mixture of pesticides divided into two groups) and internal standard solution (Heptachlor epoxide B, 1 µg/mL) were prepared in ethyl acetate and stored at –20 °C until use.

Instrumental conditions

GC conditions

GC system	Agilent 7890A GC, coupled with an Agilent 7693A Automatic Liquid Sampler
Column	Agilent VF-1701ms (30 m × 0.25 mm, 0.25 µm) (p/n CP9151)
Oven temperature	40 °C hold 1 minute, 40 °C/min to 120 °C, 5 °C/min to 240 °C, 12 °C/min to 300 °C, hold 6 minutes
Carrier gas	Helium
Flow rate	1.0 mL/min
Injection port temperature	280 °C
Injection volume	1.0 µL
Injection mode	Splitless, purge on after 1.5 minutes

MS conditions

MS system	Agilent 7000B Triple Quadrupole GC/MS System*
Ion source	EI
Ionization voltage	70 eV
Ion source temperature	280 °C
Quadrupole temperature	Q1 150 °C, Q2 150 °C
Interface temperature	280 °C
Solvent delay	3.0 minutes

*Agilent has the new GC-MS/MS model 7000C and 7010 which have better performance.

The specific MRM transitions for all the test pesticides and other parameters are given in the appendix.

Sample preparation

Weigh a portion of 5 g cereal samples (ground rice, wheat flour, and ground corn) into a 50-mL centrifuge tube. Add 10 mL of purified water into the centrifuge tube, and place in a ceramic homogenizer. Shake the centrifuge tube by hand for a few seconds to hydrate the sample.

↓

Let stand for 30 minutes, then add 15 mL of acetonitrile with 1 % acetic acid, followed by the QuEChERS extraction salt packet. Immediately, seal the tube, and shake vigorously by hand for 1 minute to prevent the formation of crystalline agglomerates during $MgSO_4$ hydration. Centrifuge the tube for 5 minutes at 8,000 rpm.

↓

Transfer 8 mL of the supernatant into a 15-mL QuEChERS dispersive centrifuge tube. Vortex the extract with the sorbent for 1 minute, then centrifuge the tube for 5 minutes at 8,000 rpm.

↓

Transfer 3 mL of the supernatant into a 10-mL glass centrifuge tube and add 75 µL of internal standard solution. Evaporate the supernatant to dryness under a stream of nitrogen in a 35 °C water bath.

↓

Redissolve the residue in 1.5 mL of ethyl acetate, and filter through a PTEE filter (0.22-µm) for GC-MS/MS analysis.

Method validation

A recovery study was carried out to determine the method accuracy and precision. For each blank matrix, six levels, 5, 10, 20, 50, 100, and 200 µg/kg were fortified. After fortification, the spiked samples were left at room temperature for 30 minutes prior to the addition of water and extraction solvent. To avoid quantitative errors, matrix-matched calibration standards were used to calculate the analyte recoveries. Solvent-based standards were also analyzed to assess the matrix effects. The limits of quantification (LOQs) for each pesticide was based on the recovery results and defined as the lowest validated spike level meeting the requirement of recovery and relative standard deviation (RSD) for different fortification levels.

Results and Discussion

Linearity and LOQs

Due to the matrix effect, a matrix-matched standard was used for quantification. Each matrix-matched standard also contained ISTD at a concentration of 50 µg/L. Linearity was determined in all matrices, and the linear range was between 2 and 200 µg/L. In the three matrices, 97.2 % of correlation coefficient of detection (R^2) was equal to, or higher than 0.99, which would guarantee accurate quantification. There were 218 pesticides spiked at 5, 10, 20, 50, 100, and 200 µg/L (n = 6) in cereal matrix for recovery and RSD analysis. The LOQs for the pesticides were determined based on the recovery and RSD results, and defined as the selected lowest validated spike level meeting the requirement of recovery and RSD for different fortification levels, as described in Document No. SANCO/12495/2013 [7]. The LOQs for the 218 pesticides ranged between 5 and 50 µg/kg and the results were presented in Figure 1. For most of the pesticides at an LOQ of 5 µg/kg, the signal-to-noise of the quantitative transition was much higher than 10. This means that it is possible to apply the method for concentrations lower than 5 µg/kg.

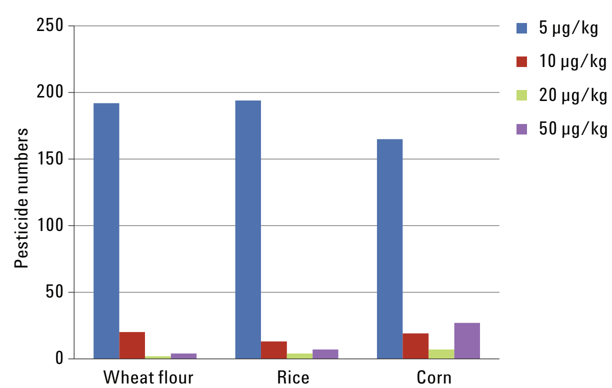

Figure 1. The distribution of LOQs in three matrices.

Recovery and precision

The proposed modified QuEChERS method was evaluated for 218 pesticides in corn, wheat flour, and rice matrices. A recovery study was carried out to determine method accuracy by comparing the real concentration of each pesticide measured by performing the complete procedure with a known pesticide concentration initially fortified to the blank matrix at six levels 5, 10, 20, 50, 100, and 200 µg/kg in replicates (n = 6). For recovery experiments, most of the 218 pesticides were in the 70–120 % range with the RSD below 20 %. There were a few exceptions, with recoveries in the 60–70 % range or the RSD in the 20–30 % range at 5 µg/kg and 10 µg/kg, such as disulfoton sulfoxide, edifenphos, ethiolate, and methamidophos. The recovery results of 100 µg/kg are presented in Figure 2A. It shows that, for most of the pesticides, the recoveries in rice were comparatively lower than in corn and flour. In general, the recoveries of the pesticides in corn and wheat flour were the same.

Real sample analysis

Ten cereal samples (two wheat flours, four corns, and four rices) from local markets were determined to validate the established method. As shown in Table 1, two pesticides were detected in the samples, including dichlorvos and isoprothiolane, but the concentrations and positive rate were very low. The extracted ion chromatograms of dichlorvos in matrix standard solution and real corn sample were given in Figure 3.

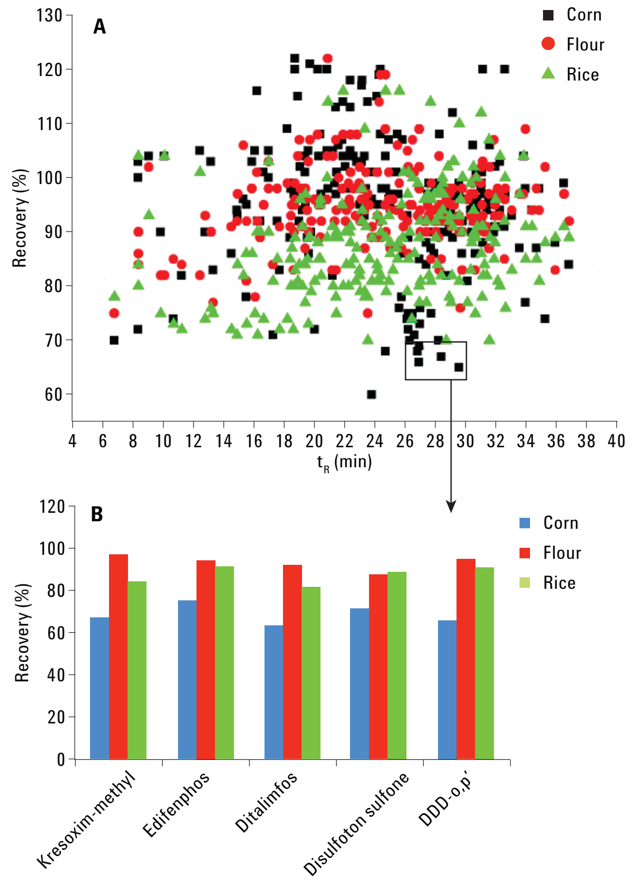

Figure 2. Recoveries of all the tested pesticides (100 µg/kg) in corn, wheat flour, and rice matrices (A) and recoveries of five pesticides with lower recoveries in corn than those in wheat flour and rice (B).

Table 1. Pesticide Levels (µg/kg) Found in Real Samples

Pesticide	Flour A	Flour B	Rice A	Rice B	Rice C	Rice D	Corn A	Corn B	Corn C	Corn D
Dichlorvos	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.	< LOQ	9.58	< LOQ
Isoprothiolane	n.d.	n.d.	< LOQ	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

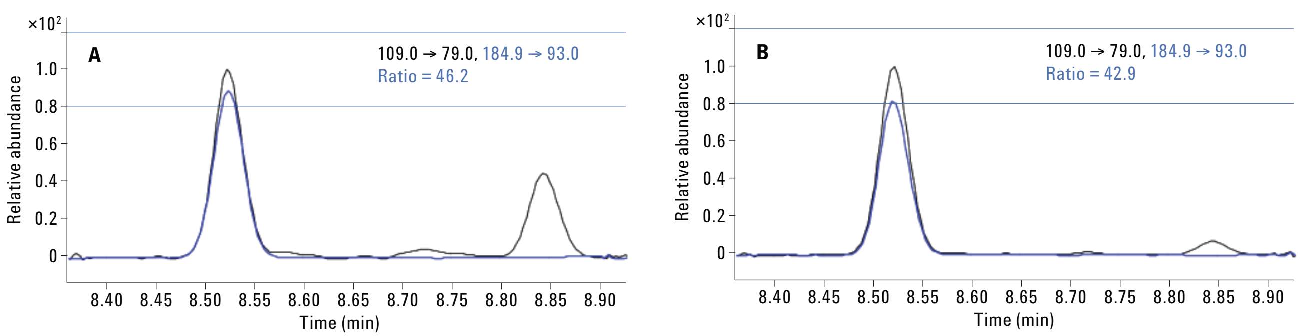

Figure 3. Extracted ion chromatograms of dichlorvos in (A) matrix-matched standard solution (5 µg/kg) and (B) real corn sample.

Comparison of the proposed method with other works

The QuEChERS method has been widely used in pesticide residue analysis, especially for vegetables and fruits. However, the application was limited for cereal. There were unique differences from other works:

- Over 200 pesticides were determined in three kinds of cereals, whereas other published works involved many fewer pesticides or matrices.
- In the extraction procedure, a ceramic homogenizer was used to improve extraction efficiency and repeatability.
- Six spiking levels were carried out to ensure good method validation.
- Less extraction time and a simpler extraction procedure was needed for sample preparation.

Conclusions

Cereals represent complex samples that are difficult to extract and clean in multipesticide residue analysis. In this study, a very simple, robust QuEChERS method combined with GC-MS/MS was developed for the determination of 218 pesticides in corn, wheat flour, and rice. Compared to other works involving pesticide residue analysis in cereal by the QuEChERS method, the proposed method has some superiorities in respect to the number of target pesticides, a simpler sample extraction procedure, and method validation. In this study, satisfactory LOQs, precision, and accuracy were obtained, demonstrating the suitability of the method for multipesticide residue analysis in cereals for regulatory and routine residue monitoring purposes.

Appendix

Acquisition and Chromatographic Parameters for the Selected Pesticides

Pesticides	RT (min)	MRM transition 1	CE1 (V)	MRM transition 2	CE2 (V)
Group A					
Dichlorvos	8.52	109 → 79	5	184.9 → 93	10
Disulfoton sulfoxide	9.09	125 → 96.9	5	213 → 97	20
Methamidophos	10.12	141 → 95	5	95 → 79	10
Dichlorobenzonitrile (2,6-(Dichlobenil))	10.71	171 → 100	25	171 → 136.1	15
Mevinphos	12.46	127 → 109	10	127 → 95	15
Methacrifos	12.8	207.9 → 180.1	5	207.9 → 93	10
Molinate	13.33	126.2 → 55.1	10	126.2 → 83.1	5
Cycloate	14.89	154.1 → 83.1	5	83 → 55.1	5
Isoprocarb	14.94	121 → 77.1	20	136 → 121.1	10
Acephate	15.32	142 → 96	5	136 → 94	10
Hexachlorobenzene	15.51	283.8 → 213.9	30	283.8 → 248.8	15
Ethoprophos	15.88	157.9 → 114	5	157.9 → 97	15
Ethalfluralin	16.21	275.9 → 202.1	15	315.9 → 275.9	10
Chlordimeform	16.42	151.9 → 117.1	10	195.9 → 181	5
Propoxur	16.97	110 → 63	25	110 → 64	15
Sulfotep	16.97	237.8 → 145.9	10	201.8 → 145.9	10
BHC-*alpha*	17.55	216.9 → 181	5	218.9 → 183	5
Atrazine-desethyl	18.40	172 → 94	15	187 → 172	5
Triallate	18.69	268 → 184.1	20	142.9 → 83	15
Profluralin	18.72	317.9 → 199	15	317.9 → 54.8	10
Fonofos	18.91	136.9 → 109	5	108.9 → 80.9	5
Tebupirimfos	19.06	233.9 → 110.1	15	260.8 → 137.2	15
Dioxathion	19.19	152.9 → 96.9	10	271 → 96.9	30

Acquisition and Chromatographic Parameters for the Selected Pesticides (cont.)

Pesticides	RT (min)	MRM transition 1	CE1 (V)	MRM transition 2	CE2 (V)
Disulfoton	19.38	88 → 60	5	153 → 97	10
Propazine	19.40	214.2 → 172.2	10	229.1 → 58.1	10
Dicloran	19.59	206.1 → 176	10	160.1 → 124.1	10
Propetamphos	19.70	138 → 110	10	138 → 64	15
Iprobenfos	20.21	203.9 → 91	5	121.9 → 121	15
Dichlofenthion	20.35	278.9 → 222.9	15	222.9 → 204.9	15
Pirimicarb	20.39	238 → 166.2	10	166 → 55.1	20
Dimethoate	20.82	86.9 → 46	15	142.9 → 111	10
Monocrotophos	20.87	127.1 → 109	10	127.1 → 95	15
Acetochlor	21.21	174 → 146.1	10	222.9 → 147.2	5
Chlorothalonil	21.43	263.8 → 168	25	263.8 → 229	20
Alachlor	21.59	188.1 → 160.2	10	160 → 132.1	10
Pirimiphos-methyl	21.82	290 → 125	20	232.9 → 151	5
Paraoxon-methyl	21.88	229.9 → 136.1	5	229.9 → 106.1	15
Vinclozolin	22.04	187 → 124	20	197.9 → 145	15
Metribuzin	22.23	198 → 82	15	198 → 55	30
Metalaxyl	22.30	234 → 146.1	20	220 → 192.1	5
Thiobencarb	22.57	100 → 72	5	124.9 → 89	15
Metolachlor	22.95	238 → 162.2	10	162.2 → 133.2	15
Formothion	22.97	170 → 93	5	197.9 → 92.9	10
o,p'-Dicofol	23.29	139 → 111	15	250.9 → 138.9	15
Bromophos	23.38	330.8 → 315.8	15	328.8 → 313.8	15
Fenthion	23.50	278 → 169	15	278 → 109	15
Heptachlor epoxide B (ISTD)	23.86	352.8 → 262.9	15	354.8 → 264.9	15
Triadimefon	24.11	208 → 181.1	5	208 → 111	20
Parathion	24.25	290.9 → 109	10	138.9 → 109	5
Isofenphos-methyl	24.34	199 → 121	10	241.1 → 199.1	10
Phorate Sulfoxide	24.66	96.9 → 64.9	20	96.9 → 78.9	15
Isofenphos	24.68	212.9 → 121.1	10	212.9 → 185.1	5
Quinalphos	24.89	146 → 118	10	146 → 91	30
Endosulfan-1	24.97	236.8 → 118.9	25	194.9 → 160	5
Penconazole	25.15	248 → 192.1	15	248 → 157.1	25
Mecarbam	25.46	130.9 → 86	10	130.9 → 74	5
Fosthiazate	25.58	195 → 103	5	195 → 60	20
DDE-p,p'	25.73	246.1 → 176.2	30	315.8 → 246	15
Fenothiocarb	25.86	160.1 → 72.1	10	72 → 56	10
Terbufos sulfone	26.12	198.9 → 143	10	152.9 → 96.9	10
DEF (Tribufos)	26.17	202 → 147	5	169 → 57.1	5
Mepanipyrim	26.18	223.2 → 222.2	10	222.2 → 207.2	15
Bromfenvinfos	26.45	266.9 → 159.1	15	268.9 → 161.1	15
Pretilachlor	26.57	262 → 202	5	162.1 → 132.2	20
DDD-o,p'	26.78	235 → 165.2	20	237 → 165.2	20
Ditalimfos	26.88	130 → 102.1	10	148 → 130.1	10
Kresoxim-methyl	26.89	116 → 89	15	116 → 63	30
Oxadiazon	26.94	174.9 → 112	15	174.9 → 76	35

Acquisition and Chromatographic Parameters for the Selected Pesticides (cont.)

Pesticides	RT (min)	MRM transition 1	CE1 (V)	MRM transition 2	CE2 (V)
DDT-o,p'	27.36	235 → 165.2	20	237 → 165.2	20
Cyflufenamid	27.62	188.1 → 88	35	118.1 → 89	25
Imazalil	27.65	214.9 → 173	5	216.8 → 175	5
Mephosfolan	27.69	196 → 139.9	15	196 → 59.9	30
Bupirimate	27.85	272.9 → 193.1	5	272.9 → 108	15
Oxyfluorfen	28.08	252 → 196	20	252 → 146	30
Isoxathion	28.19	177.1 → 130	10	177.1 → 116.1	15
Chlorthiophos	28.21	324.8 → 268.9	10	296.8 → 268.9	5
Flutolanil	28.21	173 → 145.1	15	280.9 → 173	10
DDD-p,p'	28.41	234.9 → 165.1	20	236.9 → 165.2	20
Carbophenothion	28.45	153 → 96.9	10	199 → 143	10
Endosulfan-2	28.49	206.9 → 172	15	276.7 → 240.9	10
Quinoxyfen	28.76	237 → 208.1	30	271.9 → 237.1	10
Aclonifen	28.85	212.1 → 182.2	10	264.1 → 194.2	15
Trifloxystrobin	28.88	116 → 89	15	116 → 63	30
Bioresmethrin	29.10	171 → 128	15	143 → 128	10
Piperonyl butoxide	29.18	176.1 → 103.1	25	176.1 → 131.1	15
Edifenphos	29.53	172.9 → 109	5	201 → 109	10
Fensulfothion	29.60	140 → 125	10	291.8 → 156	15
Triazophos	29.71	161.2 → 134.2	5	161.2 → 106.1	10
Bifenthrin	29.76	181.2 → 165.2	25	181.2 → 166.2	10
Tebufenpyrad	30.28	275.9 → 171.1	10	332.9 → 171	15
Bromopropylate	30.46	183 → 155	15	185 → 157	15
Epoxiconazole	30.50	192 → 138.1	10	192 → 111	25
Tetramethrin	30.63	164 → 107.1	10	164 → 77.1	25
Tebuconazole	30.64	250 → 125	20	125 → 89	15
Pyriproxyfen	30.95	136.1 → 96	15	136.1 → 78.1	20
Piperophos	30.99	320 → 122	10	140 → 98.1	10
EPN	31.07	169 → 141.1	5	169 → 77.1	25
Hexazinone	31.08	171 → 71.1	10	171 → 85.1	10
Fenamidone	31.17	238 → 237.2	10	268 → 180.2	20
Tetradifon	31.47	226.9 → 199	15	158.9 → 131	10
Anilofos	31.54	225.9 → 184	5	225.9 → 157	10
Fenamiphos-sulfoxide	31.80	304 → 196	15	196 → 93	15
Fenarimol	32.20	251 → 139.1	10	219 → 107.1	10
Permethrin	32.20	183.1 → 168.1	10	183.1 → 153	10
Pyridaben	32.53	147.2 → 117.1	20	147.2 → 132.2	10
Prochloraz	33.50	180 → 138	10	195.9 → 96.9	30
Cypermethrin	33.88	163 → 127	5	163 → 91	10
Boscalid	34.60	140 → 112	10	140 → 76	25
Fenvalerate	35.17	167 → 125.1	5	224.9 → 119	15
Deltamethrin	36.75	252.9 → 93	15	181 → 152.1	25
Group B					
Ethiolate	6.82	100 → 72	5	161 → 72	15
Naled	8.41	184.9 → 109	15	108.9 → 79	5

Acquisition and Chromatographic Parameters for the Selected Pesticides (cont.)

Pesticides	RT (min)	MRM transition 1	CE1 (V)	MRM transition 2	CE2 (V)
Biphenyl	9.88	154.1 → 153.1	15	153.1 → 152.1	15
Etridiazole	11.26	211.1 → 183	10	183 → 140	15
Chloroneb	13.19	206 → 191.1	10	208 → 193.1	10
Tecnazene (TCNB)	14.52	260.9 → 203	10	214.9 → 179	10
Thionazin	15.53	143 → 79	10	175 → 79	10
Diphenylamine	16.08	169 → 168.2	15	168 → 167.2	15
Fenobucarb	16.26	121 → 77	20	121 → 103.1	15
Benfluralin	16.65	292 → 264	5	292 → 206	10
Chlorpropham	17.26	153 → 125.1	10	153 → 90	25
Pentachloronitrobenzene	17.69	236.9 → 118.9	25	236.9 → 142.9	30
Omethoate	18.20	155.9 → 110	5	109.9 → 79	15
Atraton	18.44	211 → 169.1	5	169 → 154.1	5
Diazinon	18.50	137.1 → 84	10	137.1 → 54	20
Clomazone	18.65	204.1 → 107.1	20	125 → 89	15
Dicrotofos	18.72	127 → 109	15	127 → 95	15
pyrimethanil	19.00	198 → 183	15	198 → 118	35
BHC-gamma	19.19	216.9 → 181	5	181 → 145	15
Carbofuran	19.38	164.2 → 149.1	10	149.1 → 121.1	5
Etrimfos	19.39	181 → 153.1	5	168 → 153.1	5
Atrazine	19.52	214.9 → 58.1	10	214.9 → 200.2	5
Simazine	19.62	201.1 → 173.1	5	201.1 → 186.2	5
Terbuthylazine	19.78	228.9 → 173.1	5	172.9 → 172	5
Monolinuron	20.00	214 → 61	10	155 → 127	10
Isazofos	20.27	161 → 119.1	5	161 → 146	5
Pentachloroaniline	20.38	262.8 → 192	20	264.9 → 194	20
Pronamide	20.44	173 → 145	15	175 → 147	15
Chlorpyrifos-methyl	20.82	285.9 → 92.9	20	287.9 → 92.9	20
Aldrin	21.17	262.9 → 192.9	35	254.9 → 220	20
Ronnel (Fenchlorphos)	21.32	285 → 269.9	15	286.9 → 272	15
Desmetryn	21.39	213 → 58.1	10	213 → 171.2	5
Tolclofos-methyl	21.44	265 → 250	15	265 → 93	25
Prometryn	21.88	226 → 184.2	10	199 → 184.1	5
BHC-beta	22.10	216.9 → 181	5	181 → 145	15
Chlorpyrifos	22.36	198.9 → 171	15	196.9 → 169	15
Ametryn	22.37	227 → 170.1	10	227 → 58.1	10
Terbutryn	22.37	241.1 → 170.2	15	185 → 170.1	5
Malaoxon	22.68	126.9 → 99	5	126.9 → 55	5
Trichloronat	22.71	296.8 → 268.9	10	298.8 → 270.9	10
Dipropetryn	22.79	255.1 → 222.1	10	255.1 → 180.1	20
BHC-delta	22.99	217 → 181.1	5	181 → 145	15
Parathion-methyl	23.10	232.9 → 109	10	262.9 → 79	30
Pirimiphos-ethyl	23.10	318.1 → 166.1	10	318.1 → 182	10
Phosphamidon	23.13	127 → 95	15	127 → 109	10
Malathion	23.30	172.9 → 99	15	157.8 → 125	5
Fenitrothion	23.50	277 → 260	5	277.1 → 109	15

Acquisition and Chromatographic Parameters for the Selected Pesticides (cont.)

Pesticides	RT (min)	MRM transition 1	CE1 (V)	MRM transition 2	CE2 (V)
Methoprene	23.60	153 → 111.1	5	111.1 → 55	15
Ethofumesate	23.76	206.9 → 161.1	5	161 → 105.1	10
Cyprodinil	23.78	225.2 → 224.3	10	224.2 → 208.2	20
Heptachlor epoxide B (ISTD)	23.86	352.8 → 262.9	15	354.8 → 264.9	15
Isofenphos oxon	24.10	229 → 200.9	10	229 → 121	25
Pendimethalin	24.15	251.8 → 162.2	10	251.8 → 161.1	15
Dimepiperate	24.33	118 → 117.1	10	119 → 91	10
DDE-o,p'	24.43	246 → 176.2	30	248 → 176.2	30
Bromophos-ethyl	24.66	358.7 → 302.8	15	302.8 → 284.7	15
Propanil (DCPA)	24.70	161 → 99	30	161 → 90	25
Chlorfenvinphos	24.88	266.9 → 159.1	15	322.8 → 266.8	10
Chlordane-trans (*gamma*)	24.97	372.8 → 265.8	15	271.7 → 236.9	15
Tetraconazole	25.39	336 → 217.9	20	170.9 → 136	10
Butachlor	25.53	236.9 → 160.2	5	176.1 → 147.1	10
Prothiofos	25.78	266.9 → 239	5	266.9 → 221	20
Tetrachlorvinphose	26.10	328.9 → 109	22	330.9 → 109	22
Dieldrin	26.17	277 → 241	5	262.9 → 193	35
Beflubutamid	26.27	221 → 193.1	5	176.1 → 91.1	10
Methidathion	26.40	144.9 → 85	5	144.9 → 58.1	15
Butamifos	26.89	285.9 → 202	15	200 → 92	10
Hexaconazole	26.96	231 → 175	10	256 → 82.1	10
Chlorfenson	27.22	175 → 111	10	111 → 75	15
Paclobutrazol	27.35	236 → 125.1	10	125.1 → 89	20
Fluazifop-butyl	27.44	281.9 → 238	20	281.9 → 91	20
Isoprothiolane	27.52	162.1 → 85	20	162.1 → 134	5
Chlorobenzilate	27.97	251.1 → 139.1	15	139.1 → 111	10
Nitrofen	28.17	202 → 139.1	20	282.9 → 253	10
Disulfoton sulfone	28.33	213 → 153	5	213 → 96.9	15
Cyproconazole	29.01	139 → 111	15	139 → 75	30
DDT-p,p'	29.02	235 → 165.2	20	237 → 165.2	20
Ethion	28.45	230.9 → 129	20	230.9 → 175	10
Fluorodifen	28.68	190 → 126.1	10	190 → 75	20
Diniconazole	28.87	267.9 → 232.1	10	269.9 → 232.1	10
Myclobutanil	28.98	179 → 125.1	10	179 → 90	30
Benalaxyl	29.05	148 → 77	35	148 → 105.1	20
Methoxychlor- o,p'	29.11	227.1 → 121.1	10	227.1 → 91.1	35
Diclofop-methyl	29.51	339.9 → 252.9	10	253 → 162.1	15
Propiconazole	29.53	172.9 → 74	45	258.8 → 69	10
Fenthion sulfoxide	29.71	279 → 109	15	278 → 109	15
Fenthion sulfone	30.07	309.9 → 105	10	135.9 → 92	10
Fludioxonil	30.28	248 → 154.1	20	248 → 182.1	10
Oxadixyl	30.35	163 → 132.1	5	163 → 117.1	25
Phenothrin	30.41	183 → 168	10	183 → 155.1	5
Etoxazole	30.45	141 → 63.1	30	141 → 113	15
Famphur	30.57	218 → 109	15	217 → 92.9	10

Acquisition and Chromatographic Parameters for the Selected Pesticides (cont.)

Pesticides	RT (min)	MRM transition 1	CE1 (V)	MRM transition 2	CE2 (V)
Fenpropathrin	30.69	264.9 → 210	10	207.9 → 181	5
Leptophos	30.96	171 → 77.1	15	154.9 → 77.1	15
Pyridaphenthion	31.03	340 → 199	5	204 → 203.1	5
Phosmet	31.33	160 → 77.1	20	160 → 133.1	10
Bifenox	31.49	340.9 → 309.9	10	189.1 → 126	20
Acrinathrin	31.88	207.8 → 181.1	10	181 → 127	30
Cyhalothrin (*lambda*)	31.88	208 → 181	5	181.1 → 152	25
Phosalone	31.89	182 → 111	15	182 → 102.1	15
Mefenacet	32.05	192 → 136.1	15	192 → 109.1	30
Pyraclofos	32.49	194 → 138	15	138.9 → 97	5
Azinphos-ethyl	32.56	132 → 77.1	15	160 → 77.1	20
Fluquinconazole	32.98	340 → 298	15	108 → 57	15
Coumaphos	33.75	361.9 → 109	15	210 → 182	10
Cyfluthrin	33.88	162.9 → 127	5	198.9 → 170.1	25
Flucythrinate	34.31	156.9 → 107.1	15	198.9 → 157	10
Fenbuconazole	34.78	197.9 → 129	5	128.9 → 102.1	15
Fluvalinate-*tau*	35.83	250 → 55	40	250 → 200	40
Difenoconazole	36.42	322.8 → 264.8	15	264.9 → 202	20

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