Multiresidue Analysis of 301 Pesticides in Food Samples by LC/Triple Quadrupole Mass Spectrometry

Application Note

Pesticides

Authors

E. Michael Thurman and Imma Ferrer
Department of Civil, Environmental and Architectural Engineering
Center for Environmental Mass Spectrometry
University of Colorado
ECOT 441, 428 UCB
Boulder, CO 80309
USA

Jerry A. Zweigenbaum
Agilent Technologies Inc.
2850 Centerville Road
Wilmington, Delaware 19806
USA

Abstract

An analytical methodology for screening and confirming the presence of 301 pesticides in vegetable samples was developed using the Agilent G6410A Triple Quadrupole Mass Spectrometer (QQQ). We found that, of the 301 compounds, 90% could be identified using this procedure with a limit of detection (LOD) in vegetable matrices of 0.01 mg/kg (ppm) or below, which is the level for baby food and banned substances and is the maximum residue level (MRL) used by the European Union. These levels were reached in a single analysis using positive ion electrospray with 99 transitions per segment and a quantifying and confirming ion for each compound. The analytical performance of the method was evaluated for different types of vegetables (tomato and green pepper), showing little or no matrix effects. Linearity of response over 2 orders of magnitude was demonstrated ($r^2 > 0.99$).

Agilent Technologies

Introduction

Currently more than 900 pesticides are used worldwide, both legally and illegally, on food products and in the treatment of soil and crops. Most of these pesticides have maximum residue levels (MRLs) for both food and water to protect the consumer. The MRL concentrations have to be monitored as part of the quality control of food, especially fruits and vegetables; thus, multiresidue methods with hundreds of pesticides are needed for quality control. However, the ability to monitor hundreds of pesticides in a single analysis is a challenging problem both for chromatography and mass spectrometry.

In this application we evaluate the Agilent 6410 QQQ to not only screen but also to confirm 301 pesticides in a single analysis using a combination of the new 1.8-micron LC columns (for maximum peak capacity) and eight time segments with 100 transitions per segment in order to have both a quantifying ion and also a qualifier ion, which satisfies the European Union (EU) specifications for unequivocal identification by mass spectrometry. This study extends the tested capabilities of the instrument for limits of detection and speed of response, as well as for chromatography [1].

This study is one of the first of its kind to fully examine the Agilent QQQ for the analysis of pesticides in food for hundreds of pesticides in a single analysis. This topic was chosen because of the relevance of these compounds and their significant use on food commodities. The sensitivity of the QQQ easily meets the levels required by the regulations on pesticides in food for 90% of the compounds studied.

Experimental

Sample Preparation

Pesticide analytical standards were purchased from Chem Services, Inc. (Philadelphia, USA) and Sigma Aldrich (Louisville, USA). Individual pesticide stock solutions (approximately 1,000 µg/mL) were prepared in pure acetonitrile or methanol, depending on the solubility of each individual compound, and stored at –18 °C. From these mother solutions, working standard solutions were prepared by dilution with acetonitrile and water.

Vegetable samples were obtained from the local markets. "Blank" vegetable extracts were used to prepare the matrix-matched standards for validation purposes. In this way, two types of vegetables (green peppers and tomatoes) were extracted using the QuEChERS method [2]. The vegetable extracts were spiked with the mix of standards at different concentrations (ranging from 0.1 to 100 ng/mL or ppb) and subsequently analyzed by LC/MS/MS.

LC/MS/MS Instrumentation

LC Conditions

Column:	Agilent SB-C-18, 4.6 mm x 150 mm, 1.8 µm (p/n 829975-902)
Column temperature:	25 °C
Mobile phase:	10% ACN and 90% H_2O with 0.1% HCOOH
Flow-rate:	0.6 mL/min
Gradient:	Time 0 = 10% ACN linear to Time 28 = 98% ACN Time 30 = 100% ACN Time 31 = 100% ACN
Injection volume:	10 µL

MS Conditions

Mode:	Positive ESI using the Agilent G6410AA Triple Quadrupole Mass Spectrometer
Nebulizer:	40 psig
Drying gas flow:	9 L/min
V capillary:	4000 V
Drying gas temp:	350 °C
Fragmentor voltage:	70–120 V
Collision energy:	5–30 V
MRM:	2 transitions for every compound as shown in Table 1
Dwell time:	10 msec

Results and Discussion

Optimization of LC/MS/MS Conditions

The initial study consisted of two parts. First was to optimize the fragmentor voltage for each of the 301 compounds in order to produce the greatest signal for the precursor ion. Typically the protonated molecule was used for the precursor ion. Each compound was analyzed separately using an automated procedure to check the fragmentor at each voltage. The data were then selected for optimal fragmentor signal and each compound was injected in a programmed run at a concentration of 10 µg/mL to determine collision energies for both the quantifying and qualifying ions. Various collision energies (5, 10, 15, 20, 25, and 30 V) were applied to the compounds under study. The energies were then optimized for each of the ions and the voltages that gave the best sensitivity were selected. The MRM transitions used for this study are shown in Tables 1A and 1B along with the list of the 301 compounds that were studied.

Table 1A. Analytical Conditions, MRMs, Limits of Detection, and r^2 for Compounds Tested

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
3,4,5-Trimethacarb	194	137 122	0.9	0.5	0.999
3-Hydroxycarbofuran	238	163 220	5.0	5.0	0.999
Acephate	184	143 125	9.0	5.0	1.000
Acetamiprid	223	126 56	0.2	0.5	1.000
Aclonifen	265	248 193	20.0	10.0	0.979
Aldicarb	116	89 70	1.5	5.0	1.000
Aldicarb sulfone	223	148 76	6.0	1.0	1.000
Aldicarb sulfoxide	207	89 132	4.0	1.0	0.999
Ametryn	228	186 96	4.3	4.3	0.999
Aminocarb	209	137 152	4.5	2.0	1.000
Atrazine	216	174 132	0.8	0.6	1.000
Azamethiphos	325	183 139	0.9	0.9	0.993
Azinphos-methyl	318	132 160	1.0	1.0	0.975
Azoxystrobin	404	372 344	0.5	0.5	0.973
Benalaxyl	326	148 294	1.0	0.5	0.992
Bendiocarb	224	109 167	1.0	1.0	0.996
Bensulfuron-methyl	411	149 182	0.5	0.4	0.998
Benzoximate	364	199 105	1.0	0.5	0.999
Bifenox	342	189 310	25.0	40.0	***
Bitertanol	338	99 269	0.6	2.0	0.995
Bromacil	261	205 188	2.0	1.0	0.999

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Bromuconazole 1	376	159 70	1.0	1.0	1.000
Bromuconazole 2	376	159 70	4.0	2.0	0.983
Bupirimate	317	166 272	1.0	5.0	0.999
Buprofezin	306	201 116	0.7	0.8	0.999
Butocarboxim	213	156 75	5.0	***	0.940
Butocarboxim-sulfoxide	207	75 132	5.0	5.0	0.997
Buturon	237	84 126	1.0	0.5	0.999
Butylate	218	57 156	5.0	45.0	0.990
Carbaryl	202	145 117	5.0	5.0	0.999
Carbendazim	192	160 132	0.5	1.0	0.997
Carbetamide	237	118 192	0.5	0.5	0.996
Carbofuran	222	165 123	1.0	1.0	0.999
Carboxin	236	143 87	0.5	0.5	0.993
Carfentrazone-ethyl	412	346 366	8.0	8.0	0.998
Chlorbromuron	293	204 182	7.0	10.0	0.996
Chlorfenvinphos	359	155 127	2.0	1.0	0.990
Chlorfluazuron	540	383 158	1.0	1.0	0.989
Chloridazon	222	104 92	0.9	1.0	1.000
Chloroxuron	291	72 218	0.5	2.0	0.983
Chlorpropham	214	172 154	1.0	1.0	0.998
Chlorpyrifos methyl	322	125 290	7.0	35.0	0.978

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Chlorsulfuron	358	141 167	1.0	1.0	0.999
Cinosulfuron	414	183 157	3.0	1.0	0.998
Clethodim	360	164 268	5.0	10.0	0.940
Clodinafop-propargyl	350	266 238	5.0	1.0	0.993
Clofentezine	303	138 102	6.0	10.0	0.998
Clomazone	240	125 89	0.9	5.0	0.999
Cloquintocet-mexyl	336	238 192	0.1	0.5	0.990
Coumaphos	363	227 307	1.0	5.0	1.000
Cyanazine	241	214 174	2.0	1.0	0.999
Cycloate	216	83 154	1.0	10.0	0.999
Cymoxanil	199	128 111	6.0	5.0	1.000
Cyproconazole	292	70 125	1.0	2.0	0.993
Cyprodinil	226	93 108	5.0	7.0	1.000
Cyromazine	167	85 125	10.0	10.0	0.997
Daminozide	161	143 61	50.0	40.0	0.999
Deethylatrazine	188	146 104	1.0	1.0	0.999
Deethylterbuthylazine	202	146 110	1.0	0.5	0.999
Deisopropylatrazine	174	96 132	4.0	5.0	0.998
Demeton-S-methyl-sulfone	263	169 125	0.5	0.5	0.990
Desmedipham	301	136 182	1.0	10.0	0.999
Diazinon	305	169 153	0.5	0.2	1.000

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Dichlofenthion	315	287 259	10.0	40.0	0.520
Dichlofluanid	333	123 224	10.0	10.0	0.999
Dichlorvos	221	109 145	5.0	5.0	0.999
Diclobutrazol	328	70 159	2.0	5.0	1.000
Diethofencarb	268	152 226	0.5	1.0	0.998
Difenoconazole-1	406	251 337	0.3	0.5	0.989
Difenoconazole-2	406	251 337	0.3	0.5	0.989
Difenoxuron	287	72 123	0.6	0.2	0.980
Diflubenzuron	311	158 141	6.0	6.0	0.959
Diflufenican	395	266 246	5.0	1.0	0.999
Dimefuron	339	72 167	0.5	1.0	0.991
Dimethachlor	256	224 148	0.5	1.0	0.993
Dimethenamid	276	244 168	0.6	0.1	0.987
Dimethoate	230	199 171	0.7	0.7	0.994
Dimethomorph 1	388	301 165	0.6	0.6	0.998
Dimethomorph 2	388	301 165	0.6	0.6	0.998
Diniconazole	326	70 159	1.0	1.0	0.988
Diphenylamine	170	93 65	0.5	0.1	0.985
Disulfoton	275	89 61	5.0	10.0	0.991
Diuron	233	72 160	0.8	1.0	0.996
Dodemorph	282	116 98	10.0	10.0	0.983
EPN	324	157 296	30.0	10.0	0.991

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Epoxiconazole	330	121 141	20.0	***	***
Ethiofencarb	226	107 164	0.9	1.0	0.995
Ethiofencarb sulfone	258	107 201	6.0	6.0	0.998
Ethiofencarb sulfoxide	242	107 185	0.5	1.0	0.990
Ethion	385	171 199	1.0	5.0	1.000
Ethirimol	210	98 140	50.0	45.0	0.990
Ethofumesate	287	121 161	7.0	10.0	0.974
Ethoprophos	243	173 215	2.0	2.0	0.987
Etrimfos	293	125 265	0.7	5.0	0.999
Famoxadone	331	195 238	5.0	5.0	***
Fenamiphos	304	217 234	1.0	0.5	0.989
Fenarimol	331	81 268	5.0	6.0	0.984
Fenazaquin	307	57 161	1.0	5.0	0.999
Fenbuconazole	337	125 70	0.5	2.0	1.000
Fenfuram	202	109 83	5.0	2.0	0.999
Fenhexamid	302	97 55	3.0	9.0	1.000
Fenobucarb	208	95 152	1.0	1.0	1.000
Fenoxaprop-ethyl	362	288 244	0.6	2.0	0.999
Fenoxycarb	302	88 116	1.0	1.0	0.999
Fenpiclonil	237	202 166	1.0	10.0	0.998
Fenpropathrin	350	125 97	50.0	5.0	0.967
Fenpropimorph	304	147 130	10.0	10.0	1.000

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Fenthion 1	279	247 169	5.0	9.0	0.998
Fenthion 2	279	169 247	5.0	10.0	0.999
Fenuron	165	72 120	1.0	2.0	0.999
Fipronil	437	263 368	10.0	50.0	0.994
Flamprop-isopropyl	364	105 304	5.0	10.0	0.974
Flamprop-methyl	336	105 304	5.0	9.0	0.986
Flazasulfuron	408	182 301	8.0	5.0	0.898
Fluazifop-P-butyl	384	282 328	1.0	0.5	0.991
Flufenacet	364	152 194	0.5	1.0	0.991
Flufenoxuron	489	158 141	9.0	5.0	0.990
Fluodioxinil	229	158 185	5.0	10.0	0.987
Fluometuron	233	72 160	2.0	1.0	0.988
Fluoroglycofene-ethyl	344	223 300	25.0	10.0	0.999
Fluoroxypyr	255	209 181	10.0	5.0	0.997
Flurtamone	334	247 303	0.5	0.4	0.996
Flusilazole	316	247 165	0.1	0.1	0.991
Flutriafol	302	70 123	1.0	1.0	0.998
Folpet	260	130 232	5.0	50.0	***
Fonofos	247	109 137	1.0	5.0	***
Formetanate	222	165 120	10.0	9.0	0.995
Fuberidazole	185	157 156	1.1	1.0	1.000
Furathiocarb	383	195 252	0.5	0.1	0.991

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Haloxyfop-methyl	376	316 288	1.0	5.0	1.000
Heptenophos	251	127 125	2.0	1.0	0.999
Hexaconazole	314	70 159	1.0	0.6	0.993
Hexaflumuron	461	158 141	5.0	10.0	0.984
Hexazinone	253	171 71	0.5	1.0	0.994
Hexythiazox	353	168 228	2.0	1.0	0.996
Hydroxyatrazine	198	156 86	4.0	4.0	0.998
Imazalil	297	159 255	10.0	10.0	0.850
Imazapyr	262	217 234	1.0	1.0	0.996
Imazaquin	312	199 267	0.6	1.0	0.998
Imidacloprid	256	175 209	5.0	1.0	0.993
Indoxacarb	528	249 293	5.0	1.0	0.997
Ioxynil	372	118 245	30.0	10.0	0.998
Iprodione	330	245 288	10.0	30.0	0.999
Iprovalicarb	321	119 203	1.0	1.0	0.997
Irgarol	254	198 156	1.0	1.0	0.999
Irgarol metabolite	214	158 110	5.0	4.0	1.000
Isazofos	314	120 162	1.0	0.5	0.991
Isofenphos	346	217 245	3.0	0.5	0.996
Isoproturon	207	72 165	1.0	1.0	0.999
Isoxaflutole	360	251 69	1.0	20.0	1.000

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Kresoxim-methyl	314	206 267	5.0	5.0	0.997
Lenacil	235	153 136	5.0	25.0	0.998
Linuron	249	160 182	1.0	5.0	1.000
Lufenuron	511	158 141	5.0	10.0	0.995
Malaoxon	315	99 127	1.0	0.5	0.996
Malathion	331	99 127	0.8	2.0	0.998
Mebendazole	296	264 105	0.6	0.6	0.990
Mecarbam	330	199 227	2.0	1.0	0.989
Mepanipyrim	224	77 106	1.0	1.0	0.997
Metalaxyl	280	192 220	1.0	2.0	0.994
Metamitron	203	175 104	1.0	1.0	1.000
Metazachlor	278	134 210	1.0	1.0	0.986
Metconazole	320	70 125	1.0	0.5	0.979
Methabenzthiazuron	222	165 150	0.5	1.0	0.999
Methamidophos	142	94 125	1.0	1.0	0.999
Methfuroxam	230	137 111	0.5	0.4	1.000
Methidathion	303	85 145	1.0	0.5	0.987
Methiocarb	226	121 169	0.9	1.0	0.996
Methomyl	163	88 106	1.0	1.0	0.990
Metobromuron	259	170 148	5.0	10.0	0.999
Metolachlor	284	252 176	0.5	1.0	0.988
Metolcarb	166	109 91	3.0	1.0	1.000

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Metosulam	418	175 354	5.0	1.0	0.993
Metoxuron	229	72 156	0.5	1.0	0.996
Metribuzin	215	187 131	2.0	0.5	0.999
Metsulfuron-methyl	382	167 141	1.0	0.5	0.996
Molinate	188	126 83	2.0	5.0	0.999
Monolinuron	215	126 148	1.0	2.0	1.000
Monuron	199	72 126	1.0	5.0	0.995
Myclobutanil	289	70 125	0.5	1.0	0.997
Naled	379	127 297	10.0	10.0	0.997
Napropamide	272	129 171	1.0	1.0	1.000
Neburon	275	57 88	1.0	0.5	0.989
Nicosulfuron	411	182 213	1.0	0.6	0.937
Nuarimol	315	81 252	1.0	1.0	***
Ofurace	282	160 254	0.5	1.0	0.981
Omethoate	214	125 183	1.1	1.0	1.000
Oxadixyl	279	219 102	5.3	5.0	0.989
Oxamyl	242	72 121	45.0	50.0	0.990
Oxydemethon-methyl	263	169 109	1.1	1.0	0.990
Paclobutrazol	294	70 165	0.5	2.0	0.998
Paraoxon-methyl	248	90 202	3.0	5.0	0.994
Parathion-ethyl	292	236 264	5.0	10.0	0.999
Parathion-methyl	264	125 232	10.0	10.0	0.986

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Penconazole	284	70 159	0.5	1.0	0.986
Pencycuron	329	125 218	0.5	5.0	0.987
Pendimethalin	282	212 194	5.0	2.0	0.990
Phenmedipham	301	136 168	1.0	1.0	0.999
Phenthoate	321	163 247	5.0	9.0	0.975
Phorate	261	75 199	25.0	8.0	0.999
Phosalone	368	182 322	5.0	1.0	1.000
Phosmet	318	160 133	5.0	7.0	0.988
Phoxim	299	77 129	5.0	5.0	0.998
Picolinafen	377	238 359	1.0	1.0	0.999
Picoxystrobin	368	145 205	0.5	0.5	0.991
Pirimicarb	239	72 182	2.0	8.0	0.999
Pirimiphos-ethyl	334	198 182	0.1	0.1	0.995
Pirimiphos-methyl	306	164 108	0.1	0.1	0.934
Pirimisulfuron-methyl	469	254 199	1.0	1.0	0.980
Prochloraz	376	308 266	5.0	10.0	0.999
Procymidone	284	256 67	30.0	8.0	0.998
Profenofos	373	303 345	5.0	5.0	1.000
Promecarb	208	109 151	1.0	1.0	0.998
Prometon	226	142 184	3.0	3.0	1.000
Prometryn	242	158 200	1.0	5.0	0.999
Propachlor	212	170 152	1.0	1.0	0.998

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Propamocarb	189	102 144	8.7	9.0	0.999
Propanil	218	127 162	1.0	4.0	0.963
Propazine	230	146 188	1.0	0.5	1.000
Propetamphos	282	138 156	5.0	0.5	0.972
Propham	180	120 138	5.0	2.0	1.000
Propiconazole-1	342	159 69	0.5	1.0	0.997
Propiconazole-2	342	159 69	0.5	1.0	0.995
Propoxur	210	111 168	0.5	0.5	0.999
Propyzamide	256	190 173	3.0	1.0	0.998
Prosulfocarb	252	91 128	0.8	1.0	1.000
Prosulfuron	420	141 167	1.0	1.0	0.989
Pymetrozin	218	105 79	30.0	50.0	0.980
Pyraclostrobin	388	163 194	0.5	0.1	0.976
Pyrazophos	374	222 194	0.5	0.1	0.996
Pyridaben	365	147 309	0.1	0.5	0.997
Pyrimethanil	200	107 183	8.0	5.0	0.999
Pyriproxyfen	322	96 227	0.6	0.5	0.999
Quinalphos	299	147 163	1.0	1.0	0.999
Quinmerac	222	204 176	4.7	5.0	0.999
Quinomethionate	235	207 163	5.0	10.0	0.994
Quinoxyfen	308	197 272	1.0	0.5	0.998

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Quizalofop-ethyl	373	299 271	0.5	5.0	1.000
Rimsulfuron	432	182 325	5.0	1.0	0.810
Rotenone	395	213 192	1.0	1.0	0.999
Simazine	202	132 124	1.0	1.0	0.998
Simetryn	214	124 144	10.0	10.0	0.998
Spiromesifen	371	273 255	7.0	10.0	0.968
Sulfosulfuron	471	211 261	1.0	1.0	1.000
Sulfotep	323	171 143	1.0	5.0	0.999
Sulprofos	323	219 247	30.0	30.0	0.990
Tebuconazole	308	70 151	1.0	0.5	0.983
Tebufenozide	353	133 297	0.5	0.1	0.983
Tebutam	234	91 192	0.5	0.5	0.987
Tebuthiuron	229	172 116	0.9	1.0	1.000
Teflubenzuron	381	158 141	10.0	9.0	0.981
Terbufos	289	57 103	12.0	10.0	0.976
Terbumeton	226	170 114	5.0	5.0	1.000
Terbuthylazine	230	174 132	0.1	0.5	0.999
Terbutryn	242	186 71	5.0	2.0	1.000
Tetrachlorvinphos	365	127 239	1.0	5.0	0.999
Thiabendazole	202	175 131	6.0	1.0	0.999
Thiacloprid	253	126 186	3.0	1.0	0.998
Thiamethoxam	292	211 181	5.0	8.0	0.990

Continued

Compound	Precursor ion	Product ions	Pepper LOD (ppb)	Tomato LOD (ppb)	r^2
Thifensulfuron-methyl	388	167 141	0.9	1.0	0.998
Thiocyclam	182	137 73	54.0	54.0	0.986
Thiodicarb	355	88 163	5.0	1.0	0.980
Thiofanox	241	184 57	5.0	10.0	0.987
Thiophanate-methyl	343	151 311	10.0	1.0	0.999
Tolclofos-methyl	301	125 269	6.0	10.0	0.999
Tolyfluanid	347	137 238	10.0	1.0	0.999
Triadimefon	294	69 197	1.0	1.0	0.998
Triadimenol	296	70 227	10.0	1.0	0.976
Triasulfuron	402	167 141	2.0	0.5	0.991
Triazophos	314	162 286	0.7	1.0	0.984
Tribenuron-methyl	396	155 181	100.0	10.0	0.981
Trichlorfon	257	109 221	10.0	10.0	0.997
Triclocarban	315	162 128	1.0	1.0	0.998
Tricyclazole	190	163 136	1.0	1.0	0.998
Trietazine	230	132 202	2.0	0.8	1.000
Trifloxystrobin	409	186 206	0.5	0.5	0.997
Triflumizole	346	278 73	4.0	1.0	0.974
Triflumuron	359	156 139	4.0	1.0	0.999
Triflusulfuron-methyl	493	264 238	4.0	1.0	0.990
Vamidothion	288	146 118	0.8	2.0	0.998

Table 1B. Compounds Tested With Low Sensitivity or Poor Chromatography on SB C-18

	Precursor	Product ions	Solvent LOD (pg)	Reason
Acetochlor	270	148 224	10	Poor chromatography on SB C-18
Acibenzolar-S-methyl	211	136 91	50	Outside window
Alachlor	270	162 238	10	Poor chromatography on SB C-18
Aldoxycarb	223	149 177	50	Interference
Anilazine	275	153 178	1	Outside window
Azinphos-ethyl	346	160 132	1	Outside window
Benfuracarb	411	195 252	1.0	Outside window
Bromoxynil	278	199 223	>100	Poor sensitivity
Chlorotoluron	213	72 140	20	Outside window
Ethoxyquin	218	174 148	>100	Poor chromatography
Fenpropidin	274	147 57	100	Poor chromatography
Itraconazole	705	450 404	***	No qualifier ion
Methiocarb sulfone	258	122 217	***	No qualifier ion
Nicotine	163	130 132	***	Poor ionization
Phosphamidon	300	129 153	100	Outside window
Propargite	373 Na	81 57	>100	Poor sensitivity
Pyrifenox	295	93 263	>100	Poor sensitivity
Spinosad A	732.4	142 99	20	Not eluted from SB C-18
Spinosad D	746.4	558 142	100	Not eluted from SB C-18
Spiroxamine	298	144 100	>100	Degraded standard
Terbacil	217	161 144	>100	Poor sensitivity

The MRM transitions used a dwell time of 10 milliseconds (msec). Eight different time segments were recorded in the chromatographic run, each segment containing approximately 50 pesticides. It was necessary to overlap pesticides at each boundary of the time segment in order to monitor compounds that may elute at the exact moment of the time segment boundary. Figure 1 shows the chromatogram corresponding to 100 parts per billion (ppb) standard on column for all the 301 compounds studied. Extracted ion chromatograms are overlaid for each one of the target analytes according to their respective protonated molecule and product-ion MRM transitions.

Application to Vegetable Matrices

To confirm the suitability of the method for analysis of real samples, matrix-matched standards were analyzed in two different matrices (green pepper and tomato) and compared with solvent at six concentrations (0.1, 0.5, 1.0, 10.0, 50.0, and 100 ng/mL or ppb concentrations). Figure 2 shows an example standard curve for diazinon in the pepper matrix. The r^2 values are shown in Table 1A for the pepper matrix; similar values were found for solvent and tomato matrix. The compounds gave linear results with excellent sensitivity over more than two orders of magnitude, with r^2 values of 0.99 or greater for the majority of compounds and LODs of 1 to 10 picograms (pg) for 150 of the compounds and from 10 to 100 pg for 140 compounds. There were 11 compounds that poorly ionized or gave poor chromatography and did not respond with sufficient signal to reach the 0.010 mg/kg level. These compounds are shown in Table 1B.

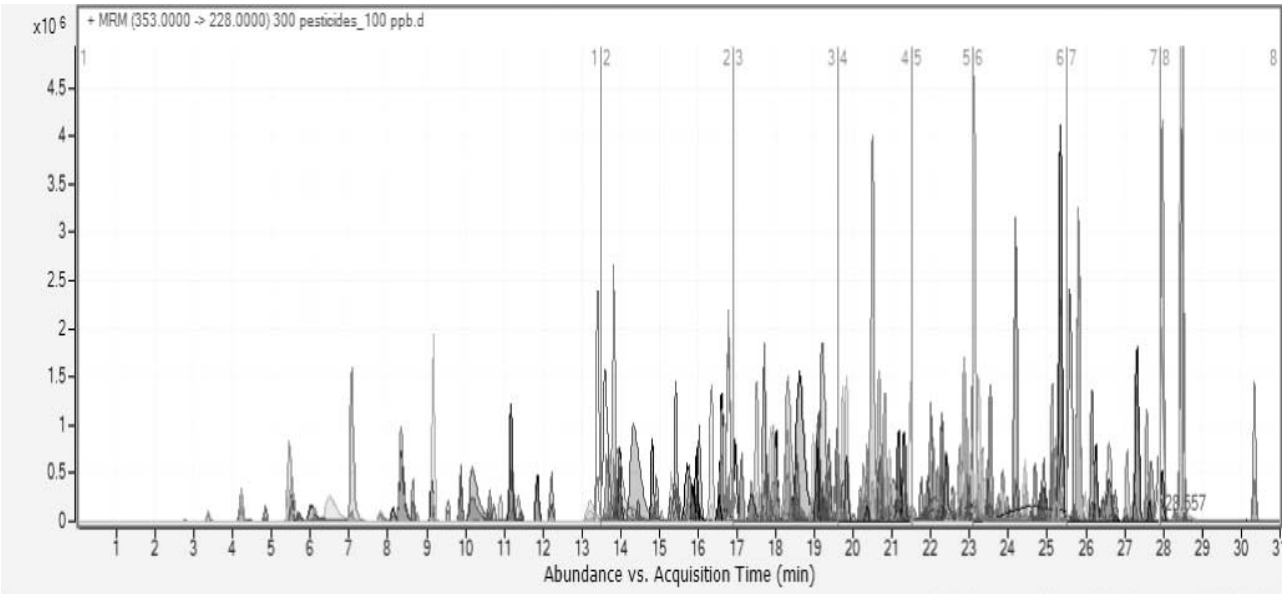

Figure 1. Product ion chromatogram (MRM) for 301 pesticides with a concentration of 100 ppb standard, which also shows the eight time segments.

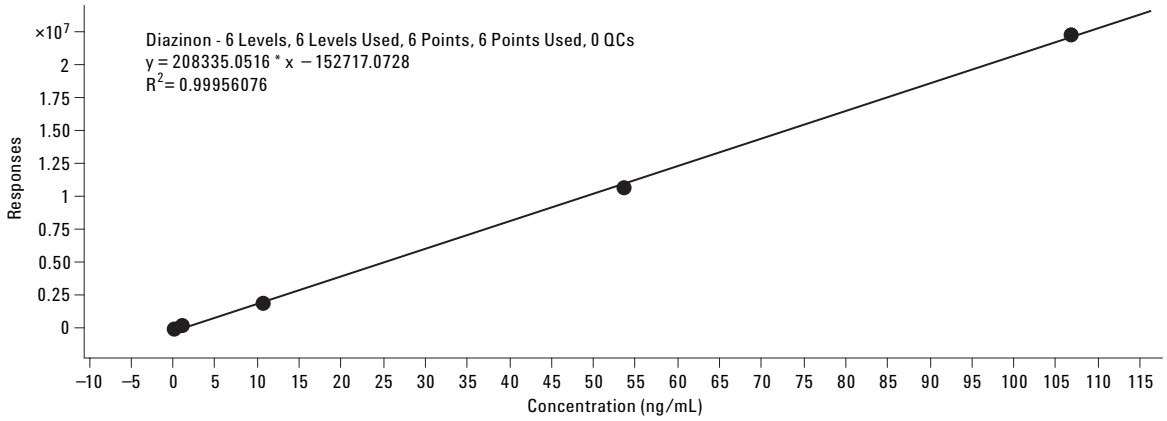

Figure 2. Calibration curve for diazinon in pepper using a six-point curve from 0.1 to 100 ng/mL (ppb) using a linear fit with no origin treatment.

Figure 3 shows the ion ratios qualifying for diazinon in an extract of green pepper spiked with the pesticide mix at 0.010 µg/g (100 pg on column). The *m/z* 169 ion was used for quantification and the *m/z* 153 ion was used as the qualifier ion, with a window set at ± 20% for the ion ratios. As shown in Figure 3 in the two ion profiles, diazinon was easily identified in this complex matrix due to the selectivity of the MRM transitions and instrument sensitivity. In general, the LODs for the 301-pesticide mix met the requirements regarding the MRL's imposed by the existing European regulations.

Furthermore, the use of 1.8-micron packing resulted in sharp chromatographic peaks of 5 to 10 seconds in width. Thus, it was important to use fast dwell times of 10 msec in order to keep the quantitation results shown in Table 1A. Finally, the analysis for repeatability of the instrument for the quantifying ion gave a relative standard deviation for five repeats of 6% (median RSD) and a mean RSD of 6.7%. These values were determined at the 0.1 mg/Kg level (100 ppb).

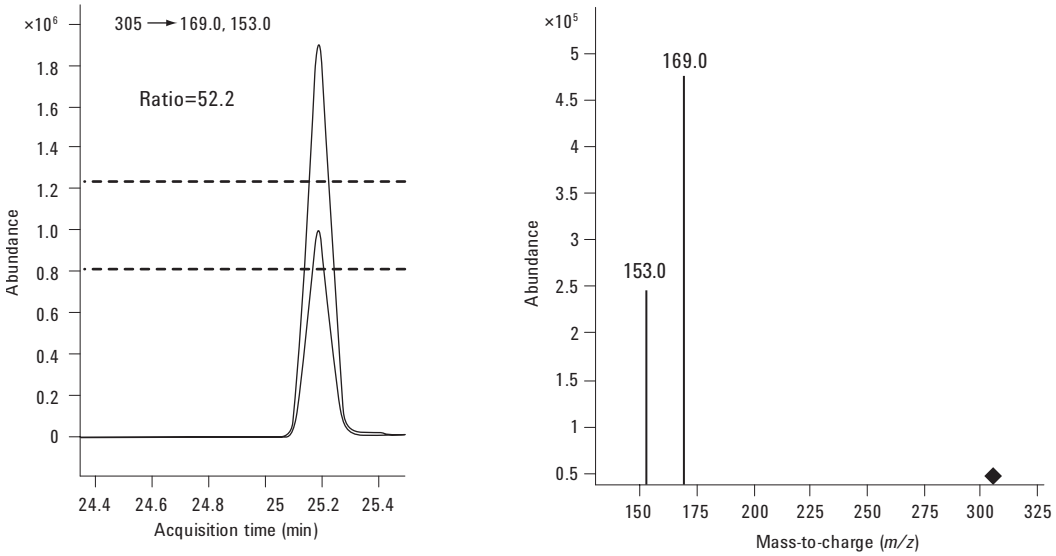

Figure 3. Shows the ion ratios for qualifier ion and the quantifying ion for diazinon in the pepper matrix.

Conclusions

The results of this study show that the Agilent 6410 Triple Quadrupole is a robust, sensitive, and repeatable instrument for the study of pesticides in food, such as vegetable extracts, using high-throughput methods. The LOD for the instrument was in the 1 to 10 pg range for 50% of the compounds and 100 pg for 90% of the compounds studied. These LODs included both the quantifying ion and the qualifying ion, which is quite important for identification. These LODs are sensitive given that the segments contained 100 transitions, which is sufficient to analyze approximately 30 to 40 compounds per segment (with an overlap of 5 to 10 compounds per segment, a minimum if good reproducibility of the method is to be obtained).

The Agilent 6410 Triple Quadrupole was capable of reaching a LOD of 0.010 mg/kg (ppm) for at least 90% of the pesticides monitored in this study using the two product ion criteria for confirmation, and a 10-µL injection, which is a typical injection volume. This MRL is the baby food limit, the limit for banned pesticides, and the typical requirement of a newly purchased LC/MS/MS system by environmental and food scientists who work on real food matrices.

References

1. Imma Ferrer, E. M. Thurman, Y. Fang, P. Zavitsanos, and J. A. Zweigenbaum, "Multiresidue Analysis of 100 Pesticides in Food Samples by LC/Triple Quadrupole Mass Spectrometry," Agilent Technologies publication 5989-5469EN, August 2006
2. M. Anastassiades, S. J. Lehotay, D. Stajnbaher, and F. J. Schenck, *J. AOAC International*, 86 (2003) 412–431.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Published in the USA
November 5, 2008
5989-8614EN

Agilent Technologies