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ARTICLE

Applications of LC/ESI-MS/MS and UHPLC QqTOF MS for the Determination of 148 Pesticides in Berries†

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Applications of liquid chromatography electrospray ionization tandem mass spectrometry (LC/ESI-MS/MS) and ultrahigh-pressure liquid chromatography electrospray ionization quadrupole time-of-flight mass spectrometry (UHPLC QqTOF MS) for the determination of 148 pesticides in berry fruits are presented in this study. Pesticides were extracted from berries using a procedure known as QuEChERS (quick, easy, cheap, effective, rugged, and safe). Quantification, with an analytical range from 5 to 500 μg/kg, was achieved using matrix-matched standard calibration curves with isotopically labeled standards or a chemical analogue as internal standards. The method performance parameters, which included overall recovery, intermediate precision, and measurement uncertainty, were evaluated according to a designed experiment, that is, the nested design. For LC/ESI-MS/MS, 95% of the pesticides studied had recoveries between 81 and 110%, 98% of the pesticides had intermediate precision of $\leq$20%, and 95% of the pesticides showed measurement uncertainty of $\leq$40%. Compared to LC/ESI-MS/MS, UHPLC QqTOF MS showed a relatively poor repeatability and large measurement uncertainty. Ninety-five percent of the pesticides analyzed by UHPLC QqTOF MS had recoveries between 81 and 110%, 86% of the pesticides had intermediate precision of $\leq$20%, and 83% of the pesticides showed measurement uncertainty of $\leq$40%. LC/ESI-MS/MS proved to be the first choice for quantification or pretarget analysis due to its superior sensitivity and good repeatability. UHPLC QqTOF MS provided accurate mass measurement and was an ideal tool for post-target screening and confirmation.

KEYWORDS: LC/ESI-MS/MS; UHPLC QqTOF; pesticides; berries; measurement uncertainty

INTRODUCTION

Berries are rich in biologically active compounds such as flavonoids, anthocyanins, phenolic acids, stilbens, tannins, carotenoids, and vitamin C (*1*, *2*). Flavonoids, anthocyanins, etc., present in berries have been shown to exhibit antioxidant, anti-inflammatory, anticarcinogenic, and estrogenic activities and to help prevent coronary heart disease (*1*−*4*). Therefore, berries, fresh or dried, have been considered to be a type of popular functional food for people's health benefits. On the other hand, pesticides are possibly used in various combinations at different stages of cultivation and during postharvest storage to protect crops against a range of pests and fungi and/or to provide quality preservation. Pesticide residues in berries might pose a risk for human health due to their potential subacute and chronic toxicity. Many foods have been tested for pesticide residues under the Canadian National Chemical Residues Monitoring Program and Food Safety Action Plan. The Canadian Food Inspection Agency requires both sensitive and confirmatory methods to test pesticides in berries and other fruits and vegetables for monitoring programs and for risk assessment of consumer exposure to pesticides.

GC and LC mass spectrometers are essential means for the determination of pesticides in foods. Their applications have been extensively reviewed elsewhere (*5*−*9*). The application of LC/ESI-MS/MS for LC-amenable pesticide analysis has been profound in the past few years because of its high sensitivity and good repeatability for trace level detection and quantification. Meanwhile, UHPLC QqTOF MS has also been recognized as an emerging technique to analyze pesticide residues in foods. It offers medium-range high-resolution, accurate mass measurement, excellent full-scan sensitivity, and complete mass spectral information, therefore making QqTOF complementary to other quadrupole and ion trap mass spectrometers for identification and quantification. In this paper, we present a study on applications of both LC/ESI-MS/MS and UPHLC QqTOF MS for the determination of 148 pesticides in berry fruits. The methods were validated according to a designed experiment, that is, a nested design (*10*−*12*), to evaluate its performance characteristics including overall recovery, intermediate precision, and measurement uncertainty. The method performances of the two techniques were compared. LC/ESI-MS/MS proved to be the first choice for quantification or pretarget analysis due to its superior sensitivity and good repeatability. UHPLC QqTOF MS

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provided accurate mass measurement and served as a practical tool for post-target screening and confirmation.

MATERIALS AND METHODS

Materials and Reagents. Six different berries or berry fruits including strawberries, Saskatoon berries, blackberries, raspberries, blueberries, and cherries were obtained from local markets. The berry samples were homogenized using a food processor, and 2 kg of each sample was prepared. Ammonium acetate (reagent grade), [Glu^1]-fibrinopeptide B (F-3261), leucine enkephalin (L-9133), magnesium sulfate anhydrous ($MgSO_4$), LC-MS water (Chromasolv, 1 L), and LC-MS acetonitrile (Chromasolv, 2.5 L) were purchased from Sigma-Aldrich Corp. (Canada). Acetic acid (glacial acetic acid, reagent grade, 99.7%), acetonitrile (distilled in glass), and methanol (distilled in glass) were obtained from Caledon Laboratories Ltd. (Canada). Water used for reagent preparation was Milli-Q water, 18 MΩ·cm from Milli-Q Reagent Water System (Millipore Corp., USA). Primary secondary amine (PSA, Bondesil PSA, 40 μm) was purchased from Varian Inc. (Canada). Sodium acetate anhydrous (ACS reagent) was from Thermo Fisher Scientific Inc. (Canada). Pesticide standards (**Table 1**, column 1) were obtained from EQ Laboratories Inc. (USA), Riedel-de Haen AG (Germany), or Chem Service (USA). Internal standards carbendazim-d_4 and carbofuran-d_3 were purchased from EQ Laboratories Inc. (USA), and thiabendazole-d_4 was from Chemical Synthesis Services (Northern Ireland). LC vials were Mini-UniPrep syringeless filter devices with polypropylene housing and PVDF 0.45 μm membrane (Whatman Inc., USA).

Preparation of Standard Solutions. Individual pesticide standard stock solutions were generally prepared at a concentration of 4000.0 μg/mL in methanol. Due to their poor solubility in methanol, carbendazim was prepared at 200.0 μg/mL and a few of pesticides were prepared at 1000.0 or 2000.0 μg/mL (**Table 1**, column 1). Intermediate pesticide standard mix working solutions were prepared at two levels, that is, 10.0 and 15.0 μg/mL, from stock solutions. Stock and intermediate solutions were stored at −20 °C. A six-level pesticide standard mix working solution was prepared by transferring 0.1, 0.5, 2.0, 4.0, 6.0, and 10.0 mL of 10.0 μg/mL intermediate working solution into six separate 50 mL volumetric flasks and making up to volume with methanol to prepare 0.02, 0.1, 0.4, 0.8, 1.2, and 2.0 μg/mL six-level standard solutions for constructing matrix-matched standard calibration curves. Four-level sample spike pesticide standard working solutions were prepared by transferring 1.0, 9.0, 24.0, and 40.0 mL of 15.0 μg/mL intermediate working solution into separate 50 mL volumetric flasks and making up to volume with methanol to prepare 0.3, 2.7, 7.2, and 12.0 μg/mL four-level standard solutions for sample spikes. Internal standard working solutions (2.0 and 100.0 μg/mL) including carbofuran-d_3, carbendazim-d_4, and thiabendazole-d_4 were prepared in a mixture of acetonitrile and methanol (50:50, v/v). All working solutions were stored at 4 °C.

LC/ESI-MS/MS Parameters. The LC/ESI-MS/MS system utilized was an Agilent 1200 SL (Agilent, Germany) coupled with an API 5000 LC/MS/MS System (Applied Biosystem, Canada). The system was controlled using Analyst 1.42 software.

LC Profile. LC mobile phase A was acetonitrile, and mobile phase B was 10 mM ammonium acetate with 2% acetonitrile in water. The LC analytical column was an Atlantis dC_{18} 100 × 2.1 mm, 3 μm column (Waters, USA), and the guard column was an Atlantis dC_{18} 10 × 2.1 mm, 3 μm column (Waters, USA). The gradient profile consisted of 0−7 min, 8−90% A; 7−25 min, 90% A; 25−28 min, 90−100% A; 28−28.1 min, 100−8% A; and 28.1−35 min, 8% A. Flow rates were controlled as 0−25 min, 0.2 mL/min; 25−28 min, 0.2−0.3 mL/min; 28−28.1 min, 0.3 mL/min; and 28.1−35 min, 0.3−0.2 mL/min. Column oven temperature was set at 35 °C, and autosampler temperature was set at 5 °C. Injection volume was 5 μL, and the total run-time was 35 min.

MS/MS Conditions. Ion source was TurboIonSpray or Turbo V electrospray ion source in positive mode. General mass spectrometric parameters were set as collision gas, 7 (arbitrary units); curtain gas (CUR), 20 psi; ion source gas 1 (GS1), 50 psi; ion source gas 2 (GS2), 50 psi; temperature (TEM), 500 °C; ion spray voltage (IS), 5500 V; and interface heater (ihe), on. Pause time between mass ranges was 5 ms. Specific mass spectrometric parameters such as dwell time, declustering potential (DP), entrance potential (EP), collision energy (CE), collision cell exit potential (CXP), and multiple reaction monitoring transitions (MRM or Q1 and Q3) are listed in **Table 1**. All MRMs were acquired in one experiment period. Parameters such as DP, EP, CE, and CXP were optimized using the Quantitative Optimization bundled with the Analyst software by infusing each individual pesticide standard (10 or 50 μg/L) to the mass spectrometer. The syringe pump (Harvard Apparatus, USA) flow rate was set at 10 μL/min for infusion.

UHPLC QqTOF Parameters. The UHPLC QqTOF system utilized was a Waters Acquity Ultra-Performance liquid chromatograph coupled with Q-Tof Premier, that is, a quadrupole and orthogonal acceleration time-of-flight tandem mass spectrometer utilizing electrospray ionization interface (UPLC QqTOF) (Waters, Milford, MA). The system was controlled using MassLynx 4.1 software.

UHPLC Profile. UHPLC mobile phase A was acetonitrile, and mobile phase B was 10 mM ammonium acetate in water. The UHPLC column utilized was an Acquity UPLC BEH C_{18} 100 mm × 2.1 mm, 1.7 μm column (Waters, USA). The gradient profile consisted of 0−9 min, 8−95% A; 9−11 min, 95−100% A; 11−12 min, 100% A; and 12−14 min, 8% A. Flow rate was 0.4 mL/min. Column oven temperature was set at 45 °C, and autosampler temperature was set at 5 °C. Injection volume was 10 μL, and the total run-time was 14 min.

QqTOF MS Conditions. The Q-Tof Premier can be operated in TOF MS mode (full-scan or MS scan only) or TOF MS/MS mode (product-ion scan or MS/MS scan only). Therefore, the QqTOF could be utilized as either a simple TOF instrument (TOF MS) or a tandem TOF mass spectrometer (TOF MS/MS). The former has the advantage of being able to capture all ions from the ESI source, and the latter is somewhat selective because it uses the first quadrupole as a mass filter to select the precursor ion of a target analyte and to record the product ion spectrum by the TOF analyzer after breakdown in the collision cell (*13*). In the current study, the Q-Tof Premier was operated in TOF MS mode only. Electrospray positive ion mode was utilized with the capillary voltage set at 3.20 kV. Source temperature was set at 120 °C, and desolvation temperature was 300 °C. Nebulizer nitrogen flow rate was regulated at 50 L/h, and desolvation nitrogen gas flow rate was set at 800 L/h. Collision gas argon pressure was regulated at 5.3×10^{-3} mbar, and collision energy was set at 5 eV when QqTOF was operated in full-scan mode. Sampling cone voltage was 20 V. LM and HM resolutions were set at 4.7 and 15, respectively. Mass range was from m/z 50 to 950. TOF resolution was about 15000 fwhm that was measured with [Glu^1]-fibrinopeptide B at $[M + 2H]^{2+} = 785.8426$ in W-mode. Lock mass reference was leucine enkephalin ($[M + H]^+ = 556.2771$, 4 μg/mL in a mixture of acetonitrile and water (2 + 8, v/v)), which was infused through the LockSpray probe at 5 μL/min. Data were acquired in centroid format with dynamic range enhancement (DRE) enabled for a dynamic range of 2 or 3 orders of magnitude for quantification under W-mode.

Sample Extraction and Cleanup Procedures. Sample extraction and cleanup procedures followed the buffered QuEChERS method (*14*−*16*) or AOAC Official Method 2007.01 (*17*). Berry samples (15.0 g/sample) were weighed into individual 50 mL polypropylene centrifuge tubes (VWR International, Canada). Five hundred microliters per four-level sample spike pesticide standard working solution was added into four centrifuge tubes to provide 10.0, 90.0, 240.0, and 400.0 μg/kg of standards equivalent in samples, followed by the addition of 15 μL of 100.0 μg/mL internal calibration standard working solution (100.0 μg/kg equivalent in samples). Then, 15 mL of acetonitrile/acetic acid (99 + 1, v/v) and 1.5 g of sodium acetate anhydrous were added to each sample, and after mixing, 6.0 g of magnesium sulfate anhydrous was added. The centrifuge tubes were capped and shaken for 45 s by hand, followed by centrifugation at 3000 rpm (∼2100*g*) for 3 min using an Allegra 6 centrifuge (Beckman Coulter Inc., USA). Supernatants were transferred (9 mL/sample) into individual 15 mL polypropylene centrifuge tubes (VWR International, Canada) that contained 0.6 g of PSA and 1.8 g of $MgSO_4$ per tube. The centrifuge tubes were capped and shaken for 45 s, and centrifuged at 3000 rpm (∼2100*g*) for 3 min. A 1 mL subsample of supernatants (1 g sample/mL) was transferred into individual 5 mL Pyrex brand centrifuge tubes, precalibrated with 1 mL volume accuracy (VWR International, Canada). Each of the sample extracts was evaporated to 0.1−0.2 mL using an N-EVAP nitrogen evaporator (Organomation Associates Inc., USA) at 30 °C under a stream of nitrogen. The extracts were then made up to 0.5 mL with methanol, vortexed for 30 s, and then

Table 1. LC/ESI-MS/MS Parameters and Method Performance Results

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
acetochlor	$[M + H]^+$	270	224	5	66	10	15	15	14		9.58	16 (5)	101.9	6.5	13.3
		270	148	5	66	10	29		20						
		270	133	5	66	10	47		16						
aclonifen[e]	$[M + H]^+$	265	182	5	101	10	41	41	24		9.78	**10** (**25**)	96.6	16.0	32.8
		265	218	5	101	10	35		22						
		265	194	5	101	10	27		18						
aldicarb	$[M + NH_4]^+$	208	116	5	26	10	13	13	16		7.21	99 (5)	99.0	13.1	31.0
		208	89	5	26	10	25		16						
		208	70	5	26	10	21		14						
aldicarb sulfone	$[M + NH_4]^+$	240	86	5	51	10	31	31	20		5.08	49 (5)	100.5	8.8	18.8
		240	148	5	51	10	21		14						
		240	76	5	51	10	19		30						
aldicarb sulfoxide	$[M + H]^+$	207	132	5	86	10	11	11	16		4.26	48 (5)	97.9	11.5	23.4
		207	89	5	86	10	21		14						
		207	41	5	86	10	49		18						
azaconazole	$[M + H]^+$	300	159	5	76	10	41	**27**	10		8.08	35 (5)	99.4	9.0	18.7
		300	231	5	76	10	25		14						
		300	89	5	76	10	97		34						
benoxacor	$[M + H]^+$	260	149	5	76	10	29	29	22	E	9.05	4 (5)	100.9	11.4	25.1
		260	134	5	76	10	43		12						
		260	120	5	76	10	49		14						
bitertanol	$[M + H]^+$	338	99	5	61	10	23	23	12		9.34	22 (5)	101.4	8.0	16.1
		338	70	5	61	10	31		26						
		338	43	5	61	10	59		16						
bromuconazole	$[M + H]^+$	376	159	5	91	10	37	37	10		9.00	15 (5)	101.5	7.3	14.8
		376	70	5	91	10	31		28						
		376	89	5	91	10	123		12						
butafenacil	$[M + NH_4]^+$	492	331	5	46	10	33	**15**	34		9.49	44 (5)	103.7	10.2	20.8
		492	180	5	46	10	61		18						
		492	349	5	46	10	23		18						
butocarboxim sulfoxide	$[M + H]^+$	207	75	5	86	10	21	21	30		3.82	29 (5)	96.1	8.0	16.8
		207	132	5	86	10	13		6						
		207	43	5	86	10	31		16						
cadusafos	$[M + H]^+$	271	159	5	81	10	21	**12**	10		10.16	43 (5)	102.6	7.4	15.7
		271	131	5	81	10	33		16						
		271	97	5	81	10	49		12						
carbaryl	$[M + H]^+$	202	145	5	91	10	17	17	18		8.04	75 (5)	103.2	8.2	18.0
		202	127	5	91	10	43		16						
		202	117	5	91	10	33		16						
carbendazim	$[M + H]^+$	192	160	5	106	10	25	**13**	16	S	6.29	413 (5)	99.2	7.7	16.3
		192	132	5	106	10	45		18						
		192	105	5	106	10	49		14						
carbendazim-d_4 (IS)	$[M + H]^+$	196	164	5	66	10	29	**21**	22		6.24				
carbofuran	$[M + H]^+$	222	165	5	81	10	19		20						
		222	**123**	5	81	10	31	**20**	14		7.84	59 (5)	103.4	8.2	16.9
		222	55	5	81	10	37		20						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
carbofuran-d_3 (IS)	$[M + H]^+$	225	123	5	96	10	33	33	14		7.79				
carfentrazone-ethyl	$[M + H]^+$	412	346	5	141	10	33	**29**	18		9.68	110 (5)	103.1	7.3	15.1
		412	366	5	141	10	25		28						
		412	384	5	141	10	21		30						
chlorbromuron	$[M + H]^+$	293	125	5	101	10	51	51	16		9.27	8 (5)	102.0	13.4	27.6
		293	63	5	101	10	101		12						
		293	62	5	101	10	23		12						
chloridazon[i]	$[M + H]^+$	222	51	5	116	10	93	93	20		6.49	55 (5)	99.2	8.1	17.2
		222	65	5	116	10	53		14						
		222	104	5	116	10	37		12						
chlorimuron-ethyl	$[M + H]^+$	415	186	5	86	10	29	**15**	24	E	6.49	59 (5)	98.2	14.4	28.9
		415	185	5	86	10	37		10						
		415	83	5	86	10	65		16						
chloroxuron	$[M + H]^+$	291	72	5	106	10	31	**19**	16		8.91	75 (5)	103.5	7.4	16.1
		291	46	5	106	10	49		20						
		291	31	5	106	10	109		12						
chlorthiamid[e,i]	$[M + H]^+$	206	189	5	66	10	27	27	26	E	7.76	**9** (**25**)	**75.4**	17.7	**67.2**
		206	119	5	66	10	61		16						
		206	154	5	66	10	49		20						
chlortoluron	$[M + H]^+$	213	72	5	66	10	37	**15**	14		7.94	50 (5)	103.8	8.3	17.5
		213	46	5	66	10	29		20						
		213	56	5	66	10	71		6						
clodinafop-propargyl	$[M + H]^+$	350	266	5	121	10	23	**15**	26		9.83	94 (5)	104.7	8.1	16.5
		350	91	5	121	10	43		8						
		350	238	5	121	10	35		24						
cloquintocet-mexyl	$[M + H]^+$	336	238	5	76	10	25	**11**	14		10.70	46 (5)	100.9	9.1	18.3
		336	192	5	76	10	41		22						
		336	179	5	76	10	45		18						
clothianidin	$[M + H]^+$	250	169	5	61	10	21	21	16	S	6.20	19 (5)	95.7	10.8	22.6
		250	132	5	61	10	27		22						
		250	113	5	61	10	37		46						
cyanofenphos	$[M + H]^+$	304	276	5	51	10	19	19	30		10.07	5 (5)	102.9	12.3	24.7
		304	157	5	51	10	33		24						
		304	120	5	51	10	31		10						
cycloxydim	$[M + H]^+$	326	280	5	111	10	21	21	32	S	9.15	34 (5)	**116.0**	9.5	24.7
		326	180	5	111	10	29		26						
		326	101	5	111	10	33		22						
cycluron	$[M + H]^+$	199	89	5	86	10	23	**15**	10		7.99	15 (5)	103.9	9.6	20.5
		199	72	5	86	10	33		12						
		199	69	5	86	10	31		16						
demeton-*S*-methyl sulfone[i]	$[M + H]^+$	263	169	5	111	10	23	23	10		5.57	97 (5)	100.6	9.0	18.5
		263	127	5	111	10	37		14						
		263	109	5	111	10	41		12						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
demeton-*S*-methyl sulfoxide[i]	$[M + H]^+$	247	169	5	86	10	21	**13**	4		4.89	71 (5)	93.8	8.9	20.0
		247	127	5	86	10	37		16						
		247	105	5	86	10	21		12						
desmedipham	$[M + H]^+$	301	182	5	116	10	15	**19**	10	E	8.71	67 (5)	100.8	8.2	16.5
		301	136	5	116	10	35		8						
		301	65	5	116	10	77		26						
diclocymet	$[M + H]^+$	313	173	5	116	10	25	25	24		9.54	8 (5)	104.1	11.5	24.1
		313	137	5	116	10	47		12						
		313	102	5	116	10	63		12						
diethofencarb	$[M + H]^+$	268	226	5	61	10	17	**23**	14		8.91	49 (5)	103.4	6.8	14.3
		268	124	5	61	10	45		14						
		268	152	5	61	10	31		20						
difenoconazole	$[M + H]^+$	406	251	5	136	10	39	**22**	26	S	9.85	21 (5)	101.1	8.0	16.3
		406	337	5	136	10	25		26						
		406	188	5	136	10	49		26						
dimethametryn	$[M + H]^+$	256	186	5	121	10	31		30						
		256	**91**	5	121	10	43	**31**	14		9.58	63 (5)	104.2	9.1	18.2
		256	96	5	121	10	45		12						
dimethomorph	$[M + H]^+$	388	301	5	76	10	31	**17**	16		8.57	41 (5)	100.9	9.9	19.9
		388	165	5	76	10	45		10						
		388	152	5	76	10	99		20						
diniconazole	$[M + H]^+$	326	70	5	136	10	37	**31**	28		9.58	73 (5)	102.5	8.3	16.6
		326	43	5	136	10	105		16						
		326	159	5	136	10	47		20						
dioxacarb	$[M + H]^+$	224	123	5	96	10	25	25	16		6.54	205 (5)	99.9	8.8	17.9
		224	167	5	96	10	15		10						
		224	95	5	96	10	39		12						
dipropetryn	$[M + H]^+$	256	144	5	101	10	41		14						
		256	**214**	5	101	10	29	**17**	22		9.73	54 (5)	103.0	9.2	18.4
		256	102	5	101	10	53		12						
diuron	$[M + H]^+$	233	72	5	56	10	35	35	28		8.18	20 (5)	103.1	7.5	15.0
		233	133	5	56	10	55		18						
		233	74	5	56	10	107		14						
dodemorph	$[M + H]^+$	282	116	5	106	10	31	**21**	16	E	18.70	31 (5)	101.4	7.8	17.0
		282	98	5	106	10	39		14						
		282	41	5	106	10	73		16						
emamectin B_{1a}	$[M + H]^+$	886	158	5	41	10	47	**33**	18	E	**15.49**	7 (5)	99.5	7.4	15.5
		886	82	5	41	10	49		10						
		886	126	5	41	10	49		14						
epoxiconazole	$[M + H]^+$	330	121	5	91	10	29	**19**	24		9.05	22 (5)	101.9	7.4	15.1
		330	123	5	91	10	31		8						
		330	91	5	91	10	49		20						
ethiofencarb	$[M + H]^+$	226	107	5	86	10	25	25	14		8.18	45 (5)	101.7	10.0	21.3
		226	164	5	86	10	13		10						
		226	77	5	86	10	49		16						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
ethiofencarb sulfone	$[M + NH_4]^+$	275	107	5	76	10	27		14						
		275	**201**	5	76	10	17	17	0		6.20	29 (5)	101.1	8.7	18.1
		275	77	5	76	10	79		32						
ethiofencarb sulfoxide	$[M + H]^+$	242	107	5	76	10	29	**15**	18		5.62	72 (5)	96.7	11.0	22.2
		242	77	5	76	10	67		32						
		242	79	5	76	10	53		32						
ethirimol[i]	$[M + H]^+$	210	140	5	56	10	33	**21**	20		7.02	24 (5)	94.6	11.0	22.5
		210	98	5	56	10	39		14						
		210	43	5	56	10	71		16						
ethoprop	$[M + H]^+$	243	131	5	86	10	29	**23**	14		9.25	42 (5)	101.2	6.7	15.9
		243	97	5	86	10	51		12						
		243	43	5	86	10	41		10						
etofenprox	$[M + NH_4]^+$	394	177	5	31	10	21	**18**	18	S	12.83	18 (5)	98.1	18.9	38.9
		394	359	5	31	10	17		26						
		394	107	5	31	10	65		12						
etoxazole	$[M + H]^+$	360	141	5	101	10	49	**22**	14	S	11.47	32 (5)	102.2	7.7	15.5
		360	304	5	101	10	27		34						
		360	57	5	101	10	43		12						
fenamidone	$[M + H]^+$	312	92	5	81	10	33	**19**	10		9.00	63 (5)	102.2	8.3	16.8
		312	236	5	81	10	25		20						
		312	65	5	81	10	49		14						
fenazaquin	$[M + H]^+$	307	57	5	91	10	35	**23**	14	S	11.76	43 (5)	101.6	8.2	16.5
		307	161	5	91	10	25		18						
		307	91	5	91	10	93		20						
fenhexamid	$[M + H]^+$	302	97	5	106	10	33	33	20		9.05	17 (5)	100.8	8.4	16.8
		302	55	5	106	10	61		14						
		302	143	5	106	10	47		14						
fenoxanil	$[M + NH_4]^+$	346	302	5	36	10	23	23	28		9.73	53 (5)	104.9	9.7	19.9
		346	86	5	36	10	39		36						
		346	189	5	36	10	43		20						
fenpropidin	$[M + H]^+$	274	147	5	76	10	39	**29**	8		**12.45**	224 (5)	103.4	10.6	23.1
		274	117	5	76	10	73		16						
		274	86	5	76	10	41		10						
fenpropimorph	$[M + H]^+$	304	147	5	76	10	45	**28**	14	E	13.65	17 (5)	103.2	8.8	18.3
		304	117	5	76	10	81		16						
		304	91	5	76	10	113		12						
fenpyroximate[i]	$[M + H]^+$	422	366	5	126	10	27	**9**	36		11.42	47 (5)	102.3	8.8	17.6
		422	135	5	126	10	45		20						
		422	107	5	126	10	81		12						
fentrazamide	$[M + H]^+$	350	154	5	111	10	17	17	16		10.07	58 (5)	100.7	15.6	31.3
		350	83	5	111	10	35		16						
		350	197	5	111	10	13		24						
fluazifop-butyl	$[M + H]^+$	384	282	5	121	10	31	**17**	18		10.79	74 (5)	102.4	9.3	18.7
		384	328	5	121	10	25		30						
		384	91	5	121	10	49		10						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
flucarbazone	$[M + NH_4]^+$	414	130	5	46	10	35	35	18	E	5.56	36 (5)	**59.4**	**27.1**	**61.2**
		414	115	5	46	10	49		18						
		414	73	5	46	10	49		30						
flutolanil	$[M + H]^+$	324	262	5	111	10	27	**17**	14		9.39	63 (5)	103.1	7.6	15.2
		324	242	5	111	10	35		12						
		324	65	5	111	10	63		30						
flutriafol	$[M + H]^+$	302	70	5	56	10	27	**17**	28		7.89	103 (5)	100.5	9.4	19.0
		302	123	5	56	10	43		16						
		302	75	5	56	10	105		16						
forchlorfenuron	$[M + H]^+$	248	129	5	31	10	27	**18**	14	S	7.94	123 (5)	99.9	9.9	21.2
		248	93	5	31	10	49		18						
		248	111	5	31	10	47		14						
fosthiazate	$[M + H]^+$	284	104	5	86	10	33	**16**	24		7.99	58 (5)	101.5	8.1	16.8
		284	228	5	86	10	17		22						
		284	200	5	86	10	25		10						
fuberidazole	$[M + H]^+$	185	157	5	96	10	33	**19**	14		6.87	27 (5)	96.8	10.9	23.6
		185	156	5	96	10	43		22						
		185	65	5	96	10	49		14						
furathiocarb	$[M + H]^+$	383	195	5	121	10	29	**13**	18		10.79	82 (5)	104.3	9.1	18.4
		383	167	5	121	10	39		22						
		383	162	5	121	10	49		16						
haloxyfop	$[M + H]^+$	362	316	5	121	10	29	29	36		6.73	8 (5)	**55.7**	18.3	**46.6**
		362	91	5	121	10	43		16						
		362	288	5	121	10	39		28						
3-hydroxycarbofuran	$[M + NH_4]^+$	255	163	5	46	10	27		16						
		255	**220**	5	46	10	17	17	12		6.20	36 (5)	101.1	10.0	20.1
		255	181	5	46	10	23		18						
imazamethabenz-methyl	$[M + H]^+$	289	144	5	66	10	49	**30**	10		7.26	50 (5)	102.2	9.3	18.6
		289	86	5	66	10	33		18						
		289	229	5	66	10	29		22						
imidacloprid	$[M + H]^+$	256	209	5	81	10	25	25	24	S	6.34	21 (5)	99.4	8.9	18.1
		256	175	5	81	10	29		22						
		256	84	5	81	10	25		12						
indoxacarb[h]	$[M + H]^+$	528	249	5	141	10	25	25	28		10.16	32 (5)	105.3	8.6	18.6
		528	293	5	141	10	21		20						
		528	203	5	141	10	49		20						
iprovalicarb	$[M + H]^+$	321	119	5	91	10	35	**11**	16		8.86	195 (5)	101.8	8.4	17.9
		321	91	5	91	10	73		14						
		321	116	5	91	10	31		14						
isocarbamide	$[M + H]^+$	186	87	5	86	10	25	25	14	S	6.15	112 (5)	96.1	9.1	18.4
		186	44	5	86	10	49		18						
		186	130	5	86	10	19		14						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
isoprocarb	$[M + H]^+$	194	95	5	86	10	23	23	18	E	8.37	41 (5)	100.3	7.9	15.9
		194	137	5	86	10	13		14						
		194	77	5	86	10	49		32						
isoxathion	$[M + H]^+$	314	105	5	111	10	25	**15**	12		10.31	66 (5)	103.2	10.8	22.5
		314	286	5	111	10	15		16						
		314	115	5	111	10	47		16						
linuron[i]	$[M + H]^+$	249	160	5	101	10	27	27	16	E	9.18	3 (5)	101.1	10.3	21.7
		249	182	5	101	10	23		18						
		249	133	5	101	10	47		18						
mepanipyrim	$[M + H]^+$	224	106	5	91	10	37	**31**	12		9.39	68 (5)	103.6	8.3	17.0
		224	77	5	91	10	49		16						
		224	42	5	91	10	49		16						
mephosfolan	$[M + H]^+$	270	140	5	91	10	33	**21**	16		7.21	56 (5)	102.1	7.8	17.7
		270	75	5	91	10	29		30						
		270	60	5	91	10	69		14						
methabenzthiazuron	$[M + H]^+$	222	165	5	71	10	27		18						
		222	**150**	5	71	10	45	**37**	20		7.84	74 (5)	102.4	7.6	15.3
		222	124	5	71	10	45		28						
methidathion[i]	$[M + H]^+$	303	145	5	91	10	13	13	20		9.14	71 (5)	101.8	10.8	22.0
		303	85	5	91	10	31		18						
		303	58	5	91	10	47		26						
methiocarb	$[M + H]^+$	226	169	5	76	10	15	15	16		8.81	39 (5)	103.3	6.9	14.3
		226	121	5	76	10	27		20						
		226	122	5	76	10	33		16						
methiocarb sulfone	$[M + NH_4]^+$	275	122	5	46	10	35	35	16	E	6.87	57 (5)	103.8	8.4	20.2
		275	201	5	46	10	19		20						
		275	107	5	46	10	49		12						
methiocarb sulfoxide[i]	$[M + H]^+$	242	185	5	111	10	21	**10**	12	S	5.91	69 (5)	96.6	10.1	20.2
		242	122	5	111	10	39		14						
		242	170	5	111	10	35		14						
methomyl	$[M + H]^+$	163	88	5	41	10	15	15	10		5.42	39 (5)	100.2	11.0	22.7
		163	106	5	41	10	17		14						
		163	58	5	41	10	31		22						
methoxyfenozide	$[M + H]^+$	369	149	5	131	10	25	**19**	14		9.25	34 (5)	104.0	9.4	21.0
		369	313	5	131	10	13		32						
		369	91	5	131	10	65		22						
metolcarb	$[M + H]^+$	166	109	5	51	10	15	15	16		7.50	35 (5)	99.8	8.4	18.7
		166	94	5	51	10	45		16						
		166	65	5	51	10	59		30						
metoxuron	$[M + H]^+$	229	72	5	111	10	27	**15**	12		7.12	26 (5)	104.0	11.5	24.4
		229	46	5	111	10	33		18						
		229	56	5	111	10	71		12						
mexacarbate[i]	$[M + H]^+$	223	151	5	86	10	35	**20**	20		9.31	37 (5)	100.8	7.7	15.9
		223	166	5	86	10	23		22						
		223	136	5	86	10	53		18						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
molinate	$[M + H]^+$	188	126	5	41	10	21	21	18	E	9.29	22 (5)	99.2	8.5	19.8
		188	55	5	41	10	39		22						
		188	83	5	41	10	27		18						
monocrotophos[i]	$[M + H]^+$	224	127	5	71	10	23	**17**	16		5.3	292 (5)	95.5	9.1	18.2
		224	193	5	71	10	13		10						
		224	98	5	71	10	19		12						
napropamide	$[M + H]^+$	272	129	5	86	10	23	**14**	18		9.29	34 (5)	103.6	8.0	16.8
		272	171	5	86	10	29		18						
		272	58	5	86	10	43		6						
neburon	$[M + H]^+$	275	88	5	106	10	25	**21**	20		9.63	110 (5)	104.0	7.4	16.7
		275	57	5	106	10	39		24						
		275	114	5	106	10	23		24						
ofurace	$[M + H]^+$	282	254	5	111	10	19	**13**	26		8.13	75 (5)	102.3	8.3	17.3
		282	160	5	111	10	37		22						
		282	236	5	111	10	23		22						
oxadixyl[i]	$[M + H]^+$	279	219	5	91	10	17	**11**	24		7.48	25 (5)	100.5	7.8	15.9
		279	132	5	91	10	47		18						
		279	133	5	91	10	31		18						
oxamyl	$[M + NH_4]^+$	237	72	5	21	10	25	25	30		5.08	172 (5)	96.5	8.3	16.8
		237	90	5	21	10	13		16						
		237	56	5	21	10	49		24						
oxamyl oxime	$[M + H]^+$	163	72	5	61	10	21	21	16		4.16	39 (5)	97.0	8.9	18.5
		163	90	5	61	10	27		18						
		163	115	5	61	10	21		16						
oxycarboxine[i]	$[M + H]^+$	268	175	5	91	10	23	**15**	18		7.21	32 (5)	99.6	11.1	22.4
		268	147	5	91	10	35		14						
		268	193	5	91	10	19		18						
paclobutrazol	$[M + H]^+$	294	70	5	86	10	25	**17**	28		8.62	59 (5)	101.5	8.0	18.0
		294	43	5	86	10	111		18						
		294	125	5	86	10	51		16						
pencycuron	$[M + H]^+$	329	125	5	96	10	39	**19**	16		10.16	56 (5)	102.8	8.2	16.7
		329	89	5	96	10	99		16						
		329	99	5	96	10	89		14						
picolinafen	$[M + H]^+$	377	238	5	146	10	45	45	24	S	10.65	28 (5)	102.4	11.5	24.1
		377	256	5	146	10	33		10						
		377	284	5	146	10	27		28						
picoxystrobin	$[M + H]^+$	368	145	5	111	10	33	**19**	20		9.78	47 (5)	104.6	8.9	18.9
		368	205	5	111	10	15		18						
		368	102	5	111	10	93		20						
piperophos	$[M + H]^+$	354	171	5	96	10	31	**19**	8		10.36	53 (5)	103.5	8.8	17.7
		354	255	5	96	10	21		12						
		354	143	5	96	10	45		14						
pretilachlor	$[M + H]^+$	312	252	5	81	10	23	**10**	26		10.50	96 (5)	102.7	6.2	12.9
		312	176	5	81	10	39		24						
		312	147	5	81	10	49		20						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
primisulfuron-methyl[h]	$[M+H]^+$	469	254	5	81	10	29	29	26		6.87	166 (5)	91.1	9.5	28.1
		469	199	5	81	10	33		10						
		469	437	5	81	10	19		46						
prodiamine	$[M+H]^+$	351	250	5	31	10	41	41	26		10.70	8 (5)	104.7	16.9	33.9
		351	267	5	31	10	27		30						
		351	291	5	31	10	25		24						
propoxur	$[M+H]^+$	210	111	5	76	10	23	**16**	12		7.79	75 (5)	101.5	7.3	16.1
		210	168	5	76	10	13		22						
		210	65	5	76	10	49		26						
pymetrozine	$[M+H]^+$	218	105	5	91	10	27	**19**	22	S	4.94	49 (5)	84.0	11.6	28.0
		218	78	5	91	10	49		18						
		218	79	5	91	10	47		18						
pyraclostrobin	$[M+H]^+$	388	194	5	81	10	19	**10**	10		10.02	22 (5)	103.0	11.0	22.0
		388	163	5	81	10	33		16						
		388	104	5	81	10	85		22						
pyraflufen-ethyl	$[M+H]^+$	413	339	5	136	10	29	**27**	22		9.83	78 (5)	103.0	8.4	17.2
		413	253	5	136	10	45		14						
		413	289	5	136	10	43		40						
pyridalyl[i]	$[M+H]^+$	490	109	5	126	10	43	43	12	S	14.09	6 (5)	85.3	**40.3**	**81.8**
		490	183	5	126	10	27		10						
		490	204	5	126	10	31		22						
pyridaphenthion	$[M+H]^+$	341	189	5	141	10	31	**17**	22		9.15	31 (5)	104.3	9.6	21.3
		341	92	5	141	10	57		12						
		341	205	5	141	10	31		28						
pyridate	$[M+H]^+$	379	207	5	76	10	23	**18**	10	S	13.05	31 (5)	**50.5**	17.4	**134.0**
		379	77	5	76	10	75		18						
		379	57	5	76	10	41		22						
pyrifenox	$[M+H]^+$	295	93	5	106	10	37	**19**	10		9.54	56 (5)	105.6	8.2	16.9
		295	93	5	106	10	79		34						
		295	67	5	106	10	83		14						
pyrimethanil	$[M+H]^+$	200	107	5	91	10	35	35	14		8.91	55 (5)	101.1	7.3	14.8
		200	82	5	91	10	37		18						
		200	42	5	91	10	49		18						
pyriproxyfen	$[M+H]^+$	322	96	5	81	10	23	**13**	12		10.94	50 (5)	100.7	8.5	17.3
		322	78	5	81	10	81		32						
		322	51	5	81	10	111		22						
quinoxyfen	$[M+H]^+$	308	197	5	51	10	47	**35**	26	S	10.94	25 (5)	101.3	7.3	15.4
		308	214	5	51	10	49		22						
		308	272	5	51	10	39		30						
quizalofop	$[M+H]^+$	345	299	5	61	10	27	27	38		6.44	15 (5)	**59.7**	**63.9**	**202.0**
		345	91	5	61	10	43		18						
		345	271	5	61	10	35		30						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
quizalofop-ethyl	$[M + H]^+$	373	299	5	126	10	29	**17**	34		10.50	na[f]	102.6	11.7	23.9
		373	271	5	126	10	35		28						
		373	91	5	126	10	49		18						
schradan[h]	$[M + H]^+$	287	135	5	116	10	39	**21**	12		5.71	21 (5)	95.6	9.8	19.9
		287	242	5	116	10	19		24						
		287	44	5	116	10	69		10						
spinosyn A	$[M + H]^+$	732	142	5	186	10	41	**29**	20	E	15.54	12 (5)	102.0	9.7	22.6
		732	98	5	186	10	93		22						
		732	99	5	186	10	71		16						
spinosyn D	$[M + H]^+$	746	142	5	186	10	43	**29**	20	E	16.89	11 (5)	101.5	12.0	24.3
		746	99	5	186	10	75		12						
		746	98	5	186	10	101		18						
spirodiclofen	$[M + H]^+$	411	71	5	136	10	33	33	12		12.10	6 (5)	101.9	8.2	18.1
		411	313	5	136	10	17		16						
		411	43	5	136	10	49		16						
spiromesifen	$[M + NH_4]^+$	388	273	5	51	10	21	**9**	26		11.91	42 (5)	91.2	13.5	**41.5**
		388	255	5	51	10	39		26						
		388	187	5	51	10	43		26						
spiroxamine	$[M + H]^+$	298	144	5	86	10	31	**17**	16		**14.18**	49 (5)	103.3	8.5	18.6
		298	100	5	86	10	43		42						
		298	58	5	86	10	67		24						
sulfentrazone	$[M + H]^+$	387	307	5	146	10	31	31	18		7.50	23 (5)	104.0	8.6	18.4
		387	273	5	146	10	41		28						
		387	308	5	146	10	31		32						
tebufenozide	$[M + H]^+$	353	133	5	86	10	33		20						
		353	**297**	5	86	10	13	**23**	32		9.58	90 (5)	106.0	10.4	22.5
		353	105	5	86	10	59		40						
tebufenpyrad	$[M + H]^+$	334	145	5	121	10	39	**31**	18		10.60	27 (5)	101.8	7.6	15.7
		334	117	5	121	10	49		10						
		334	147	5	121	10	37		18						
tebupirimfos	$[M + H]^+$	319	277	5	51	10	21	**11**	22		11.13	103 (5)	100.8	7.9	15.9
		319	153	5	51	10	39		16						
		319	231	5	51	10	39		20						
tepraloxydim	$[M + H]^+$	342	250	5	61	10	19	19	34	S	6.63	33 (5)	**138.8**	11.1	22.3
		342	250	5	61	10	19		28						
		342	166	5	61	10	33		18						
tetraconazole	$[M + H]^+$	374	161	5	126	10	51	51	10		9.05	38 (5)	102.8	7.1	14.5
		374	70	5	126	10	37		28						
		374	89	5	126	10	109		18						
thiabendazole	$[M + H]^+$	202	175	5	51	10	39	**25**	18	S	6.68	68 (5)	102.4	9.8	20.5
		202	131	5	51	10	47		26						
		202	65	5	51	10	61		14						
thiabendazole-d_4 (IS)	$[M + H]^+$	206	179	5	131	10	39	39	18		6.68				

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
thiacloprid	$[M + H]^+$	253	126	5	101	10	33	**20**	12		7.07	122 (5)	101.5	9.7	19.7
		253	90	5	101	10	49		12						
		253	99	5	101	10	49		12						
thiamethoxam	$[M + H]^+$	292	211	5	76	10	19		18	S					
		292	**181**	5	76	10	33	33	18		5.71	17 (5)	98.9	9.9	21.7
		292	132	5	76	10	33		8						
thiazopyr	$[M + H]^+$	397	377	5	146	10	31	**26**	36		10.02	177 (5)	102.0	7.5	15.1
		397	335	5	146	10	39		40						
		397	61	5	146	10	49		28						
thiodicarb[i]	$[M + H]^+$	355	88	5	106	10	23	23	16		7.55	143 (5)	103.5	8.0	16.0
		355	108	5	106	10	23		14						
		355	73	5	106	10	73		14						
thiofanox	$[M + Na]^+$	241	184	5	76	10	17	17	18		8.08	16 (5)	101.2	11.5	26.6
		241	98	5	76	10	19		12						
		241	106	5	76	10	21		22						
thiofanox sulfone	$[M + NH_4]^+$	268	57	5	51	10	19	19	4		6.49	42 (5)	98.6	10.2	20.8
		268	76	5	51	10	17		10						
		268	41	5	51	10	55		6						
thiofanox sulfoxide	$[M + H]^+$	235	104	5	46	10	15	15	12		5.66	115 (5)	97.1	10.7	21.5
		235	57	5	46	10	29		14						
		235	64	5	46	10	41		12						
tolylfluanid[i]	$[M + H]^+$	347	238	5	106	10	17	17	26		10.37	3 (5)	96.1	16.9	34.1
		347	137	5	106	10	35		18						
		347	137	5	106	10	67		18						
tralkoxydim	$[M + H]^+$	330	284	5	86	10	19	**15**	28		9.49	105 (5)	**123.4**	9.0	19.6
		330	138	5	86	10	31		14						
		330	96	5	86	10	45		20						
trichlorfon	$[M + H]^+$	257	127	5	101	10	29	29	18		5.91	31 (5)	97.7	9.1	18.3
		257	221	5	101	10	17		24						
		257	109	5	101	10	31		10						
tricyclazole[i]	$[M + H]^+$	190	163	5	111	10	33	**24**	16		6.74	119 (5)	99.8	11.8	23.7
		190	136	5	111	10	43		18						
		190	109	5	111	10	51		14						
trietazine	$[M + H]^+$	230	99	5	101	10	35	**30**	22		9.54	79 (5)	103.3	7.4	16.1
		230	43	5	101	10	49		18						
		230	202	5	101	10	29		10						
trifloxysulfuron	$[M + H]^+$	438	182	5	106	10	29	**14**	26		6.49	41 (5)	100.3	13.6	27.7
		438	257	5	106	10	29		28						
		438	176	5	106	10	47		18						
triforine[g,h]	$[M + H]^+$	435	390	5	71	10	19	19	12	S	8.08	37 (5)	102.2	12.9	26.2
		435	98	5	71	10	49		10						
		435	83	5	71	10	91		12						
trimethacarb[i]	$[M + H]^+$	194	137	5	86	10	17		18						
		194	**122**	5	86	10	37	37	16		8.37	34 (5)	101.5	6.4	13.8
		194	107	5	86	10	53		12						

Table 1. Continued

pesticide 1[d]	ionization 2	Q1 mass (amu) 3	Q3 mass[n] (amu) 4	dwell time (ms) 5	DP (V) 6	EP (V) 7	CE (V) 8	CE[a] (V) 9	CXP (V) 10	matrix effects[j] 11	retention time[b] (min) 12	LCL S/N PtP[c] 13	recovery[k] (%) 14	precision[l] (%) 15	measurement uncertainty[m] (%) 16
zinophos	$[M + H]^+$	249	97	5	51	10	41	41	12	E	8.71	16 (5)	101.2	9.0	19.7
		249	193	5	51	10	21		26						
		249	221	5	51	10	17		24						
zoxamide	$[M + H]^+$	336	187	5	131	10	33	**19**	20	E	10.02	53 (5)	103.2	8.6	17.5
		336	159	5	131	10	49		22						
		336	204	5	131	10	25		22						

[a] Collision energy (bold and underlined) was attenuated to avoid the saturation of the detector at the highest concentration level, i.e., 500.0 μg/kg. Transitions in the corresponding row were used for quantification. [b] Retention time may vary from column to column. Bold and underlined pesticides had retention times that drifted within a batch run. [c] Signal-to-noise (peak-to-peak) ratio was determined at the lowest concentration level (μg/kg, in parentheses) in a strawberry matrix. Bold and underlined pesticides had signal-to-noise ratios that determined to be above 5 μg/kg. [d] Column number. Bold pesticides typically have poor sensitivity. [e] Method performance was based on three spike levels, i.e., 90.0, 240.0, and 400.0 μg/kg, due to poor sensitivity. [f] There was a small interference peak. S/N was not able to be determined. [g] An ion with Cl^{37} was selected as a precursor ion. [h] Pesticides have a relatively low solubility in methanol. Stock solution was prepared in 1000.0 μg /mL. [i] Pesticides have a relatively low solubility in methanol. Stock solution was prepared in 2000.0 μg/mL. [j] S or E indicates either ion suppression (S) or enhancement (E) in at least one of the matrices. [k] Bold and underlined pesticides have recoveries not in the range of 81−110%. [l] Bold and underlined pesticides have intermediate precision of >20%. [m] Bold and underlined pesticides have MU > 40%. [n] Bold and underlined pesticides have second transition that is used for quantification.

made up to 1.0 mL with 0.1 M ammonium acetate and vortexed again for 30 s. One hundred microliters of each extract was transferred into a Mini-UniPrep vial (Whatman Inc., USA), and 500 μL of solvent buffer (a mixture of 0.1 M ammonium acetate/methanol, 50 + 50, v/v) was added. The vials were capped, vortexed for 30 s, and pressed to filter. Sample extracts were ready for LC/ESI-MS/MS injection. Another 600 μL of the extracts (without dilution) was transferred into a Mini-UniPrep vial for UHPLC QqTOF MS injection.

Preparation of Matrix-Matched Calibration Standards and Calculation. Matrix-matched calibration standards were prepared by adding standards and internal standards to blank sample extracts after sample extraction and cleanup. A blank berry sample (15.0 g/sample) was weighed into a 50 mL centrifuge tube, and the sample was processed through the extraction procedure as described above. Two hundred and fifty microliters of each six-level pesticide standard mix working solution was transferred into each of six blank sample extracts (1.0 mL/tube), providing 5.0, 25.0, 100.0, 200.0, 300.0, and 500.0 μg/kg of standard equivalent in samples. Then, 50 μL of 2.0 μg/mL internal calibration working solution was added to each sample (100.0 μg/kg equivalent in samples). The extracts were made up to 0.5 mL with methanol, vortexed for 30 s, made up volume to 1.0 mL with 0.1 M ammonium acetate, and vortexed again for 30 s. The extracts were diluted six times prior to LC/ESI-MS/MS injection. The extracts were injected to UHPLC QqTOF MS without dilution. Matrix-matched standard calibration curves were prepared fresh for each day's samples.

LC/ESI-MS/MS Quantification. LC/ESI-MS/MS matrix-matched standard calibration curves for each individual pesticide were constructed using the "Quantitate" function bundled with the Analyst software. The quantitation integration algorithm applied was IntelliQuan with no data smoothing. Deuterium-labeled standards carbendazim-d_4, carbofuran-d_3, and thiabendazole-d_4 were used as internal standards for their respective native compounds for quantification. All other pesticides used carbofuran-d_3 as an internal standard for quantification. A quadratic function was applied to the calibration curves based on the line of best fit. The $1/x$ weighting was used to accurately quantify pesticides at low concentrations. Responses for the unknown or fortified samples were compared to the curves to calculate the amount of pesticide residues (μg/kg) in samples.

UHPLC QqTOF MS Quantification. UHPLC QqTOF MS matrix-matched standard calibration curves for each individual pesticide were constructed using QuanLynx. The uses of internal standards and weighting ($1/x$) were the same as for LC/ESI-MS/MS. In general, a quadratic function was applied to the calibration curves based on the line of best fit. Occasionally, linear regression may be used for quantification for a few pesticides.

Experimental Design and Method Validation. The method was validated according to the nested experimental design, which was described elsewhere (*10*−*12*). In this study, there were a total of six berry fruits. For each matrix, samples were spiked at four levels, that is, 10.0, 90.0, 240.0, and 400.0 μg/kg, in triplicate. Spike experiments were repeated on two different days. Overall recovery, intermediate precision, and measurement uncertainty were calculated using a compiled computer program that consisted of SAS codes (SAS Software Release 9.1, SAS Institute Inc., USA) along with a Microsoft Excel (Microsoft Office 2002) workbook (*10*). The compiled program was built using SAS EIS/OLAP Application Builder.

RESULTS AND DISCUSSION

Extraction. Pesticides were extracted from berry samples (15 g/sample) following the buffered QuEChERS method (*14*−*16*) or AOAC Official Method 2007.01 (*17*). The whole procedure entailed step 1, extraction with acetonitrile containing 1% acetic acid, $MgSO_4$, and sodium acetate; step 2, a simple cleanup step using dispersive solid-phase extraction (dispersive-SPE) with $MgSO_4$ and PSA; and step 3, concentration, reconstitution, and filtration. The QuEChERS method proved to be simple and adequate to extract most pesticides from berries for LC/ESI-MS/MS and UHPLC QqTOF MS analysis. Compared to conventional reversed-phase solid-phase extraction, QuEChERS

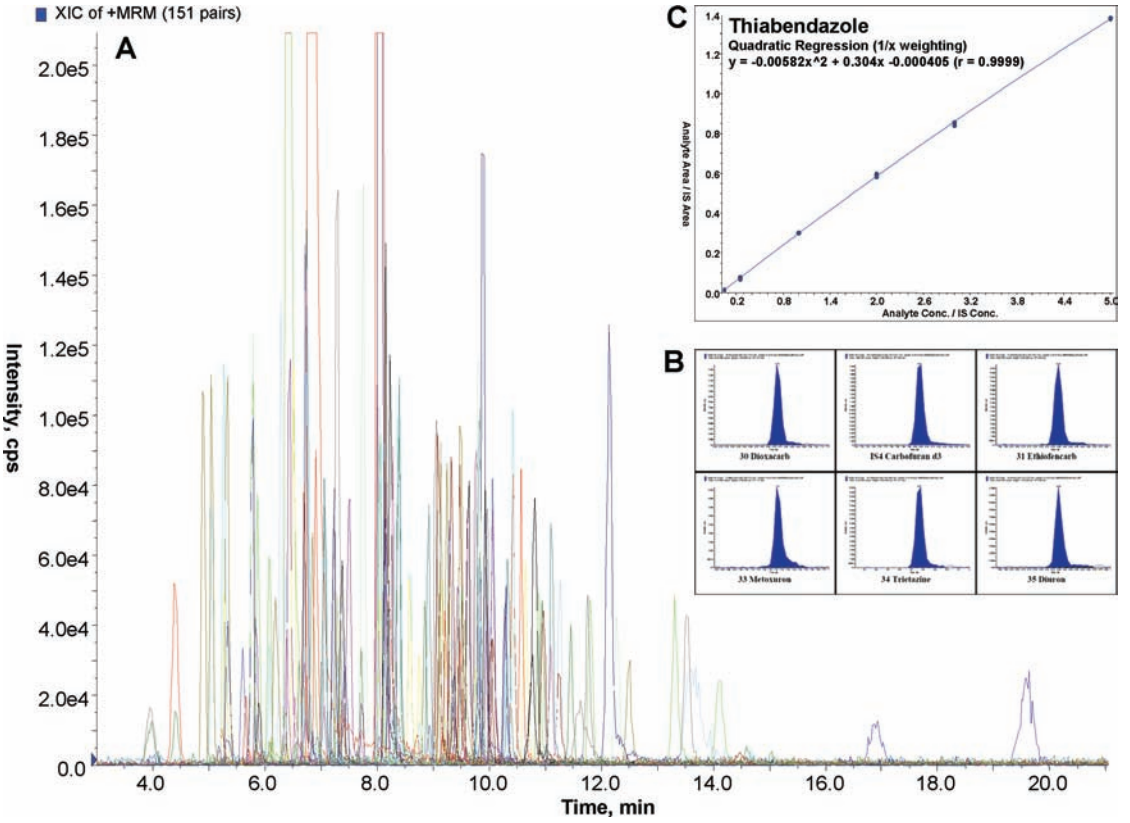


Figure 1. LC/ESI-MS/MS chromatogram of pesticides (10 μg/kg) spiked in strawberry: (**A**) total ion chromatogram (TIC) of 151 MRM transitions including 148 pesticides and 3 internal standards; (**B**) example of extracted ion chromatograms (XIC) [first row left to right, dioxacarb (224/123, 6.73 min), carbofuran-d_3 (225/123, 8.04 min), and ethiofencarb (228/107, 8.39 min); second row, left to right, metoxuron (229/72, 7.31 min), trietazine (230/99, 9.77 min), and diuron (233/72, 8.40 min)]; (**C**) matrix-matched standard calibration curve for thiabendazole.

effectively removed anthocyanins (dark red or blue in color) in samples and, therefore, reduced the ion source contamination.

LC/ESI-MS/MS Data Acquisition. LC/ESI-MS/MS was considered to be pretarget analysis, and its data acquisition was based on the multiple reaction monitoring (MRM) transitions that were predetermined by infusing 148 pesticides and 3 isotopically labeled standards (**Table 1**, column 1) into an API 5000 mass spectrometer. **Table 1** (columns 3 and 4) lists MRM transitions of 148 pesticides for either quantification or confirmation. Pesticides were ionized in the form of $[M + H]^+$, $[M + NH_4]^+$, or $[M + Na]^+$ (**Table 1**, column 2) in the positive electrospray mode depending on their chemical structures in the presence of ammonium acetate (10 mM) in LC mobile phase. In routine practice, the first transition, that is, the most intense product ion of its corresponding precursor, was used for quantification or screening, and the second or third transition along with retention time was utilized for confirmation. Some pesticides shared the same transitions and eluted at approximately the same time, and, therefore, the second transition was chosen for quantification. For example, isoprocarb and trimethacarb both had 194/137 transition and eluted at 8.37 min; the second transition of trimethacarb, that is, 194/122, was selected for quantification; and its third transition was used for confirmation. The same scenarios were observed for methabenzthiazuron and carbofuran and for dimethametryn and dipropetryn.

A conventional LC (Aglient 1200 SL) along with an Atlantis dC_{18} analytical column demonstrated a satisfactory chromatographic performance to separate pesticides under the given gradient condition. The LC peaks were narrow and sharp with Gaussian distribution (**Figure 1A**,**B**). Mobile phase B (acetonitrile) was ramped from 8 to 90% in 7 min, and then it was kept at 90% until 25 min before the column was regenerated. The total run time was 35 min. The LC pesticide retention times are listed in **Table 1** (column 12). The first pesticide eluted from the column was butocarboxim sulfoxide at 3.82 min, and the last pesticide was dodemorph at 18.70 min. Most pesticides (97%) were eluted between 4 and 15 min. Only four pesticides, that is, dodemorph (18.70 min), emamectin B_{1a} (15.49 min), spinosyn A (15.54 min), and spinosyn D (16.89 min), were eluted after 15 min. The retention times, within- and between-batches, were reproducible for most of the pesticides, but those of emamectin B_{1a}, fenpropidin, and spiroxamine drifted in within-batch analysis. Nevertheless, the tolerance of retention time matching did not exceed 2.5% relative to the retention time of a standard in the same batch under all circumstances.

UHPLC QqTOF MS Data Acquisition. QqTOF was operated in QqTOF MS (full-scan) mode rather than QqTOF MS/MS (product-ion scan) mode. Although the QqTOF MS/MS product-ion spectra provided much more specific and unequivocal information for confirmation, QqTOF MS full-scan data proved to be practical and flexible and allowed for either post-target analysis or unknown identification in a retrospective manner (*13*). The UHPLC QqTOF MS instrumental parameters were optimized for analytes in a mass range of 50−950 Da. This generic setup made it an easy and powerful tool for method development. New analytes could be simply added to the list for data acquisition data without a prerequisite for analyte tuning beforehand. This was in contrast to a QqQ instrument that must be optimized for analytes prior to MRM data acquisition. QqTOF MS data processing was based on accurate mass measurement with mass error of $\leq$50 mDa. Pesticides were ionized in positive electrospray mode and formed mainly $[M + H]^+$ and/or $[M + NH_4]^+$ (**Table 2**,

Table 2. Elemental Composition, Exact Mass, and Retention Time of the Studied Pesticides and UHPLC/QqTOF MS Method Performance Results

pesticide 1[a]	elemental composition 2	ionization 3	exact mass 4	fragment 5	exact mass of extracted ion for quantification 6	matrix effects[h] 7	retention time (min) 8	LCL S/N PtP[d] 9	recovery[i] (%) 10	precision[j] (%) 11	measurement uncertainty[k] (%) 12
acetochlor	$C_{14}H_{20}ClNO_2$	$[M+H]^+$	270.1261	$C_{12}H_{15}ClNO^+$	224.0842		6.20	13 (5)	103.0	11.4	23.1
aclonifen[f]	$C_{12}H_9ClN_2O_3$	$[M+H]^+$	265.0380		265.0380	NA	6.42	**6** (**100**)	99.6	**27.9**	**60.5**
aldicarb	$C_7H_{14}N_2O_2S$	$[M+H]^+$	191.0854	$C_5H_{10}NS^+$	116.0534		3.39	8 (5)	99.4	13.5	27.6
aldicarb sulfone	$C_7H_{14}N_2O_4S$	$[M+H]^+$	223.0753		223.0753	S	1.67	6 (5)	98.5	14.7	31.4
aldicarb sulfoxide	$C_7H_{14}N_2O_3S$	$[M+H]^+$	207.0803	$C_5H_{10}NOS^+$	132.0483		1.35	5 (5)	92.7	11.7	23.4
azaconazole	$C_{12}H_{11}Cl_2N_3O_2$	$[M+H]^+$	300.0307		300.0307	S	4.61	47 (5)	101.9	11.9	24.0
benoxacor[e]	$C_{11}H_{11}Cl_2NO_2$	$[M+H]^+$	260.0245		260.0245	E	5.50	**5** (**25**)	107.7	**32.3**	**65.0**
bitertanol	$C_{20}H_{23}N_3O_2$	$[M+H]^+$	338.1869		338.1869		6.16	6 (5)	99.6	14.1	28.3
bromuconazole	$C_{13}H_{12}BrCl_2N_3O$	$[M+H]^+$	375.9619	A+2[g]	377.9590	S	5.55	20 (5)	103.1	11.3	22.7
butafenacil	$C_{20}H_{18}ClF_3N_2O_6$	$[M+NH_4]^+$	492.1149		492.1149	S	6.38	40 (5)	101.8	14.0	31.1
butocarboxim sulfoxide	$C_7H_{14}N_2O_3S$	$[M+H]^+$	207.0803	$C_5H_{10}NOS^+$	132.0483	S	1.23	7 (5)	92.1	12.9	25.8
cadusafos	$C_{10}H_{23}O_2PS_2$	$[M+H]^+$	271.0955		271.0955		6.83	27 (5)	103.0	10.6	21.6
carbaryl	$C_{12}H_{11}NO_2$	$[M+H]^+$	202.0868	$C_{10}H_9O^+$	145.0653	S	4.34	21 (5)	102.3	12.5	25.8
carbendazim	$C_9H_9N_3O_2$	$[M+H]^+$	192.0773		192.0773	S	2.58	39 (5)	103.3	10.6	22.7
carbendazim-d_4 (IS)	$C_9H_5D_4N_3O_2$	$[M+H]^+$	196.1024		196.1024		2.52				
carbofuran	$C_{12}H_{15}NO_3$	$[M+H]^+$	222.1130		222.1130		4.15	23 (5)	99.9	9.7	20.0
carbofuran-d_3 (IS)	$C_{12}H_{12}D_3NO_3$	$[M+H]^+$	225.1318		225.1318		4.13				
carfentrazone-ethyl	$C_{15}H_{14}Cl_2F_3N_3O_3$	$[M+H]^+$	412.0443		412.0443		6.49	14 (5)	104.2	10.8	22.7
chlorbromuron[e]	$C_9H_{10}BrClN_2O_2$	$[M+H]^+$	292.9692		292.9692	E	5.53	**9** (**25**)	105.5	**38.5**	**80.0**
chloridazon	$C_{10}H_8ClN_3O$	$[M+H]^+$	222.0434		222.0434	S	2.59	9 (5)	96.3	17.0	38.1
chlorimuron-ethyl	$C_{15}H_{15}ClN_4O_6S$	$[M+H]^+$	415.0479		415.0479	E	3.21	45 (5)	97.6	11.7	23.5
chloroxuron	$C_{15}H_{15}ClN_2O_2$	$[M+H]^+$	291.0900		291.0900		5.55	74 (5)	105.7	11.5	23.2
chlorthiamid[f]	$C_7H_5Cl_2NS$	$[M+H]^+$	205.9598		205.9598	S	3.55	**4** (**100**)	81.6	**24.5**	**70.1**
chlortoluron	$C_{10}H_{13}ClN_2O$	$[M+H]^+$	213.0795		213.0795	E	4.30	56 (5)	103.6	10.6	21.3
clodinafop-propargyl	$C_{17}H_{13}ClFNO_4$	$[M+H]^+$	350.0595		350.0595		6.70	19 (5)	103.0	17.3	34.7
cloquintocet-mexyl	$C_{18}H_{22}ClNO_3$	$[M+H]^+$	336.1366		336.1366		7.45	100 (5)	99.7	11.5	24.1
clothianidin	$C_6H_8ClN_5O_2S$	$[M+H]^+$	250.0165		250.0165	S	2.47	5 (5)	91.6	**24.5**	**49.6**
cyanofenphos[e]	$C_{15}H_{14}NO_2PS$	$[M+H]+$	304.0561		304.0561	E	6.91	**3** (**25**)	106.4	**32.7**	**65.8**
cycloxydim	$C_{17}H_{27}NO_3S$	$[M+H]^+$	326.1790		326.1790	S	4.90	8 (5)	**111.7**	10.7	22.8
cycluron	$C_{11}H_{22}N_2O$	$[M+H]^+$	199.1810		199.1810		4.41	19 (5)	102.2	9.5	19.5
demeton-*S*-methyl sulfone	$C_6H_{15}O_5PS_2$	$[M+H]^+$	263.0177		263.0177		2.04	80 (5)	95.5	9.1	20.2
demeton-*S*-methyl sulfoxide	$C_6H_{15}O_4PS_2$	$[M+H]^+$	247.0228		247.0228		1.65	31 (5)	90.9	10.6	21.2
desmedipham	$C_{16}H_{16}N_2O_4$	$[M+H]^+$	301.1188		301.1188		5.28	15 (5)	100.5	12.1	25.5
diclocymet[e]	$C_{15}H_{18}Cl_2N_2O$	$[M+H]^+$	313.0874		313.0874		6.36	**7** (**25**)	100.1	**27.0**	**54.5**
diethofencarb	$C_{14}H_{21}NO_4$	$[M+H]^+$	268.1549	$C_{11}H_{16}NO_4^+$	226.1079		5.44	14 (5)	103.0	12.3	25.3
difenoconazole	$C_{19}H_{17}Cl_2N_3O_3$	$[M+H]^+$	406.0725		406.0725	S	6.68	17 (5)	98.9	9.4	20.2
dimethametryn	$C_{11}H_{21}N_5S$	$[M+H]^+$	256.1596		256.1596		6.19	86 (5)	102.3	8.5	17.1
dimethomorph	$C_{21}H_{22}ClNO_4$	$[M+H]^+$	388.1316		388.1316	E	5.33	42 (5)	101.7	12.4	25.1
diniconazole	$C_{15}H_{17}Cl_2N_3O$	$[M+H]^+$	326.0827		326.0827	S	6.30	40 (5)	100.9	14.4	30.0
dioxacarb	$C_{11}H_{13}NO_4$	$[M+H]^+$	224.0923	$C_9H_{11}O_3^+$	167.0708	S	2.78	16 (5)	98.0	11.1	22.3
dipropetryn	$C_{11}H_{21}N_5S$	$[M+H]^+$	256.1596		256.1596		6.36	58 (5)	99.7	10.4	20.8
diuron	$C_9H_{10}Cl_2N_2O$	$[M+H]^+$	233.0248		233.0248	S	4.58	44 (5)	104.0	15.9	33.5
dodemorph	$C_{18}H_{35}NO$	$[M+H]^+$	282.2797		282.2797		10.27	196 (5)	97.2	11.1	22.3
emamectin B_{1a}	$C_{49}H_{75}NO_{13}$	$[M+H]^+$	886.5317		886.5317	E	7.80	40 (5)	96.9	12.9	26.3
epoxiconazole	$C_{17}H_{13}ClFN_3O$	$[M+H]^+$	330.0809		330.0809		5.71	48 (5)	105.9	14.7	32.5

Table 2. Continued

pesticide 1[a]	elemental composition 2	ionization 3	exact mass 4	fragment 5	exact mass of extracted ion for quantification 6	matrix effects[h] 7	retention time (min) 8	LCL S/N PtP[d] 9	recovery[i] (%) 10	precision[j] (%) 11	measurement uncertainty[k] (%) 12
ethiofencarb	$C_{11}H_{15}NO_2S$	$[M + H]^+$	226.0902	$C_7H_7O^+$	107.0497		4.52	19 (5)	100.5	15.1	30.8
ethiofencarb sulfone	$C_{11}H_{15}NO_4S$	$[M + H]^+$	258.0800	$C_9H_{13}O_3S^+$	201.0585		2.49	15 (5)	100.9	12.8	26.3
ethiofencarb sulfoxide	$C_{11}H_{15}NO_3S$	$[M + H]^+$	242.0851	$C_9H_{13}O_2S^+$	185.0636		2.20	6 (5)	96.1	11.6	23.2
ethirimol	$C_{11}H_{19}N_3O$	$[M + H]^+$	210.1606		210.1606		3.71	73 (5)	93.7	10.7	22.6
ethoprop	$C_8H_{19}O_2PS_2$	$[M + H]^+$	243.0642		243.0642		5.82	38 (5)	100.5	10.8	22.8
etofenprox	$C_{25}H_{28}O_3$	$[M + NH_4]^+$	394.2382		394.2382	S	9.00	5 (5)	87.7	**44.4**	**89.1**
etoxazole	$C_{21}H_{23}F_2NO_2$	$[M + H]^+$	360.1775		360.1775		8.12	92 (5)	98.7	14.2	28.6
fenamidone	$C_{17}H_{17}N_3OS$	$[M + H]^+$	312.1171		312.1171		5.71	109 (5)	105.7	12.3	27.0
fenazaquin	$C_{20}H_{22}N_2O$	$[M + H]^+$	307.1810		307.1810	S	7.93	68 (5)	100.2	17.7	36.0
fenhexamid	$C_{14}H_{17}Cl_2NO_2$	$[M + H]^+$	302.0715		302.0715	S	5.79	4 (5)	97.7	**27.3**	**58.2**
fenoxanil	$C_{15}H_{18}Cl_2N_2O_2$	$[M + H]^+$	329.0824		329.0824		6.53	21 (5)	103.1	12.5	25.6
fenpropimorph	$C_{20}H_{33}NO$	$[M + H]^+$	304.2640		304.2640	E	9.06	66 (5)	99.8	12.3	24.8
fenpyroximate	$C_{24}H_{27}N_3O_4$	$[M + H]^+$	422.2080		422.2080		7.99	51 (5)	99.7	19.3	38.7
fentrazamide	$C_{16}H_{20}ClN_5O_2$	$[M + H]^+$	350.1384	$C_{10}H_{17}N_2O_2^+$	197.1290		6.85	42 (5)	99.8	10.9	24.4
fluazifop-butyl	$C_{19}H_{20}F_3NO_4$	$[M + H]^+$	384.1423		384.1423	E	7.75	126 (5)	102.5	15.3	30.7
flucarbazone	$C_{12}H_{11}F_3N_4O_6S$	$[M + H]^+$	397.0430		397.0430	E	2.42	4 (5)	**55.1**	**24.7**	**64.4**
flutolanil	$C_{17}H_{16}F_3NO_2$	$[M + H]^+$	324.1211		324.1211		6.12	52 (5)	103.8	12.2	25.1
flutriafol	$C_{16}H_{13}F_2N_3O$	$[M + H]^+$	302.1105		302.1105	S	4.45	67 (5)	106.0	12.3	26.1
forchlorfenuron	$C_{12}H_{10}ClN_3O$	$[M + H]^+$	248.0591		248.0591	S	4.39	20 (5)	100.5	12.6	26.6
fosthiazate	$C_9H_{18}NO_3PS_2$	$[M + H]^+$	284.0544		284.0544	E	4.46	112 (5)	100.9	7.5	16.6
fuberidazole	$C_{11}H_8N_2O$	$[M + H]^+$	185.0715		185.0715		3.06	33 (5)	96.6	10.7	21.8
furathiocarb	$C_{18}H_{26}N_2O_5S$	$[M + H]^+$	383.1641		383.1641	E	7.61	156 (5)	102.9	10.7	21.9
haloxyfop[e]	$C_{15}H_{11}ClF_3NO_4$	$[M + H]^+$	362.0407		362.0407	S	4.03	**5** (**25**)	**58.5**	16.9	**44.5**
3-hydroxycarbofuran	$C_{12}H_{15}NO_4$	$[M + H]^+$	238.1079	$C_{12}H_{14}NO_3^+$	220.0974		2.57	21 (5)	101.8	13.4	29.7
imazamethabenz-methyl	$C_{16}H_{20}N_2O_3$	$[M + H]^+$	289.1552		289.1552		3.75	18 (5)	99.6	8.1	17.9
imidacloprid	$C_9H_{10}ClN_5O_2$	$[M + H]^+$	256.0601		256.0601	S	2.64	4 (5)	97.8	14.8	29.8
indoxacarb	$C_{22}H_{17}ClF_3N_3O_7$	$[M + H]^+$	528.0785		528.0785	E	7.23	46 (5)	98.5	**22.8**	**48.9**
iprovalicarb	$C_{18}H_{28}N_2O_3$	$[M + H]^+$	321.2178		321.2178	E	5.60	52 (5)	101.9	10.5	21.0
isocarbamide[e]	$C_8H_{15}N_3O_2$	$[M + H]^+$	186.1243		186.1243	S	2.57	**17** (**25**)	97.3	16.8	38.4
isoprocarb	$C_{11}H_{15}NO_2$	$[M + H]^+$	194.1181		194.1181		4.78	3 (5)	100.2	9.6	19.7
isoxathion	$C_{13}H_{16}NO_4PS$	$[M + H]^+$	314.0616		314.0616		7.12	38 (5)	103.8	19.1	38.7
linuron[e]	$C_9H_{10}Cl_2N_2O_2$	$[M + H]^+$	249.0198		249.0198	E	5.40	**7** (**25**)	106.1	16.4	33.9
mepanipyrim	$C_{14}H_{13}N_3$	$[M + H]^+$	224.1188		224.1188	E	5.90	52 (5)	101.8	11.0	22.5
mephosfolan	$C_8H_{16}NO_3PS_2$	$[M + H]^+$	270.0388		270.0388	E	3.68	82 (5)	105.6	11.5	24.4
methabenzthiazuron	$C_{10}H_{11}N_3O_3$	$[M + H]^+$	222.0879		222.0879	S	4.22	46 (5)	100.1	13.0	27.9
methidathion	$C_6H_{11}N_2O_4PS_3$	$[M + H]^+$	302.9697	$C_4H_5N_2O_2S^+$	145.0072		5.32	4 (5)	102.8	15.3	31.1
methiocarb	$C_{11}H_{15}NO_2S$	$[M + H]^+$	226.0902	$C_9H_{13}OS^+$	169.0687	S	5.32	9 (5)	104.1	10.8	22.7
methiocarb sulfone	$C_{11}H_{15}NO_4S$	$[M + H]^+$	258.0800		258.0800	E	3.08	3 (5)	104.0	15.5	32.9
methiocarb sulfoxide	$C_{11}H_{15}NO_3S$	$[M + H]^+$	242.0851		242.0851	S	2.38	22 (5)	94.7	12.5	26.2
methomyl	$C_5H_{10}N_2O_2S$	$[M + H]^+$	163.0541	$C_3H_6NS^+$	88.0221	S	1.85	4 (5)	96.2	**34.7**	**72.6**
methoxyfenozide	$C_{22}H_{28}N_2O_3$	$[M + H]^+$	369.2178	$C_{18}H_{21}N_2O_3^+$	313.1552		5.99	18 (5)	104.7	10.5	24.9
metolcarb[e]	$C_9H_{11}NO_2$	$[M + H]^+$	166.0868	$C_7H_9O^+$	109.0653		3.71	**6** (**25**)	104.4	17.5	36.8
metoxuron	$C_{10}H_{13}ClN_2O_2$	$[M + H]^+$	229.0744		229.0744		3.40	47 (5)	100.4	9.5	19.0
mexacarbate	$C_{12}H_{18}N_2O_2$	$[M + H]^+$	223.1447		223.1447		5.65	44 (5)	102.8	10.0	20.8

Table 2. Continued

pesticide 1[a]	elemental composition 2	ionization 3	exact mass 4	fragment 5	exact mass of extracted ion for quantification 6	matrix effects[h] 7	retention time (min) 8	LCL S/N PtP[d] 9	recovery[i] (%) 10	precision[j] (%) 11	measurement uncertainty[k] (%) 12
molinate[f]	$C_9H_{17}NOS$	$[M+H]^+$	188.1109		188.1109	E	5.63	**6** (**100**)	101.5	14.2	28.7
monocrotophos	$C_7H_{14}NO_5P$	$[M+H]^+$	224.0688	$C_6H_{10}O_5P^+$	193.0266		1.80	18 (5)	93.3	10.5	21.7
napropamide	$C_{17}H_{21}NO_2$	$[M+H]^+$	272.1651		272.1651		5.92	97 (5)	104.4	9.5	19.4
neburon	$C_{12}H_{16}Cl_2N_2O$	$[M+H]^+$	275.0718		275.0718		6.28	69 (5)	105.4	13.5	27.2
ofurace	$C_{14}H_{16}ClNO_3$	$[M+H]^+$	282.0897		282.0897		4.53	34 (5)	102.9	11.6	23.9
oxadixyl	$C_{14}H_{18}N_2O_4$	$[M+H]^+$	279.1345		279.1345		3.68	5 (5)	102.9	7.9	17.0
oxamyl	$C_7H_{13}N_3O_3S$	$[M+H]^+$	220.0756	$C_3H_8NO_2^{+c}$	90.0549	S	1.74	4 (5)	91.2	17.5	35.4
oxamyl-oxime[e]	$C_5H_{10}N_2O_2S$	$[M+H]^+$	163.0541		163.0541	E	1.37	**4** (**25**)	93.0	13.6	32.2
oxycarboxine	$C_{12}H_{13}NO_4S$	$[M+H]^+$	268.0644		268.0644	E	3.30	29 (5)	99.9	12.0	25.0
paclobutrazol	$C_{15}H_{20}ClN_3O$	$[M+H]^+$	294.1373		294.1373	S	5.25	40 (5)	105.3	12.8	27.1
pencycuron	$C_{19}H_{21}ClN_2O$	$[M+H]^+$	329.1421		329.1421	E	7.00	87 (5)	101.4	11.0	22.1
picolinafen	$C_{19}H_{12}F_4N_2O_2$	$[M+H]^+$	377.0913		377.0913	E	7.46	5 (5)	99.9	**38.1**	**76.4**
picoxystrobin	$C_{18}H_{16}F_3NO_4$	$[M+H]^+$	368.1110	$C_{12}H_{13}O_3^+$	205.0865	E	6.62	35 (5)	102.3	9.6	19.6
piperophos	$C_{14}H_{28}NO_3PS_2$	$[M+H]^+$	354.1327		354.1327		7.19	74 (5)	103.5	9.2	19.1
pretilachlor	$C_{17}H_{26}ClNO_2$	$[M+H]^+$	312.1730		312.1730		7.24	11 (5)	99.7	9.1	19.7
primisulfuron-methyl	$C_{15}H_{12}F_4N_4O_7S$	$[M+H]^+$	469.0441		469.0441	E	3.99	15 (5)	92.1	17.6	36.5
prodiamine[e]	$C_{13}H_{17}F_3N_4O_4$	$[M+H]^+$	351.1280		351.1280		7.57	**3** (**25**)	98.9	**31.2**	**62.7**
propoxur	$C_{11}H_{15}NO_3$	$[M+H]^+$	210.1130	$C_8H_{10}NO_3^+$	168.0661		4.08	29 (5)	102.3	9.1	20.2
pymetrozine	$C_{10}H_{11}N_5O$	$[M+H]^+$	218.1042		218.1042	S	1.57	7 (5)	81.0	12.6	32.3
pyraclostrobin	$C_{19}H_{18}ClN_3O_4$	$[M+H]^+$	388.1064		388.1064	E	6.86	107 (5)	98.2	12.6	27.9
pyraflufen-ethyl	$C_{15}H_{13}Cl_2F_3N_2O_4$	$[M+H]^+$	413.0283		413.0283	E	6.70	21 (5)	101.8	**21.6**	**43.3**
pyridalyl[e]	$C_{18}H_{14}Cl_4F_3NO_3$	$[M+H]^+$	489.9758	A+2[g]	491.9729	E or S	9.44	**31** (**25**)	104.8	**98.1**	**208.9**
pyridaphenthion	$C_{14}H_{17}N_2O_4PS$	$[M+H]^+$	341.0725		341.0725		5.82	65 (5)	102.0	11.5	23.1
pyridate	$C_{19}H_{23}ClN_2O_2S$	$[M+H]^+$	379.1247		379.1247	E or S	9.06	52 (5)	**45.6**	**44.7**	**145.6**
pyrifenox	$C_{14}H_{12}Cl_2N_2O$	$[M+H]^+$	295.0405		295.0405	S	5.99	43 (5)	104.6	12.7	27.1
pyrimethanil	$C_{12}H_{13}N_3$	$[M+H]^+$	200.1188		200.1188		5.26	12 (5)	100.9	11.4	22.9
pyriproxyfen	$C_{20}H_{19}NO_3$	$[M+H]^+$	322.1443		322.1443	S	7.74	137 (5)	97.5	19.6	39.4
quinoxyfen	$C_{15}H_8Cl_2FNO$	$[M+H]^+$	308.0045		308.0045		7.47	56 (5)	99.2	18.1	**41.8**
quizalofop[e]	$C_{17}H_{13}ClN_2O_4$	$[M+H]^+$	345.0642		345.0642	S	3.63	**8** (**25**)	**50.9**	19.6	**54.3**
quizalofop-ethyl	$C_{19}H_{17}ClN_2O_4$	$[M+H]^+$	373.0955		373.0955	S	7.32	7 (5)	95.8	16.2	39.0
schradan	$C_8H_{24}N_4O_3P_2$	$[M+H]^+$	287.1402		287.1402		2.52	15 (5)	95.3	9.1	18.7
spinosyn A[b]	$C_{41}H_{65}NO_{10}$	$[M+H]^+$	732.4687		732.4687	E	8.73	27 (5)	101.6	10.2	20.5
spinosyn D[b]	$C_{42}H_{67}NO_{10}$	$[M+H]^+$	746.4843		746.4843	E	9.19	3 (5)	99.7	12.2	24.5
spirodiclofen	$C_{21}H_{24}Cl_2O_4$	$[M+H]^+$	411.1130		411.1130		8.58	10 (5)	97.8	18.0	36.3
spiromesifen	$C_{23}H_{30}O_4$	$[M+H]^+$	371.2222	$C_{17}H_{21}O_3^+$	273.1491		8.47	36 (5)	87.7	15.4	**40.2**
spiroxamine	$C_{18}H_{35}NO_2$	$[M+H]^+$	298.2746		298.2746	E	7.06	12 (5)	100.4	12.8	26.1
sulfentrazone	$C_{11}H_{10}Cl_2F_2N_4O_3S$	$[M+NH_4]^+$	404.0162		404.0162	E or S	3.90	3 (5)	103.0	11.8	23.6
tebufenozide	$C_{22}H_{28}N_2O_2$	$[M+H]^+$	353.2229	$C_{18}H_{21}N_2O_2^+$	297.1603		6.43	76 (5)	105.5	10.8	22.6
tebufenpyrad	$C_{18}H_{24}ClN_3O$	$[M+H]^+$	334.1686		334.1686		7.39	40 (5)	103.1	13.1	29.4
tebupirimfos	$C_{13}H_{23}N_2O_3PS$	$[M+H]^+$	319.1245		319.1245		7.85	16 (5)	99.8	11.5	23.3
tepraloxydim	$C_{17}H_{24}ClNO_4$	$[M+H]^+$	342.1472		342.1472	S	2.96	3 (5)	**126.0**	17.4	35.0
tetraconazole	$C_{13}H_{11}Cl_2F_4N_3O$	$[M+H]^+$	372.0294		372.0294		5.87	24 (5)	104.5	15.9	32.3
thiabendazole	$C_{10}H_7N_3S$	$[M+H]^+$	202.0439		202.0439	S	2.86	35 (5)	102.0	9.1	18.4
thiabendazole-d_4 (IS)	$C_{10}H_3D_4N_3S$	$[M+H]^+$	206.0690		206.0690		2.83				

Table 2. Continued

pesticide 1[a]	elemental composition 2	ionization 3	exact mass 4	fragment 5	exact mass of extracted ion for quantification 6	matrix effects[h] 7	retention time (min) 8	LCL S/N PtP[d] 9	recovery[i] (%) 10	precision[j] (%) 11	measurement uncertainty[k] (%) 12
thiacloprid	$C_{10}H_9ClN_4S$	$[M + H]^+$	253.0315		253.0315	S	3.28	38 (5)	98.5	12.2	26.6
thiamethoxam	$C_8H_{10}ClN_5O_3S$	$[M + H]^+$	292.0271		292.0271	S	2.15	19 (5)	88.0	13.5	30.2
thiazopyr	$C_{16}H_{17}F_5N_2O_2S$	$[M + H]^+$	397.1009		397.1009		6.88	43 (5)	100.7	13.6	28.9
thiodicarb	$C_{10}H_{18}N_4O_4S_3$	$[M + H]^+$	355.0568		355.0568	E	4.10	50 (5)	101.4	10.5	21.1
thiofanox[f]	$C_9H_{18}N_2O_2S$	$[M + H]^+$	219.1167		219.1167		4.45	**6** (**100**)	100.1	16.1	32.6
thiofanox sulfone	$C_9H_{18}N_2O_4S$	$[M + H]^+$	251.1066		251.1066		2.83	3 (5)	101.6	10.1	20.4
thiofanox sulfoxide	$C_9H_{18}N_2O_3S$	$[M + H]^+$	235.1116	$C_3H_6NOS^+$	104.0170	S	2.28	22 (5)	96.5	11.2	22.5
tolylfluanid[e]	$C_{10}H_{13}Cl_2FN_2O_2S_2$	$[M + H]^+$	346.9858	$C_8H_7Cl_2FNS^+$	237.9660	E	6.96	**3** (**25**)	98.2	**42.4**	**88.3**
tralkoxydim	$C_{20}H_{27}NO_3$	$[M + H]^+$	330.2069		330.2069		5.46	21 (5)	**112.1**	10.5	24.0
trichlorfon	$C_4H_8Cl_3O_4P$	$[M + H]^+$	256.9304	A+2[g]	258.9275	S	2.38	3 (5)	100.1	**24.4**	**48.8**
tricyclazole	$C_9H_7N_3S$	$[M + H]^+$	190.0439		190.0439		2.92	50 (5)	97.2	13.6	27.5
trietazine	$C_9H_{16}ClN_5$	$[M + H]^+$	230.1172		230.1172		5.95	40 (5)	101.0	10.4	20.9
trifloxysulfuron	$C_{14}H_{14}F_3N_5O_6S$	$[M + H]^+$	438.0695		438.0695	E	2.93	44 (5)	102.8	14.2	29.0
triforine	$C_{10}H_{14}Cl_6N_4O_2$	$[M + H]^+$	432.9326	$C_9H_{12}Cl_5{}^{35}Cl^{37}N_3O^+$	389.9082	S	4.70	9 (5)	102.3	12.8	28.1
trimethacarb	$C_{11}H_{15}NO_2$	$[M + H]^+$	194.1181	$C_9H_{13}O^+$	137.0966		4.78	10 (5)	101.1	9.9	20.0
zinophos[e]	$C_8H_{13}N_2O_3PS$	$[M + H]^+$	249.0463		249.0463	E	5.06	**8** (**25**)	102.7	**21.0**	**42.2**
zoxamide	$C_{14}H_{16}Cl_3NO_2$	$[M + H]^+$	336.0325	A+2[g]	338.0295		6.77	33 (5)	103.3	**20.1**	**40.3**

[a] Column number. Bold pesticides typically have poor sensitivity. [b] Spinosad is a mixture of spinosyns A and D. Quantification can be based on either one. [c] Elemental composition was determined by the MassLynx Elemental Composition calculator, but it was not able to be confirmed by the chemical structure related to possible fragmentation. [d] Signal-to-noise (peak-to-peak) ratio was determined at the lowest concentration level (μg/kg, in parentheses) in a strawberry matrix. Bold and underlined pesticides have signal-to-noise ratios were determined to be above 5 μg/kg. [e] Method performance was based on three spike levels, i.e., 90.0, 240.0, and 400.0 μg/kg, due to its poor sensitivity. [f] Method performance was based on two spike levels, i.e., 240.0 and 400.0 μg/kg, due to its poor sensitivity. [g] Ion with one ^{37}Cl was selected for quantification. [h] NA, not available. S or E indicates either ion suppression (S) or enhancement (E) in at least one of the matrices. [i] Bold and underlined pesticides have recoveries not in the range of 81−110%. [j] Bold and underlined pesticides are of intermediate precision, >20%. [k] Bold and underlined pesticides have MU > 40%.

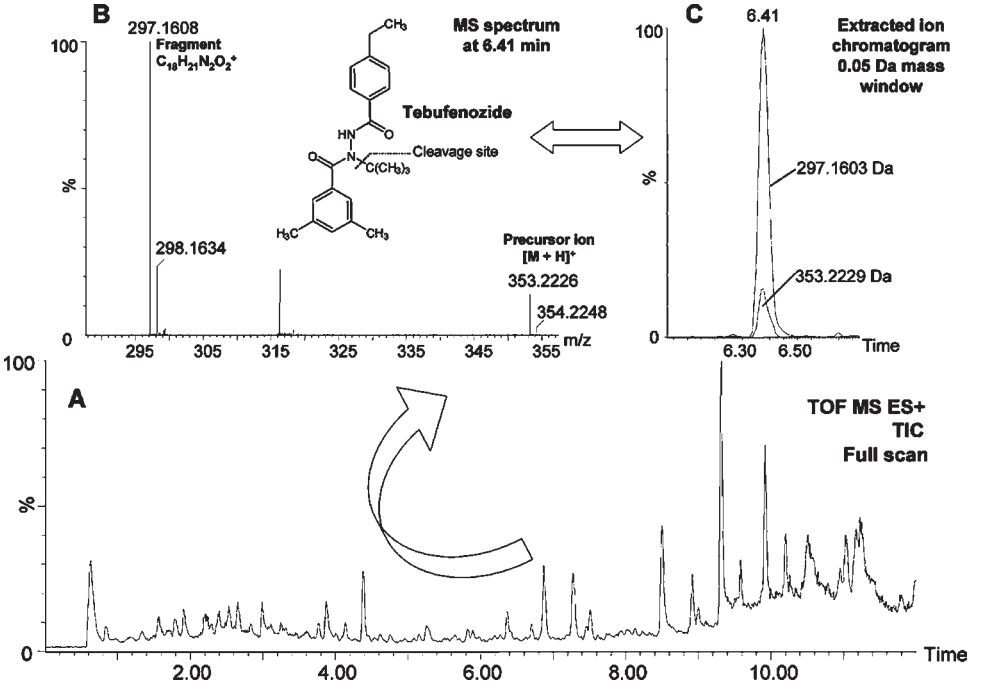


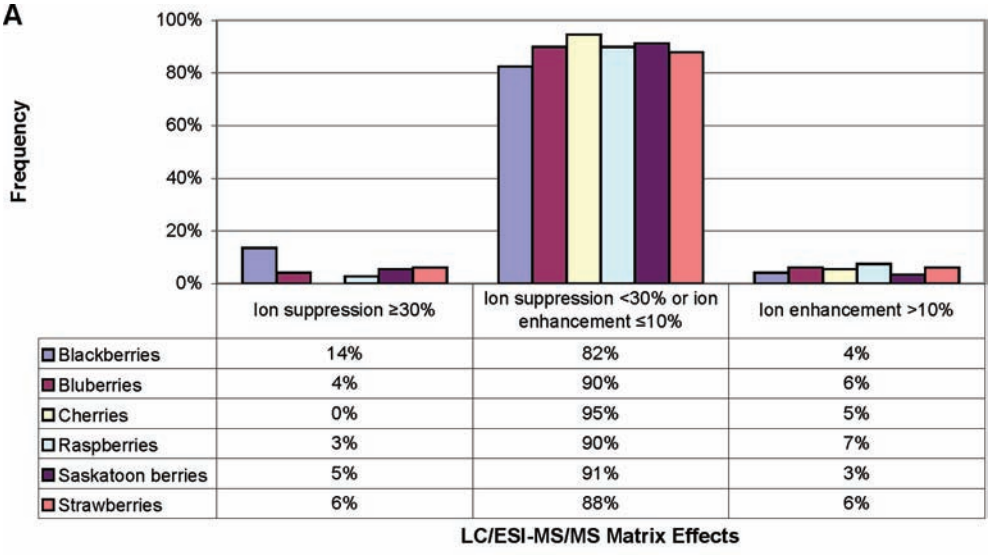
Figure 2. UHPLC QqTOF MS chromatogram and spectrum of pesticides (10 μg/kg) spiked in strawberry: (**A**) total ion current chromatogram (TIC); (**B**) mass spectrum of tebufenozide and its fragmentation pattern and fragment elemental composition; (**C**) extracted ion chromatogram of tebufenozide with a mass error window of 50 mDa.

column 3) in the presence of ammonium acetate (10 mM) in UHPLC mobile phase. The target ions listed in **Table 2** (column 6) were used to extract chromatograms for quantification. Twenty-seven pesticides experienced significant in-source decay or in-source collision-induced dissociation, and consequently their fragments became the predominate ions that were chosen for quantification to lower the method detection limits. The possible elemental compositions of fragments (**Table 2**, column 5) were determined using MassLynx Elemental Composition, isotopical pattern (or i-FIT), and/or chemical structure as described elsewhere (*13*).

UHPLC (Acquity UPLC) served as a fast LC and demonstrated its efficiency to separate 147 pesticides using a UPLC BEH C_{18} column in a relatively short period of time and, therefore, to increase sample throughput. The peak shapes were of Gaussian distribution with baseline peak width between 5 and 10 s, and retention times proved to be very reproducible at under $\pm$0.2 min within- and between-batches. All pesticides, expect for dodemorph (10.27 min), were eluted between 2 and 10 min with a total run time of 14 min. The UHPLC QqTOF MS run time was two-fifths that of the LC/ESI-MS/MS. **Figure 2** shows an example of total ion current (TIC) chromatogram (**Figure 2A**) of pesticides (10 μg/kg) spiked in strawberry. The chromatograms of tebufenozide (**Figure 2C**) were extracted from TIC (**Figure 2A**) on the basis of exact masses, that is, either m/z 353.2229 or 297.1603. The combined spectrum (**Figure 2B**) from peaks at 6.41 min (**Figure 2C**) provided accurate masses of ions, which allowed for identification of both the precursor ion ($[M + H]^+$) of tebufenozide and its fragment ($C_{18}H_{21}N_2O_2^+$).

Matrix Effects and Calibration Curves. It was commonly known that matrix effects, resulting in either ion enhancement or suppression, were one of the major challenges for quantification when ESI was used to couple an LC to a mass spectrometer. Matrix effects might vary from sample to sample and ultimately affected the LC/ESI-MS/MS and UHPLC QqTOF MS quantitative results. In this study, matrix effects (**Figure 3**) were evaluated by comparing the responses of pesticides in sample extracts (post extraction spike) to those pesticide standards prepared in solvent buffer at the same concentration level, for example, 100 μg/kg equivalent in samples. **Table 1** (column 11) and **Table 2** (column 7) indicated the pesticides that might encounter either ion suppression or enhancement in at least one of six berry matrices. When injected to LC/ESI-MS/MS, 82−95% of the pesticides in all six berry matrices experienced ion suppression $<30\%$ or enhancement $\leq 10\%$. As a comparison, when injected to UHPLC QqTOF MS, 73−82% of the pesticides experienced the same effects (**Figure 3**). About 10% fewer pesticides had $\geq 30\%$ suppression or $>10\%$ enhancement by LC/ESI-MS/MS than UHPLC QqTOF MS. This was expected because an additional 6 times sample extract dilution and small volume injection (i.e., 5 μL) were used in LC/ESI-MS/MS analysis. Overall, matrix effects were compensated for or reduced by the uses of matrix-matched standard calibration curves and/or isotopically labeled standards (**Figure 1C**), and, therefore, the quantitative accuracy was improved.

Method Validation and Method Performance. Both LC/ESI-MS/MS and UHPLC QqTOF MS methods were validated according to a statistical experimental design or the nested design, which included four factors, that is, pesticide concentrations or spike levels, matrix effects, day-to-day variation, and within-day variation. The designed experiment provided validation data to study and to evaluate method performance parameters that covered accuracy expressed as overall recovery, intermediate precision, and measurement uncertainty (MU). Pesticides were spiked into six berry matrices at 10, 90, 240, and 400 μg/kg in triplicate, and each experiment was repeated on a separate day. The performance parameters were calculated using a compiled SAS statistical program. Detailed calculations and equations were described elsewhere (*10*−*12*). The method performance results are summarized in **Table 1** (columns 14−16) and **Table 2** (columns 10−12) and are depicted in **Figure 4**. Generally, 95% of the pesticides (**Figure 4A**) had recoveries between 81 and 110% by both LC/ESI-MS/MS and UHPLC QqTOF MS. However, LC/ESI-MS/MS demonstrated better intermediate precision and less



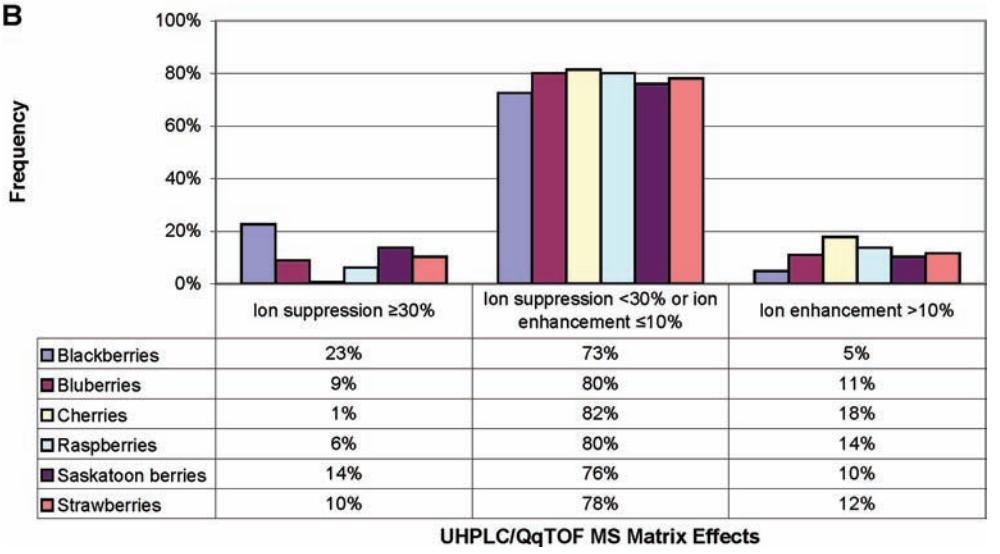


Figure 3. Matrix effects: (**A**) LC/ESI-MS/MS (data from 148 pesticides); (**B**) UHPLC QqTOF MS (data from 146 pesticides). Aclonifen was not included due to its poor sensitivity. Fenpropidin was not included due to interference. Pesticides were spiked at 100 μg/kg equivalent in samples.

measurement uncertainty than UHPLC QqTOF MS. For example, 69% of the pesticides had intermediate precision ≤10% by LC/ESI-MS/MS, whereas this was only 12% by UHPLC QqTOF MS (**Figure 4B**). Consequently, 61% of the pesticides possessed MU ≤ 20% by LC/ESI-MS/MS compared to 10% by UHPLC QqTOF MS (**Figure 4C**). LC/ESI-MS/MS successfully quantified up to 97% of the pesticides with MU ≤ 50%, whereas UHPLC QqTOF MS was up to 89% in the same limit, which was recommended as a default value in European Union Document SANCO/2007/3131 for pesticide analysis and enforcement decisions (MRL-exceedances) (*18*). The validation data and results indicated that LC/ESI-MS/MS was superior to UHPLC QqTOF MS for quantification.

Sensitivity. The method sensitivity was evaluated according to the signal-to-noise (S/N) ratios (peak-to-peak) at the lowest concentration level (**Table 1**, column 13, and **Table 2**, column 9). Generally, LC/ESI-MS/MS was at least 10 times more sensitive than UHPLC QqTOF MS. Most pesticides were able to be detected and quantified below or at 5 μg/kg, except for aclonifen and chlorthiamid by LC/ESI-MS/MS, and aclonifen, benoxacor, chlorbromuron, chlorthiamid, cyanofenphos, diclocymet, haloxyfop, isocarbamide, linuron, metolcarb, molinate, oxamyl-oxime, prodiamine, pyridalyl, quizalofop, thiofanox, tolylfluanid, and zinophos by UHPLC QqTOF MS.

Problematic Pesticides. Pesticides, which had MU > 50% by LC/ESI-MS/MS analysis, consisted of chlorthiamid, flucarbazone, pyridalyl, pyridate, and quizalofop. Pesticides, which showed MU > 50% by UHPLC QqTOF MS analysis, included aclonifen, benoxacor, chlorbromuron, chlorthiamid, cyanofenphos, diclocymet, etofenprox, fenhexamid, flucarbazone, methomyl, picolinafen, prodiamine, pyridalyl, pyridate, quizalofop, and tolylfluanid. Those pesticides were problematic pesticides by LC/ESI-MS/MS and/or UHPLC QqTOF MS as a result of insufficient sensitivity, low or high recovery, and/or poor repeatability. Further study on extraction and/or the applications of different mass spectrometric techniques, especially different ionization methods, is necessary to obtain better quantitative results.

In conclusion, the LC/ESI-MS/MS method reported in this paper was able to determine 148 pesticides in berry fruits in a range from 5 to 500 μg/kg with the lowest concentration level at 5 μg/kg for all pesticides (S/N > 10), except for aclonifen and chlorthiamid. Most pesticides (95%) by LC/ESI-MS/MS had overall recoveries in a range from 81 to 110%; 98% of the

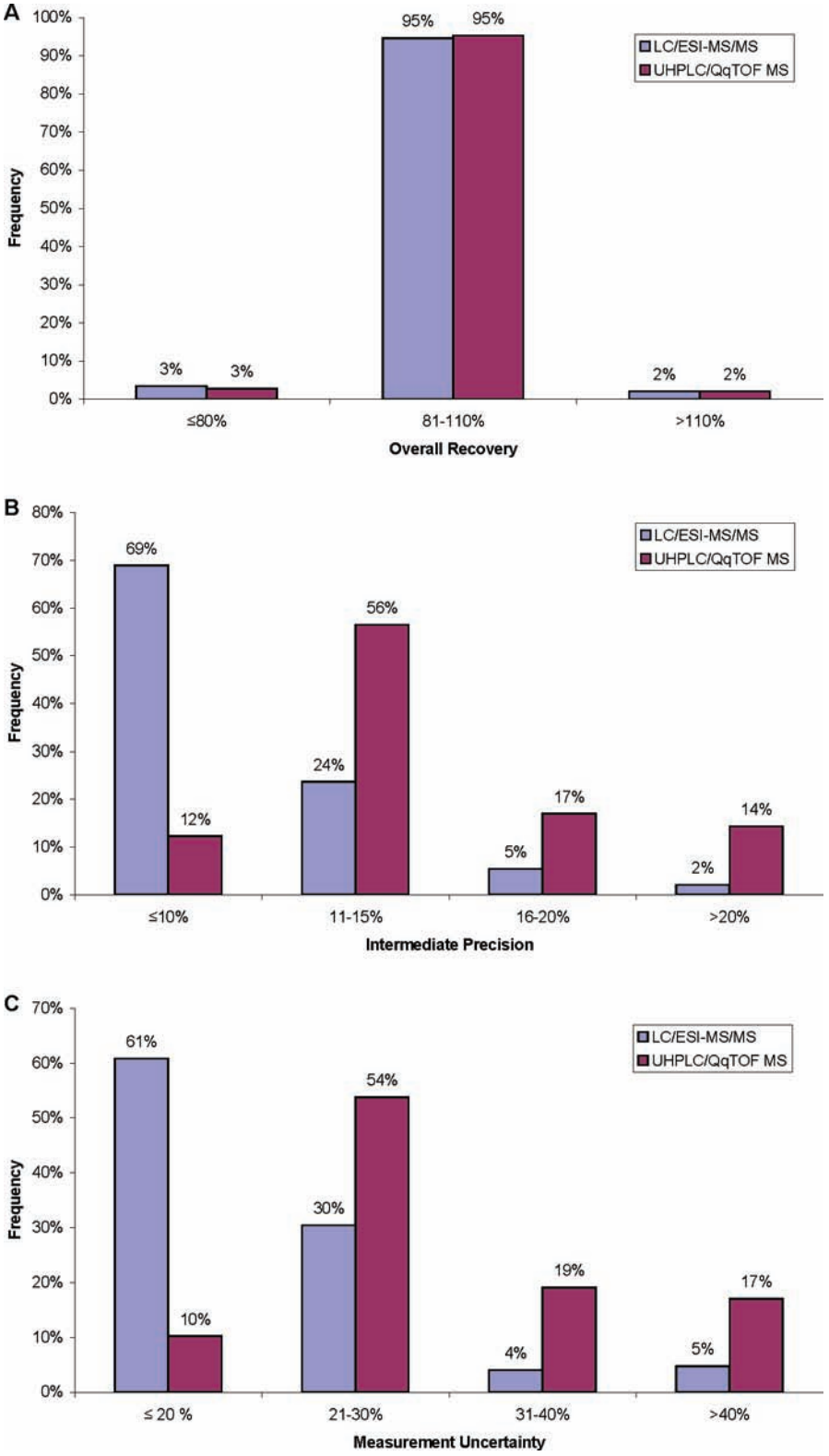


Figure 4. LC/ESI-MS/MS (148 pesticides) and UHPLC QqTOF MS (147 pesticides, fenpropidin excluded due to interference) method performance: (**A**) overall recovery; (**B**) precision; (**C**) measurement uncertainty.

pesticides had method intermediate precisions of ≤20%; and 95% of the pesticides showed measurement uncertainties of ≤40%. The UHPLC QqTOF MS method was able to determine the same group of pesticides, of which 88% were possible to detect at 5 μg/kg. Most pesticides (95%) by UHPLC QqTOF MS had overall recoveries in a range from 81 to 110%; 86% of the pesticides had method intermediate precisions of ≤20%; and 83% of the pesticides showed measurement uncertainties of ≤40%. LC/ESI-MS/MS proved to be the first choice for quantification or pretarget analysis due to its superior sensitivity and good repeatability. UHPLC QqTOF MS provided accurate mass measurement and was a practical tool for post-target screening and confirmation. LC/ESI-MS/MS and UHPLC QqTOF MS were complementary to each other for pesticide analysis.

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