

Multiresidue Pesticide Analysis in Fresh Produce by Capillary Gas Chromatography–Mass Spectrometry/Selective Ion Monitoring (GC-MS/SIM) and –Tandem Mass Spectrometry (GC-MS/MS)[†]

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A multiresidue method for the analysis of pesticides in fresh produce has been developed using salt-out acetonitrile extraction, solid-phase dispersive cleanup with octadecyl-bonded silica (C₁₈), and graphitized carbon black/primary–secondary amine (GCB/PSA) sorbents and toluene, followed by capillary gas chromatography–mass spectrometry in selected ion monitoring mode (GC-MS/SIM) or –tandem mass spectrometry (GC-MS/MS). Quantitation was determined from calibration curves using matrix-matched standards ranging from 3.3 to 6667 ng/mL with $r^2 > 0.99$, and geometric mean limits of quantitation were typically 8.4 and 3.4 $\mu\text{g}/\text{kg}$ for GC-MS/SIM and GC-MS/MS, respectively. Identification was determined by using target and qualifier ions and qualifier-to-target ratios for GC-MS/SIM and two ion transitions for GC-MS/MS. Fortification studies (10, 25, 100, and 500 $\mu\text{g}/\text{kg}$) were performed on 167 organohalogen, organophosphorus, and pyrethroid pesticides in 10 different commodities (apple, broccoli, carrot, onion, orange, pea, peach, potato, spinach, and tomato). The mean percent recoveries were 90 ± 14 , 87 ± 14 , 89 ± 14 , and $92 \pm 14\%$ for GC-MS/SIM and 95 ± 22 , 93 ± 14 , 93 ± 13 , and $97 \pm 13\%$ for GC-MS/MS at 10, 25, 100, and 500 $\mu\text{g}/\text{kg}$, respectively. GC-MS/MS was shown to be more effective than GC-MS/SIM due to its specificity and sensitivity in detecting pesticides in fresh produce samples. The method, based on concepts from the multiresidue procedure used by the Canadian Food Inspection Agency and QuEChERS (*Quick, Easy, Cheap, Effective, Rugged, and Safe*), was shown to be efficient in screening, identifying, and quantitating pesticides in fresh produce samples.

KEYWORDS: Multiresidue methods; GC-MS/SIM; GC-MS/MS; modified QuEChERS

INTRODUCTION

Pesticides are considered to be necessary and essential for food production and protection, but there is public concern about their presence in foods. Laboratories must use cost-effective procedures that reliably detect and measure as many pesticides as possible. The most effective approach for pesticide residue analysis is to apply multiresidue methods that provide the capability to identify and quantitate a large number of pesticides in different types of food matrices. The first notable pesticide method was the Mills method developed at the U.S. Food and

Drug Administration, which utilizes acetonitrile salt-out extraction (1). Many other notable procedures based on acetonitrile salt-out extraction have been developed in government laboratories that addressed pesticide analysis for risk exposure assessment and residue tolerance enforcement (2–12). Fillion et al. (4, 6) developed a procedure using salting-out acetonitrile extraction, followed by a dual cleanup procedure involving octadecyl-bonded silica (C₁₈) and tandem graphitized carbon black/aminopropyl-bonded silica (GCB/ABS) solid-phase extraction (SPE) and toluene, and analysis by capillary gas chromatography–mass spectrometry in selective ion monitoring (GC-MS/SIM) or high-performance liquid chromatography with postcolumn derivatization/fluorescence detection (HPLC-PCD/FLD). The method is currently used by the Canadian Food

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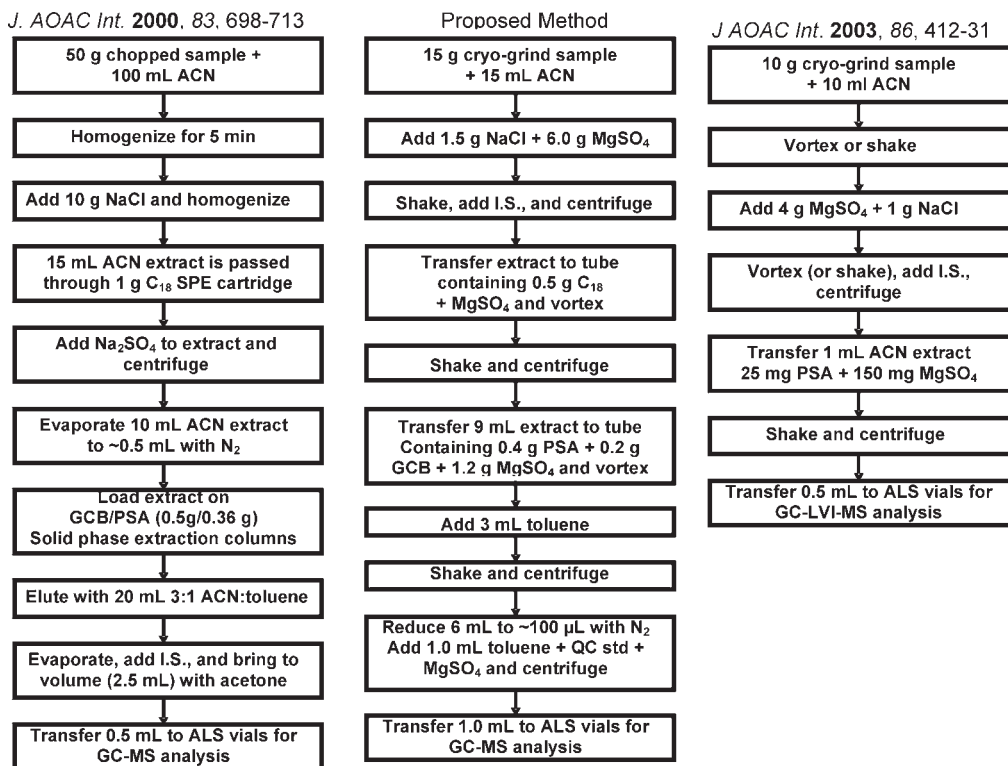


Figure 1. Flow diagrams describing and comparing the procedures of Fillion et al. (6) (left), nonbuffered QuEChERS (15) (right), and the proposed method (middle). I.S., internal standard; QC, quality control; ALS, automated liquid sample; LVI, large volume injection.

Inspection Agency to screen for 285 pesticides in fresh fruits and vegetables (12). The success of this multiresidue procedure has led other pesticide groups such as Pang et al. (11) and Okimashi et al. (10, 13, 14) to screen for larger numbers and different classes of pesticides using GC, GC-MS/SIM, GC-tandem mass spectrometry (GC-MS/MS), and high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS).

Anastassiades et al. (15) developed a multiresidue procedure known as QuEChERS (*Quick, Easy, Cheap, Effective, Rugged, and Safe*) to optimize extraction and cleanup procedures with an emphasis on minimizing cost, sample size, and preparation time. QuEChERS involves the extraction of pesticides from a homogenized composite sample using acetonitrile and salts in a centrifuge tube, followed by a solid-phase dispersive cleanup step performed in a second test tube containing sorbents to remove interfering matrix components. The authors (15) reported excellent recoveries and repeatabilities for pesticides in fruits and vegetables. To demonstrate the speed in sample preparation, Schenck and Hobbs (16) were able to prepare a complete batch of 6–12 QuEChERS in 20–30 min. Versions of QuEChERS utilizing different buffering salts have been approved as official pesticide residue methods by AOAC International (17, 18) and the European Community (19).

QuEChERS is a flexible procedure, which allows it to be modified for specific purposes. During the solid-phase dispersive cleanup stage of QuEChERS, many sorbent combinations such as C₁₈, primary–secondary amine, graphitized carbon black, florisol, and chlorophyll-removing sorbents have been used to improve the cleanup (20–26). This work combines the benefits of the efficiency of QuEChERS and the effective cleanup procedures used by Fillion et al. (4, 6), in which two solid-phase dispersive cleanup steps are used involving (1) octadecyl-bonded silica (C₁₈) and (2) graphitized carbon black/primary–secondary amine-bonded silica (GCB/PSA) sorbents and toluene. **Figure 1** shows a schematic listing and comparisons of the proposed method with

the Fillion et al. and nonbuffered QuEChERS procedures. The method described is intended to be used for routine monitoring for pesticides in fruits and vegetables using GC-MS/SIM and GC-MS/MS. GC equipped with a single-quadrupole mass spectrometer (GC-MS) is commonly used in laboratories to analyze semivolatile pesticides because of their low cost, reliability, and effectiveness. The instrument is commonly operated in selective ion monitoring mode (GC-MS/SIM) because of its increased sensitivity. Several laboratories have developed multiresidue procedures for the analysis of pesticides in fresh produce (4–12, 27, 28). Although GC-MS/SIM provides qualitative and quantitative MS information on pesticide residues in foods, there are difficulties with this approach. Official pesticide identification criteria in SIM mode call for one target and three qualifier ions at the proper ion ratios in combination with the correct GC retention time (29). However, the ion abundance associated with the pesticide analyte in SIM mode is not specific and could originate from components from the sample matrix, which could lead to false positives or negatives of a pesticide. The analyte can no longer be correctly identified when ion ratios are altered due to component contributions from the matrix.

To improve the selectivity of GC-MS detection, GC equipped with triple-quadrupole or tandem mass spectrometry (GC-MS/MS) can operate in selective or multiple reaction monitoring mode, where the precursor ion (or ions) of the target analyte from the matrix is isolated from the other analytes in the first quadrupole and is allowed to enter a second quadrupole, where it undergoes collision-induced dissociation and fragments into various product ions. Only the selected product ions unique to the target analyte are allowed to enter the third quadrupole, where they are filtered and finally detected. The selection of the product ions from the analyte precursor ion (or ions) results in a process that is more specific and sensitive due to less background than GC-MS/SIM. Identification of the analyte is usually determined by the ratio of the two product ions generated from the analyte

precursor ion or ions, which is more reliable than the qualifier-to-target ion ratios used in GC-MS/SIM. In multiple reaction monitoring mode, several analytes can be simultaneously selected and screened so that multiresidue analysis by GC-MS/MS can be accomplished. There are several groups that have already developed multiresidue pesticide procedures, including QuEChERS, using GC-MS/MS for a variety of food products, such as fresh produce (13, 24, 25, 30–34).

The purpose of this work is to present, evaluate, and validate a procedure based on the successes of the Fillion et al. and QuEChERS methods. We have already applied the modified procedure for the analysis of organophosphorus and organohalogen pesticides on fresh produce, infant foods, and powdered ginseng root (35–37); this involved using GC-pulsed flame photometric detection (GC-PFPD), GC-halogen selective detection (GC-XSD), GC-MS/SIM, and GC-flame photometric detection (GC-FPD). In this work, we expand the method to the analysis of organohalogen, organophosphorus, and pyrethroid pesticides, their isomers, and metabolites by GC-MS/SIM and GC-MS/MS.

MATERIALS AND METHODS

Reagents and Materials. The majority of the pesticide standards were obtained from the U.S. Environmental Protection Agency National Pesticide Standard Repository (U.S. EPA, Ft. Meade, MD), whereas pesticides unavailable from the Repository were obtained from ChemServices (West Chester, PA), Sigma/Aldrich/Fluka Chemicals (St. Louis, MO), or Crescent Chemicals (Islandia, NY). Solvents such as ACS- or pesticide-grade acetonitrile, acetone, and toluene; HPLC-grade water; Nalgene Teflon centrifuge tubes with screw caps; and ACS-grade anhydrous magnesium sulfate and sodium chloride were purchased from Fisher Scientific (Pittsburgh, PA). The internal standard, tris(1,3-dichloroisopropyl) phosphate, was purchased from TCI America (Portland, OR), and the quality control standards, naphthalene-*d*₈, acenaphthalene-*d*₁₀, phenanthrene-*d*₁₀, and chrysene-*d*₁₂, were purchased from Sigma/Aldrich/Fluka Chemicals (Milwaukee, WI). Octadecyl-bonded silica (C₁₈) and primary–secondary amine-bonded silica (PSA) sorbents were purchased from Varian (Harbor City, CA) and United Chemical Technologies (Bristol, PA). Graphitized carbon black (GCB) sorbent was purchased from Supelco (Bellefonte, PA) and United Chemical Technologies. The magnesium sulfate was baked at 550 °C in a muffle oven for at least 8 h to remove plasticizers.

Preparation of Standard and Calibration Solutions. Standard solutions were prepared in acetonitrile and toluene for fortification and calibration standards, respectively. Individual pesticide standards were prepared by dissolving 25–100 mg of the pesticide in 25 mL in each solvent. The standards were stored in amber glass bottles with Teflon-lined screw caps and stored at –40 °C until further use. The standards used for calibration or fortification were prepared by making 250 mL stock solutions containing approximately 50 pesticides by adding the appropriate volume of each pesticide standard to a 250 mL volumetric flask and adjusting the final volume with toluene or acetonitrile to prepare 20 µg/mL stock solutions. Successive dilutions of the stock pesticide standards were used to prepare 6.67, 3.33, 1.67, 0.833, 0.333, 0.167, 0.083, 0.033, 0.017, 0.0083, 0.0033, and 0.00167 µg/mL calibration standards in toluene (50 mL standards each). Fortification solutions were prepared by diluting the 20 µg/mL acetonitrile stock solutions to 7.5, 1.5, and 0.5 µg/mL with acetonitrile. The internal and quality control standards were prepared by dissolving tris(1,3-dichloroisopropyl) phosphate to a 3.4 µg/mL working solution in acetonitrile and the deuterated polycyclic hydrocarbons to a 20 µg/mL working solution in toluene. Care must be taken to ensure that tris(1,3-dichloroisopropyl)phosphate is not an incurred residue by pre-screening samples without addition of the standard. Naphthalene-*d*₈, acenaphthalene-*d*₁₀, phenanthrene-*d*₁₀, and chrysene-*d*₁₂ were used as quality control standards to identify any changes in analyte peak shapes and chromatographic performance.

Sample Preparation. The middle flowchart in Figure 1 of the proposed method is shown to illustrate the overall procedure to prepare

the sample for GC-MS/SIM and GC-MS/MS analysis. Pesticide-free produce samples (10 pounds each of bell pepper, broccoli, cantaloupe, carrot, onion, orange, peach, potato, spinach, and tomato) purchased from local markets were ground with dry ice using a Blixer 4 V blender (Robot Coupe, USA, Inc., Ridgeland, MS); the homogenized composites were stored in Mason jars with metal screw caps or in freezer plastic bags and stored at –40 °C until further use (the jars and freezer bags were left open to allow for any trapped CO₂ to escape before containers were capped or sealed before freezing). A portion of the sample, 15 g, was weighed into 50 mL Teflon centrifuge tubes (Nalgene, Rochester, NY). Acetonitrile (15 mL), anhydrous magnesium sulfate (6.0 g), and sodium chloride (1.5 g) were added to the homogenate and shaken vigorously by hand for 2 min. An internal standard, 500 µL of a 3.4 µg/mL solution of tris(1,3-dichloroisopropyl) phosphate, was added to the mixture. The mixture was centrifuged (ThermoElectron Corp., Milford, MA) at 4500 rpm for 5 min to separate the organic acetonitrile phase from the aqueous phase and the solid plug. The upper layer (~12 mL) of the acetonitrile supernatant was transferred to a second centrifuge Teflon tube containing 500 mg of C₁₈ sorbent and 1.2 g of anhydrous magnesium sulfate, and the tube was shaken for 1 min and centrifuged at 4500 rpm for 5 min. The extract, 9.0 mL, was quantitatively transferred into another 50 mL Teflon centrifuge tube containing 400 mg of PSA sorbent, 200 mg of GCB, and 1.2 g of anhydrous magnesium sulfate. The centrifuge tube was vortexed for approximately 15 s, 3.0 mL of toluene was added, and the tube was shaken vigorously for 2 min. The centrifuge tube was centrifuged at 4500 rpm for 5 min. The extract (6.0 mL) was transferred to a clean 15 mL glass centrifuge tube, and the extract volume was reduced using a nitrogen evaporator (Organomation Associates, Berlin, MA) to ~100 µL in a 35 °C water bath. To the centrifuge tube were added 1.0 mL of toluene and 25 µL of quality control solution (20 µg/mL deuterated polycyclic hydrocarbons). Approximately 50 mg of anhydrous magnesium sulfate was added, and the centrifuge tube was vortexed and centrifuged at 1500 rpm for 5 min. The clarified extract was transferred to automated liquid sample (ALS) vials via Pasteur pipet.

Fortification Studies. Cryo-ground pesticide-free produce was prepared, and the samples were stored in a –40 °C freezer until further use. Samples were screened for incurred residues by screening the matrix blanks. These samples were fortified with 300 µL of 0.5 µg/mL, 750 µL of 0.5 µg/mL, 1.0 mL of 1.5 µg/mL, or 1.0 mL of 7.5 µg/mL (solutions prepared in acetonitrile) to form fortified samples of concentrations of 10, 25, 100, and 500 µg/kg, respectively. The samples were vortexed vigorously to ensure thorough mixing of the pesticide with the composite and prepared according to the proposed procedure in the previous section.

Preparation of Matrix-Matched Standards. For the quantitative analysis of pesticides in produce samples, matrix-matched calibration standards were used rather than standards prepared in solvent to compensate for matrix enhancement effects (40). The coextractives in the sample matrix have been shown to cause an enhancement of the pesticide peak response in the matrix compared to that of the same amount of the pesticide in the matrix-free solvent. Pesticide-free matrices were prepared by processing the composite and adding the internal standard as described under Sample Preparation. After the 6 mL acetonitrile/toluene composite extract had been reduced to ~100 µL, 1.0 mL of the calibration standard (6.67, 3.33, 1.67, 0.833, 0.333, 0.167, 0.083, 0.033, 0.017, 0.0083, and 0.0033 µg/mL) and 25 µL of the quality control standard (20 µg/mL), both prepared in toluene, were added to the evaporated extract. Approximately 50 mg of anhydrous magnesium sulfate was added, and the centrifuge tube was vortexed and centrifuged at 1500 rpm for 5 min. The clarified matrix-matched standard was transferred to ALS vials via Pasteur pipet.

GC-MS/SIM Analysis. An Agilent 6890N gas chromatograph was equipped with an Agilent 5973 mass selective detector (MSD, Agilent Technologies, Little Falls, DE) and fitted with a deactivated guard column (5 m × 0.25 mm i.d., Restek Corp., Bellefonte, PA) and HP-5MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness, Agilent Technologies). The 5973 MSD was upgraded with software and hardware components to allow up to 60 ions per time segment when operating in the SIM mode. The temperature program consisted of a ramp from 105 °C (1 min hold) to 130 °C at a rate of 10 °C/min, increased to 230 °C at 4 °C/min, followed by a final ramp to 290 °C at 20 °C/min (7 min hold) using He as the carrier gas at a flow rate of 1.9 mL/min. The MSD was operated in electron impact (EI) mode at 70 eV. The injector, transfer line, MSD source, and

quadrupole temperatures were 250, 290, 230, and 150 °C, respectively. The produce extracts, standards, and blanks were injected (1 μ L) into the GC operated in pulsed splitless mode (pulsed pressure = 35.0 psi; pulsed time = 2.00 min) using an Agilent 7683 series autoinjector. The MSD system was routinely programmed in selective ion monitoring (SIM) mode using one target and three qualifier ions as listed in Table 1. Quantitation by GC-MS/SIM was based on the peak area ratios of the target ions of the analyte to that of the internal standard, tris(1,3-dichloroisopropyl) phosphate, and compared to concentrations of matrix-matched calibration standards using ChemStation G1701DA rev D.03.00 software. Identification was established by the retention time of the target ion and the presence of two to three qualifier-to-target ratios as given in Table 1 of the Supporting Information. The target and qualifier abundances were determined by injection of individual pesticide standards using full scan with mass/charge scan ranging from m/z 40 to 500. The qualifier-to-target percentage was then determined by dividing the abundance of the selected qualifier ions by that of the target ion multiplied by 100%. Identification of pesticides in fortified and incurred samples by GC-MS/SIM was determined by comparing the percentage ratios of the qualifier ion to target ions obtained from matrix-matched standards and the criteria for identification established by the European Union (19).

GC-MS/MS Analysis. A Varian CP-3800 series gas chromatograph coupled with a Varian 1200 L triple-quadrupole mass spectrometer and a CTC COMBI PAL autosampler (Varian Inc., Palo Alto, CA) were employed for all sample analyses. Analytes were separated with a Varian 30 m \times 0.25 mm \times 0.25 μ m, VF-5 fused silica capillary column preceded by a deactivated guard column (5 m \times 0.25 mm i.d., Restek Corp.). The column head pressure was set at 13.2 psi, and flow rate was 1.2 mL/min using He as the carrier gas. The column temperature was programmed as follows: the initial temperature was 105 °C for 6 min and increased to 130 °C at 10 °C/min, ramped to 230 °C at 4 °C/min and to 290 °C at 10 °C/min, which was held for 5.5 min. The total run time was 45 min. Injector temperature was maintained at 280 °C, and the injection volume was 1.0 μ L in the splitless mode. The ion source and transfer line temperatures were 240 and 300 °C, respectively. Electron multiplier voltage was set to 1400 V by automatic tuning. Argon was used as the collision gas for all MS/MS experiments and the pressure in the collision cell was set at 1.8 mTorr. The optimal two ion transitions (primary and secondary transitions of a precursor to product ion) for each pesticide were determined via collision tests. Determined precursor ion to product ion transitions and corresponding collision energies are listed in Table 1. Figure 1 of the Supporting Information shows a schematic of the MS/MS program used to detect the pesticides in multiple reaction monitoring mode. Varian Workstation software, version 6.9, was used for instrument control and data acquisition and processing. Quantitation by GC-MS/MS was based on the peak area ratios of the primary transition of the analyte product to that of the primary transition of the internal standard, tris(1,3-dichloroisopropyl) phosphate, and compared to concentrations of matrix-matched calibration standards using the Varian Workstation software. Identification of pesticides in fortified and incurred samples by GC-MS/MS was determined by comparing the ratio of the two transition (primary/secondary) results to matrix-matched standards and the criteria for identification established by the European Union (29).

Statistics Analysis, Principal Component Analysis (PCA), and Calculations. Averages and standard deviations from fortification studies and linear regressions and correlation coefficients for calibration curves were determined using Microsoft Excel 2003. Pesticide concentrations were quantitated against calibration curves of peak area response ratios of the primary ion transitions of the pesticide analyte to the internal standard (tris(1,3-dichloroisopropyl) phosphate) versus the concentration of pesticide calibration standards; GC-MS/SIM and GC-MS/MS data were processed with ChemStation G1701DA rev. D.03.00 and Varian Workstation, version 6.9, software, respectively. The recovery data from each fortification level were analyzed by a two-tailed Student's *t* test at the 95% confidence level. The data were grouped in eight sets, namely, four fortification levels each for SIM and MS/MS analysis modes. The data set for each set was tested for homogeneity of variance using an *F* test at the 95% confidence level. All calculations were performed using Microsoft Excel 2003. PCA was carried out using the Pirouette 4.0 software package (Informetrix Inc., Bothell, WA) to compare GC-MS/SIM and GC-MS/MS analyses of the fortification results obtained from the different produce commodities.

RESULTS AND DISCUSSION

Sample Extraction and Preparation. The proposed method outlined in Figure 1 (middle procedure) involves extraction of pesticides from cryo-ground fruit and vegetable samples with acetonitrile, sodium chloride, and magnesium sulfate. The extraction procedure is scaled-down and performed in a centrifuge tube and avoids the use of a large-volume blender, minimizing contamination from improperly rinsed blenders. Solid-phase dispersion is used for the cleanup, and it is also performed in centrifuge tubes by treating the acetonitrile extract with C₁₈-bonded silica, followed by a combination of GCB/PSA and toluene. These sorbents have been previously characterized to remove matrix coextractives such as organic acids, chlorophyll, pigments, lipids, and sterols that may interfere with GC-MS analysis (22, 40, 41).

The modified procedure performed in this study is based on the Canadian and QuEChERS methods. The Canadian procedure (Figure 1, left procedure) developed by Fillion et al. (4, 6) uses acetonitrile extraction with NaCl and cleanup with C₁₈ and tandem GCB/ABS solid-phase extraction cartridges with toluene elution. This procedure is currently used by the Canadian government and has been widely used and modified by other laboratories, which suggests the popularity and effectiveness of this method. The QuEChERS procedure (Figure 1, right procedure) developed by Anastassiades et al. (15) was developed to optimize pesticide multiresidue procedures by using lower sample sizes, reducing organic solvent consumption, eliminating the use of various types of glassware, and decreasing the costs in sample preparation. Whereas materials costs for typical multiresidue procedures are ~\$10 per sample using solid-phase extraction cartridges (38), materials for the QuEChERS and the proposed procedure using the modified Canadian and QuEChERS procedure cost about ~\$1–2 per sample, resulting in substantial savings.

The proposed procedure here is based on the benefits of both procedures, and this concept has already been adopted by Okihashi et al. (10). The work of Okihashi et al. suggested that the original QuEChERS procedure was not suitable for GC analysis; additional cleanup was required for effective GC analysis, and there was a need to incorporate the tandem solid-phase extraction cleanup procedure used by Fillion et al. (4, 6) in the sample preparation procedure. Their modification utilized the salt-out acetonitrile extraction of the sample with anhydrous magnesium sulfate and sodium chloride in a 50 mL centrifuge tube as described by the QuEChERS procedure, followed by cleanup using a tandem GCB/PSA SPE cartridge and the 3:1 acetonitrile/toluene elution described by the Canadian procedure. Okihashi et al. used the SPE cleanup procedure to remove matrix components such as chlorophyll, carotenoids, and acetonitrile/water-soluble coextractives such as sugars and salts. Their work resulted in effective methods for the determination of 180 pesticide residues in produce by GC-FPD and GC-MS/SIM (10) and 260 pesticides in produce by GC-MS/MS (13). The proposed method illustrated in Figure 1 follows more of the QuEChERS concepts for the cleanup and tries to take into account the concerns of Okihashi et al. by using two dispersive solid-phase cleanup steps (C₁₈ and PSA/GCB) instead of traditional solid-phase extraction and saving preparation time by eliminating the acetonitrile evaporation step prior to GCB/PSA SPE cleanup used in both the Fillion and Okihashi procedures. Enough toluene is added to the mixture to achieve a 3:1 acetonitrile/toluene mixture, the effective solvent ratio used in GCB/PSA SPE solvent elution (22, 40). Less acetonitrile solvent eliminates the need of

Table 1. Pesticide Name, Molecular Formula and Weight, GC-MS/SIM and GC-MS/MS Retention Times, Target and Qualifier Ions, Percentage of Qualifier-to-Target Ratios (GC-MS/SIM Only), Primary and Secondary Ion (Precursor→Product) Transitions, and Ion Ratios (GC-MS/MS Only) Used in the Study^a

pesticide	mol formula	mol wt	GC-MS/SIM						GC-MS/MS						
			RT	target	Q ₁	Q ₂	Q ₃	Q ₄	RT	primary	CE 1	secondary	CE 2	MRM	ion
			(min)	(T)	(%Q _i /T)	(%Q _i /T)	(%Q _i /T)	(%Q _i /T)	(min)	transition	(eV)	transition	(eV)	group	ratio
acenaphthene-d ₁₀	C ₁₂ D ₁₀	164.29	12.75	164	162 (91.1)	160 (41.1)	163 (14.5)	13.50	164→162	15	164→134	25	4	33	
acrinathrin	C ₂₆ H ₂₁ F ₆ NO ₅	541.45	36.64	181	208 (72.2)	209 (48.8)	289 (28.2)	37.31	181→152	15	290→93	10	29	1.9	
akton	C ₁₂ H ₁₄ Cl ₃ O ₃ PS	375.64	27.54	283	339 (91.6)	285 (70.6)	341 (58.8)	28.78	339→184	30	339→283	10	19	2.7	
alachlor	C ₁₄ H ₂₀ CINO ₂	269.77	22.56	160	188 (70.0)	146 (33.9)	237 (22.5)	23.74	188→130	35	160→77	45	13	3.5	
aldrin	C ₁₂ H ₆ Cl ₆	364.91	23.82	263	265 (66.3)	293 (42.6)	298 (27.4)	24.92	298→193	35	263→191	40	14	1.7	
allethrin	C ₁₉ H ₂₆ O ₃	302.41	26.70	136	123 (408.5)	168 (19.6)	107 (108.1)	28.04	123→81	5	136→108	5	18	7.5	
atrazine	C ₆ H ₁₄ CIN ₅	215.67	18.98	200	215 (54.4)	202 (30.3)	173 (21.5)	20.27	200→94	15	200→71	15	8	2.1	
azamethiophos	C ₉ H ₁₀ CIN ₂ O ₅ PS	324.68	31.67	215	183 (50.5)	155 (48.7)	324 (29.7)	33.45	324→171	25	215→171	10	24	2.4	
azinhos-ethyl	C ₁₂ H ₁₆ N ₃ O ₃ PS ₂	345.38	36.51	132	160 (68.7)	77 (66.0)	104 (19.4)	35.70	160→132	5	160→77	15	29	0.9	
azinhos-methyl	C ₁₀ H ₁₂ N ₃ O ₃ PS ₂	317.33	35.49	160	132 (86.4)	77 (71.5)	104 (22.5)	37.77	160→132	5	160→77	15	28	0.4	
α-BHC	C ₆ H ₆ Cl ₆	290.83	17.61	181	183 (94.1)	219 (97.3)	217 (75.5)	18.89	181→146	20	219→183	10	7	83	
β-BHC	C ₆ H ₆ Cl ₆	290.83	18.89	219	183 (99.7)	181 (96.1)	217 (47.3)	20.31	181→146	20	219→183	10	8	1.2	
δ-BHC	C ₆ H ₆ Cl ₆	290.83	20.33	219	183 (93.8)	181 (97.6)	217 (80.6)	22.09	181→146	20	219→183	10	11	3.1	
benfluralin	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	335.26	17.35	292	264 (18.1)	276 (13.8)	293 (12.7)	335 (4.9)							
bifenthrin	C ₂₃ H ₂₂ ClF ₃ O ₂	422.87	34.55	181	165 (21.6)	166 (25.6)	182 (14.5)	35.73	181→165	20	181→166	15	27	2.2	
bromophos	C ₁₀ H ₁₂ BrCl ₂ O ₃ PS	394.05	25.27	331	329 (84.3)	333 (30.3)	125 (31.2)	316 (5.7)	26.60	331→316	15	331→286	30	16	1.5
bromophos-ethyl	C ₈ H ₈ BrCl ₂ O ₃ PS	366.00	31.12	359	303 (79.6)	242 (39.2)	331 (40.1)	357 (84.2)	28.58	357→301	20	357→222	30	19	1.4
bromopropylate	C ₁₇ H ₁₆ Br ₂ O ₃	428.12	34.34	339	341 (198.7)	183 (70.4)	185 (68.3)	343 (96.0)	35.75	341→185	15	341→183	15	27	1.9
captafol	C ₁₀ H ₈ Cl ₄ NO ₂ S	349.06	32.89	79	77 (21.9)	80 (28.1)	183 (8.1)	34.74	151→79	20	79→77	15	26	12	
captan	C ₈ H ₈ Cl ₃ NO ₂ S	300.59	26.13	79	80 (25.3)	149 (16.9)	114 (12.11)	28.01	79→77	15	107→79	15	18	9.1	
carbophenothion	C ₁₁ H ₁₆ ClO ₂ PS ₃	326.74	31.75	342	157 (195.4)	199 (51.4)	121 (87.7)	33.49	342→157	5	342→143	15	25	1.1	
cis-chlordane	C ₁₀ H ₆ Cl ₈	409.78	27.47	373	375 (94.1)	377 (50.5)	371 (41.8)	28.54	373→266	35	373→337	10	19	17	
trans-chlordane	C ₁₀ H ₆ Cl ₈	409.78	26.80	373	375 (94.7)	377 (52.9)	371 (42.3)	29.13	373→266	15	373→232	40	20	4.0	
α-chlordene	C ₁₀ H ₆ Cl ₆	338.87	22.64	303	230 (66.1)	338 (27.9)	301 (57.8)	24.07	303→232	30	338→232	25	13	1.9	
β-chlordene	C ₁₀ H ₆ Cl ₆	338.87	24.10	338	230 (112.0)	303 (157.4)	301 (96.7)	25.48	230→160	20	338→230	20	14	2.7	
γ-chlordene	C ₁₀ H ₆ Cl ₆	338.87	23.97	338	230 (171.4)	303 (125.4)	301 (86.8)	25.48	230→160	20	338→230	20	14	1.9	
β-chlorfenvinphos	C ₁₂ H ₁₄ Cl ₃ O ₄ P	359.57	26.51	323	267 (143.7)	269 (101.2)	295 (35.5)	325 (65.9)	27.82	267→159	20	267→123	35	17	6.2
chlorobenzilate	C ₁₆ H ₁₄ Cl ₂ O ₃	325.19	30.15	251	253 (69.4)	139 (71.2)	111 (26.9)	31.91	251→139	20	251→111	45	23	1.9	
chloroneb	C ₈ H ₈ Cl ₂ O ₂	207.06	13.45	206	208 (68.2)	141 (48.1)	191 (182.4)	14.08	191→113	15	206→191	10	4	1.5	
chlorothalonil	C ₉ Cl ₄ N ₂	265.91	20.48	266	264 (76.4)	268 (46.7)	270 (10.3)	21.47	264→133	50	264→168	20	9	1.5	
chlorpyrifos	C ₉ H ₁₁ Cl ₃ NO ₃ PS	350.59	24.59	314	286 (40.7)	258 (58.1)	260 (40.2)	316 (72.6)	25.63	314→258	15	197→169	15	15	2.0
chlorpyrifos-methyl	C ₇ H ₇ Cl ₃ NO ₃ PS	322.54	22.28	286	288 (70.4)	125 (43.9)	197 (5.9)	290 (17.4)	23.35	286→93	20	286→241	15	12	8.8
chlorthiophos	C ₁₁ H ₁₅ Cl ₂ O ₃ PS ₂	361.25	31.09	269	325 (65.7)	360 (44.0)	297 (39.8)	32.47	325→269	10	325→271	20	23	2.5	
chrysene-d ₁₂	C ₁₈ D ₁₂	240.39	33.86	240	241 (20.0)	236 (23.0)	239 (12.2)	35.75	240→212	15	240→208	50	27	2.7	
coumaphos	C ₁₄ H ₁₆ ClO ₆ P	346.70	37.54	362	226 (43.9)	210 (36.3)	334 (16.8)	364 (44.8)	38.57	362→226	25	362→99	10	30	1.4
cyanazine	C ₉ H ₁₃ CIN ₆	240.68	24.70	225	212 (165.5)	240 (56.8)	198 (69.7)	26.03	198→91	10	138→69	15	15	6.5	
cyanophos	C ₉ H ₁₃ Cl ₂ O ₃ PS	243.22	19.59	243	109 (95.1)	125 (59.5)	180 (8.4)	20.83	243→127	20	243→79	25	9	5.6	
cyfluthrin 1	C ₂₂ H ₁₈ Cl ₂ FNO ₃	434.29	38.01	163	206 (61.9)	226 (57.0)	199 (50.1)	39.06	163→91	30	163→127	15	30	3.0	
cyfluthrin 2	C ₂₂ H ₁₈ Cl ₂ FNO ₃	434.29	38.14	163	206 (62.1)	226 (37.6)	199 (42.5)	39.19	163→91	30	163→127	15	30	3.0	
cyfluthrin 3	C ₂₂ H ₁₈ Cl ₂ FNO ₃	434.29	38.23	163	206 (68.0)	226 (44.1)	199 (39.4)	39.22	163→91	30	163→127	15	30	3.0	
cyfluthrin 4	C ₂₂ H ₁₈ Cl ₂ FNO ₃	434.29	38.28	163	206 (68.7)	226 (40.3)	199 (49.1)	39.25	163→91	30	163→127	15	30	3.0	
λ-cyhalothrin	C ₂₃ H ₁₉ ClF ₃ NO ₃	449.86	36.26	181	197 (77.2)	208 (56.1)	199 (26.5)	209 (46.6)	35.95	197→119	10	197→91	10	27	4.6
cypermethrin 1	C ₂₂ H ₁₉ Cl ₂ NO ₃	416.30	38.40	163	181 (89.0)	165 (66.8)	209 (30.4)	39.45	163→91	30	163→127	15	30	3.0	
cypermethrin 2	C ₂₂ H ₁₉ Cl ₂ NO ₃	416.30	38.53	163	181 (77.6)	165 (61.3)	209 (42.8)	39.58	163→91	30	163→127	15	30	3.0	
cypermethrin 3	C ₂₂ H ₁₉ Cl ₂ NO ₃	416.30	38.61	163	181 (73.1)	165 (55.2)	209 (21.9)	39.60	163→91	30	163→127	15	30	2.3	
cypermethrin 4	C ₂₂ H ₁₉ Cl ₂ NO ₃	416.30	38.66	163	181 (81.1)	165 (71.2)	209 (32.5)	39.65	163→91	30	163→127	15	30	2.4	
dachal (DCPA)	C ₁₀ H ₆ Cl ₄ O ₄	331.97	24.65	301	299 (83.0)	303 (57.7)	332 (25.8)	25.81	332→167	50	332→223	40	15	1.8	
<i>o,p'</i> -DDD	C ₁₄ H ₁₀ Cl ₄	320.04	28.97	235	237 (65.1)	165 (37.3)	199 (13.5)	212 (8.8)	32.33	235→165	35	235→115	50	23	7.1
<i>p,p'</i> -DDD	C ₁₄ H ₁₀ Cl ₄	320.04	30.46	235	237 (64.0)	165 (37.6)	199 (10.8)	212 (8.7)	32.33	235→165	35	235→115	50	23	6.7
<i>o,p'</i> -DDE	C ₁₄ H ₈ Cl ₄	320.04	27.37	246	248 (68.4)	318 (42.7)	316 (33.5)	28.76	246→176	30	318→176	40	19	50	
<i>p,p'</i> -DDE	C ₁₄ H ₈ Cl ₄	318.03	28.86	246	248 (62.7)	318 (93.4)	316 (73.1)	30.35	246→177	30	318→177	40	22	1.0	
<i>o,p'</i> -DDT	C ₁₄ H ₈ Cl ₅	354.49	30.59	235	237 (64.3)	165 (35.3)	199 (12.9)	212 (7.3)	32.33	235→165	35	235→115	50	23	6.7
<i>p,p'</i> -DDT	C ₁₄ H ₈ Cl ₅	354.49	32.09	235	237 (64.6)	165 (32.3)	199 (8.7)	212 (9.0)	33.94	235→165	35	235→115	50	25	5.0
DEF (tribufos)	C ₁₂ H ₂₇ OPS ₃	314.52	28.81	202	169 (175.0)	226 (48.5)	258 (51.3)	314 (21.8)	30.48	202→147	5	258→112	25	22	3.7
deltamethrin	C ₂₂ H ₁₉ Br ₂ NO ₃	505.21	40.54	181	253 (100.3)	255 (48.2)	251 (50.5)	41.88	172→93	10	251→93	20	30	1.1	
demeton-S	C ₈ H ₁₃ O ₃ PS ₂	258.34	18.20	88	170 (16.2)	143 (12.3)	258 (3.2)								
demeton-S-methyl	C ₆ H ₁₅ O ₃ PS ₂	230.29	15.39	88	109 (26.3)	142 (19.9)	230 (3.0)	16.92	88→60	5	142→79	10	5	3.2	
dialifor	C ₁₄ H ₁₇ CINO ₄ PS ₂	393.85	36.70	208	357 (12.0)	173 (35.6)	186 (8.9)	210 (35.3)	37.82	208→89	15	208→125	15	29	1.4
diallate 1	C ₁₀ H ₇ Cl ₂ NOS	270.22	17.36	86	128 (26.8)	234 (68.7)	236 (25.9)	18.71	234→150	20	234→192	10	7	3.6	
diallate 2	C ₁₀ H ₇ Cl ₂ NOS	270.22	17.72	86	128 (28.2)	234 (74.5)	236 (27.4)	19.13	234→150	20	234→192	10	7	3.6	
diamidafos (nellite)	C ₈ H ₁₃ N ₂ O ₂ P	200.18	21.30	107	94 (40.7)	200 (9.6)	170 (5.2)	19.64	200→107	20			7	NA	
diazinon	C ₁₂ H ₂₁ N ₂ O ₃ PS	304.35	20.34	304	276 (36.3)	227 (45.8)	248 (37.2)	21.24	304→179	10	179→121	25	9	4.4	
diethyl chlorendate	C ₁₇ H ₂₀ Cl ₆ O ₄	501.06	35.60	388	371 (68.3)	317 (45.3)	237 (31.2)	36.72	388→207	45	388→182	35	28	8.5	
dicapthion	C ₉ H ₉ CINO ₃ PS	297.65	24.74	262	125 (38.3)	216 (10.0)	79 (13.2)	232 (19.1)	26.13	262→216	10	262→123	40	15	3.0
dichlobenil	C ₇ H ₃ Cl ₂ N	172.01	10.18	171	173 (67.5)	100 (20.7)	136 (17.8)	10.07	171→100	20	171→126	10	2	7.1	
dichlofenthion	C ₁₀ H ₁₃ Cl ₂ O ₃ PS	315.16	21.89	279	223 (93.2)	162 (39.1)	251 (39.0)	281 (46.0)	23.08	279→223	30	279→205			

Table 1. Continued

pesticide	mol formula	mol wt	GC-MS/SIM							GC-MS/MS						
			RT (min)	target (T)	Q ₁ (%Q ₁ /T)	Q ₂ (%Q ₂ /T)	Q ₃ (%Q ₃ /T)	Q ₄ (%Q ₄ /T)	RT (min)	primary transition	CE 1 (eV)	secondary transition	CE 2 (eV)	MRM group	ion ratio	
			SIM						MS/MS							
3,4'-dichloroaniline	<chem>C6H5Cl2N</chem>	162.01	11.77	161	163 (61.5)	165 (10.3)	99 (15.2)		12.21	163→90	20	161→125	10	3	2.1	
4,4'-dichlorobenzophenone	<chem>C13H8Cl2O</chem>	251.11	24.45	139	250 (30.2)	111 (35.7)	141 (37.2)	252 (21.2)	26.33	139→111	20	139→75	45	16	5.2	
dichlorvos	<chem>C4H7ClO4P</chem>	185.52	8.66	185	109 (281.0)	220 (20.0)	79 (45.6)	145 (28.6)	7.92	185→93	15	185→109	20	1	1.9	
dicloran	<chem>C6H4Cl2N2O2</chem>	207.01	18.24	206	178 (70.2)	176 (108.0)	208 (77.8)		19.56	206→176	15	206→148	15	7	3.1	
dieldrin	<chem>C12H8Cl6O</chem>	380.91	28.46	263	277 (75.6)	380 (37.6)	79 (266.9)	345 (28.5)	30.53	202→113	20	202→95	20	22	1.6	
dimethachlor	<chem>C13H18ClNO2</chem>	255.74	21.79	134	197 (41.0)	210 (10.8)	199 (16.9)		23.09	197→120	20	197→148	20	12	1.7	
dioxabenzofos	<chem>C8H9O3PS</chem>	216.20	20.25	216	183 (41.1)	201 (23.8)	153 (25.8)	171 (4.0)	18.43	216→201	10	216→137	25	6	10	
dioxathion	<chem>C12H26O6P2S4</chem>	456.55	37.70	270	153 (115.6)	125 (149.5)	97 (205.9)	271 (148.9)	20.56	125→97	5	270→169	10	8	4.1	
disulfoton	<chem>C8H18O2PS3</chem>	274.41	20.36	88	186 (14.7)	142 (18.6)	274 (16.3)		21.63	88→60	5	88→73	5	10	2.0	
ditalimfos	<chem>C12H14NO4PS</chem>	299.28	27.87	299	130 (248.6)	148 (114.6)	243 (85.8)	209 (82.8)	29.50	243→130	25	148→130	15	20	2.4	
edifenphos	<chem>C14H15O2PS2</chem>	310.38	31.89	310	173 (104.4)	109 (154.4)	201 (44.5)	218 (22.2)	33.63	310→109	20	109→65	5	25	3.3	
α-endosulfan	<chem>C9H6Cl6O3S</chem>	406.93	27.27	241	195 (74.5)	237 (90.0)	339 (46.3)		29.13	241→206	20	243→136	30	20	2.1	
β-endosulfan	<chem>C9H6Cl6O3S</chem>	406.93	29.82	195	237 (78.0)	241 (91.5)	339 (51.4)		32.08	241→206	20	243→136	30	23	2.2	
endosulfan ether	<chem>C9H6Cl6O</chem>	342.86	20.95	241	277 (88.9)	307 (83.2)	342 (45.2)		22.61	307→69	5	272→143	30	11	6.9	
endosulfan sulfate	<chem>C9H6Cl6O4S</chem>	422.93	31.76	272	387 (65.3)	274 (82.7)	229 (64.7)	422 (21.3)	33.72	272→143	40	385→219	30	20	2.1	
endrin	<chem>C12H8Cl6O</chem>	380.91	29.38	263	345 (42.8)	317 (80.0)	281 (64.5)	245 (58.0)	30.36	281→211	25	263→191	15	22	2.2	
endrin aldehyde	<chem>C12H8Cl6O</chem>	380.91	30.75	345	279 (32.2)	347 (77.4)	250 (68.8)		32.43	248→177	30	345→253	10	23	13	
endrin ketone	<chem>C12H8Cl6O</chem>	380.91	33.82	317	345 (31.8)	315 (73.8)	281 (33.6)		35.43	317→175	45	317→219	35	27	1.1	
EPN	<chem>C14H14NO4PS</chem>	323.31	34.36	157	169 (56.0)	185 (31.9)	141 (32.1)		35.75	169→77	20	157→110	20	27	3.0	
ethalfuralin	<chem>C13H14F3N3O4</chem>	333.25	16.94	316	276 (123.7)	292 (45.5)	333 (31.3)		17.70	276→105	15	316→201	30	5	2.7	
ethion	<chem>C9H22O4P2S4</chem>	384.48	30.94	231	384 (14.5)	153 (54.6)	125 (36.7)	233 (14.4)	20.78	231→129	25	231→185	10	9	4.8	
ethoprop	<chem>C8H19O2PS2</chem>	242.34	16.25	158	139 (48.1)	200 (32.4)	242 (22.6)		17.28	158→97	15	158→81	20	5	4.4	
etridazole	<chem>C5H5Cl3N2OS</chem>	247.53	12.26	211	183 (78.6)	213 (68.2)	185 (54.8)		12.61	211→108	40	211→183	20	3	21	
famphur	<chem>C10H16NO5PS2</chem>	325.34	31.77	218	125 (21.0)	93 (17.6)	109 (8.0)	217 (20.2)	33.41	218→127	15	218→91	5	24	3.4	
fenamiphos	<chem>C13H22NO3PS</chem>	303.36	28.30	303	154 (75.6)	288 (24.5)	260 (22.2)		29.78	303→154	15	303→195	10	21	2.1	
fenarimol	<chem>C17H12Cl2N2O</chem>	331.19	36.19	139	219 (74.8)	251 (61.8)	330 (37.1)		37.58	139→75	20	219→107	10	29	1.5	
fenchlorphos (ronnel)	<chem>C8H8Cl3O3PS</chem>	321.55	22.93	285	287 (70.5)	125 (29.2)	167 (4.6)	289 (13.2)	24.16	285→270	15	285→240	25	13	1.2	
fenitrothion	<chem>C9H12NO3PS</chem>	277.24	23.59	277	260 (75.1)	109 (75.2)	125 (98.7)	247 (43.2)	24.91	277→109	15	277→127	25	14	3.1	
fensulfotthion	<chem>C11H17O4PS2</chem>	308.37	30.44	292	308 (6.7)	293 (38.2)	188 (9.8)	156 (48.9)	32.16	293→97	40	308→109	20	23	3.9	
fenthion	<chem>C10H15O3PS2</chem>	278.33	24.48	278	125 (26.0)	109 (17.6)	169 (17.6)	279 (11.2)	25.86	277→109	15	277→127	20	15	5.2	
fenvalerate 1	<chem>C25H22ClNO3</chem>	419.91	39.50	419	167 (255.4)	181 (160.5)	225 (118.6)		40.67	167→125	10	419→167	25	30	24	
fenvalerate 2	<chem>C25H22ClNO3</chem>	419.91	39.77	419	167 (315.1)	181 (182.7)	225 (132.7)		40.98	167→125	10	419→167	25	30	23	
fluchloralin	<chem>C12H13ClF3N3O4</chem>	355.68	20.46	306	145 (14.9)	264 (46.1)	326 (84.3)		21.38	306→160	20	306→264	5	9	3.3	
flucythrinate 1	<chem>C26H23F2NO4</chem>	451.47	38.70	199	225 (16.6)	209 (15.5)	181 (36.1)	451 (31.7)	39.66	199→107	35	157→107	15	30	1.4	
flucythrinate 2	<chem>C26H23F2NO4</chem>	451.47	38.94	199	225 (15.9)	209 (9.8)	181 (34.2)	451 (27.1)	39.81	199→107	35	157→107	15	30	1.4	
fluridone	<chem>C19H14F3NO</chem>	329.32	39.20	328	329 (46.3)	189 (1.6)	310 (2.4)	330 (8.2)	40.40	328→189	35	328→233	40	30	3.3	
fluvalinate τ-1	<chem>C26H22ClF3N2O3</chem>	502.92	39.79	250	252 (34.1)	181 (26.5)	251 (15.9)		40.82	502→250	15	181→152	30	30	1.3	
fluvalinate τ-2	<chem>C26H22ClF3N2O3</chem>	502.92	39.88	250	252 (30.4)	181 (21.8)	251 (12.4)		40.82	502→250	15	181→152	30	30	2.0	
folpet	<chem>C6H4Cl3NO2S</chem>	296.56	26.47	260	104 (131.6)	76 (107.3)	130 (50.5)		28.39	260→130	20	262→234	10	18	5.1	
fonophos	<chem>C10H15OPS2</chem>	246.33	19.65	246	109 (190.43)	137 (91.1)	110 (49.1)	174 (13.0)	20.94	246→109	25	137→109	5	9	1.0	
heptachlor	<chem>C10H5Cl7</chem>	373.32	23.05	272	100 (68.2)	274 (75.9)	237 (36.7)		23.89	100→65	20	272→237	15	13	1.3	
heptachlor epoxide	<chem>C10H5Cl7O</chem>	389.32	25.71	353	355 (80.4)	351 (49.0)	357 (37.9)		27.43	353→263	20	353→265	15	17	1.6	
hexachlorobenzene	<chem>C6Cl6</chem>	284.78	17.91	284	286 (82.2)	282 (52.8)	288 (34.1)		18.96	284→144	50	284→179	30	7	2.4	
iprobenfos (IBP)	<chem>C13H21O3PS</chem>	288.34	21.11	204	123 (25.0)	288 (14.1)	246 (19.4)		22.37	204→91	15	204→121	35	11	1.6	
iprodione	<chem>C13H13Cl2N3O3</chem>	330.16	34.04	314	316 (71.4)	187 (53.0)	189 (35.2)		35.57	314→245	10	314→271	10	27	1.9	
isazophos	<chem>C9H17ClN3O3PS</chem>	313.74	20.87	161	119 (75.1)	257 (55.4)	285 (27.7)	313 (14.9)	21.78	161→119	10	162→120	10	10	1.5	
isofenfos	<chem>C15H24NO4PS</chem>	345.40	26.52	255	213 (202.7)	185 (89.5)	245 (32.0)	345 (7.4)	27.65	213→121	15	213→185	5	17	5.0	
jodfenphos (iodofenphos)	<chem>C8H9Cl2IO3PS</chem>	413.00	28.27	377	379 (37.2)	125 (16.7)	109 (7.5)	250 (5.3)	29.83	377→93	25	377→157	30	28	37	
leptophos	<chem>C13H10BrCl2O2PS</chem>	412.07	35.57	377	171 (90.7)	375 (75.2)	379 (26.7)		36.74	377→157	40	171→77	15	28	37.0	
lindane (γ-BHC)	<chem>C6H6Cl6</chem>	290.83	19.12	181	219 (83.0)	183 (105.8)	217 (63.9)		20.51	181→146	20	219→183	10	10	1	
malathion	<chem>C10H19O6PS2</chem>	330.36	24.22	173	125 (82.8)	158 (42.9)	211 (7.2)	127 (90.1)	25.42	127→99	5	173→99	15	14	2.1	
methidathion	<chem>C6H11N2O4PS3</chem>	302.34	27.11	145	85 (62.5)	125 (16.0)	93 (17.9)		28.70	145→85	5	145→58	15	19	1.2	
o,p'-methoxychlor	<chem>C16H15Cl3O2</chem>	345.65	32.96	227	121 (90.7)	228 (17.3)	152 (10.3)		35.96	227→115	50	227→141	30	27	1.4	
p,p'-methoxychlor	<chem>C16H15Cl3O2</chem>	345.65	34.57	227	228 (15.7)	212 (3.9)	152 (5.1)		34.24	227→121	15	227→91	30	25	5.0	
metolachlor	<chem>C15H22ClNO2</chem>	283.79	24.44	238	162 (117.2)	240 (42.3)	146 (25.2)		25.50	238→162	10	238→133	20	14	1.6	
mevinphos	<chem>C7H13O6P</chem>	224.15	11.86	127	192 (25.6)	109 (21.2)	164 (6.0)		12.06	192→127	10	192→109	20	3	3.1	
mirex	<chem>C10Cl12</chem>	545.54	35.53	272	237 (41.4)	332 (11.5)	274 (75.7)		37.19	272→237	15	272→143	35	29	3.1	
naphthalene-d ₆	<chem>C10D8</chem>	136.24	7.68	136	108 (7.7)	134 (9.0)	137 (10.4)		6.78	136→108	15	136→82	25	1	2.9	
cis-nonachlor	<chem>C10H5Cl9</chem>	444.24	30.49	409	407 (86.6)	411 (61.1)	405 (35.9)		29.27	409→300	30	409→230	50	23	1.7	
trans-nonachlor	<chem>C10H5Cl9</chem>	444.24	27.73	409	407 (90.5)	411 (64.5)	405 (35.0)		32.08	409→302	25	409→230	50	20	2.3	
oxadiazon	<chem>C15H18Cl2N2O3</chem>	345.23	29.30	258	175 (182.8)	260 (64.0)	302 (75.9)		30.47	175→112	15	175→77	45	22	63	
parathion	<chem>C10H14NO3PS</chem>	291.26	24.61	291	263 (13.2)	235 (12.6)	186 (22.0)	218 (9.2)	26.03	291→109	10	139→109	5	15	6.5	
parathion-methyl	<chem>C8H10NO3PS</chem>	263.21	22.27	263	233 (24.5)	247 (11.4)	264 (9.9)	200 (6.3)	23.69	263→109	5	263→127	10	13	1.8	
pentachloroaniline	<chem>C6H2Cl5N</chem>	265.35	21.20	265												

Table 1. Continued

pesticide	mol formula	mol wt	GC-MS/SIM							GC-MS/MS						
			RT	target	Q ₁	Q ₂	Q ₃	Q ₄	RT	CE 1	secondary	CE 2	MRM	ion		
			(min)						(min)						MS/MS	transition
pentachlorophenyl methyl ester	C ₇ H ₃ Cl ₅ O	280.36	18.26	280	265 (97.1)	282 (74.4)	267 (56.6)		19.28	280→237	20	280→265	10	7	3.0	
pentachlorothioanisole	C ₇ H ₃ Cl ₅ S	296.43	23.47	296	246 (45.5)	263 (31.2)	298 (59.7)		24.92	296→263	10	246→103	30	14	6.1	
<i>cis</i> -permethrin	C ₂₁ H ₂₀ Cl ₂ O ₃	391.29	37.23	183	165 (17.3)	163 (17.5)	184 (17.3)		38.35	183→128	30	163→127	5	30	2.1	
<i>trans</i> -permethrin	C ₂₁ H ₂₀ Cl ₂ O ₃	391.29	37.39	183	165 (19.8)	163 (23.5)	184 (16.1)		38.53	183→128	30	163→127	5	30	2.1	
phenanthrene- <i>d</i> ₁₀	C ₁₄ D ₁₀	188.31	19.32	188	189 (14.5)	187 (22.7)	184 (13.5)		21.04	188→161	15	188→176	25	10	1.4	
phenothrin	C ₂₃ H ₂₆ O ₃	350.46	35.40	183	123 (160.5)	184 (21.5)	124 (16.3)	350 (9.2)	36.45	123→77	30	123→81	10	28	10	
phorate	C ₇ H ₁₇ O ₂ PS ₃	260.38	17.64	260	121 (168.7)	97 (94.9)	231 (63.7)	75 (376.2)	18.73	260→75	10	121→93	5	7	7.4	
phosalone	C ₁₂ H ₁₅ ClNO ₄ PS ₂	367.81	35.52	182	184 (35.5)	367 (28.2)	154 (25.7)		36.79	121→65	10	182→75	30	28	0.8	
phosmet	C ₁₁ H ₁₂ NO ₄ PS ₂	317.33	34.17	160	161 (12.0)	133 (5.4)	317 (4.7)		35.70	160→77	15	160→133	10	27	1.6	
phenthoate	C ₁₂ H ₁₇ O ₄ PS ₂	320.36	26.59	274	246 (30.8)	275 (26.8)	320 (5.1)									
pirimiphos-ethyl	C ₁₁ H ₂₀ N ₃ O ₃ PS	333.39	25.76	318	333 (104.6)	304 (68.1)	290 (23.3)		26.76	333→168	20	333→97	45	16	4.0	
pirimiphos-methyl	C ₁₁ H ₂₀ N ₃ O ₃ PS	305.33	23.80	290	305 (76.0)	276 (84.1)	233 (30.8)		24.83	290→125	20	290→233	10	14	2.6	
procymidone	C ₁₃ H ₁₁ Cl ₂ NO ₂	284.14	26.73	283	285 (65.0)	287 (13.0)	255 (10.2)	212 (9.4)	28.22	283→96	10	283→255	5	18	50	
profenofos	C ₁₁ H ₁₅ BrClO ₃ PS	373.63	28.61	339	208 (158.7)	295 (40.1)	337 (97.8)	374 (59.9)	30.24	337→188	35	337→269	15	22	0.8	
propachlor	C ₁₄ H ₁₄ ClNO	247.72	15.67	176	120 (243.8)	169 (39.2)	211 (25.6)		16.56	176→77	20	176→120	10	5	1.5	
propazine	C ₉ H ₁₆ ClN ₅	229.70	19.15	214	172 (53.3)	229 (60.8)	216 (32.2)	187 (28.1)	20.46	214→172	10	214→79	10	8	15	
propetamphos	C ₁₀ H ₂₀ NO ₄ PS	281.31	19.81	138	194 (50.7)	222 (24.9)	236 (37.0)		20.92	138→110	10	236→138	20	9	1.7	
propyzamide	C ₁₂ H ₁₁ Cl ₂ NO	256.13	19.72	173	145 (31.4)	175 (61.0)	255 (26.2)		21.07	173→74	35	173→145	10	9	0.5	
prothiophos	C ₁₁ H ₁₅ Cl ₂ O ₂ PS ₂	345.25	28.46	309	267 (92.0)	311 (47.9)	269 (41.9)		30.41	309→239	15	309→221	35	21	71	
pyraclofos	C ₁₄ H ₁₈ ClN ₂ O ₃ PS	360.80	36.75	360	194 (55.2)	362 (32.6)	138 (57.2)		37.97	360→97	30	360→138	35	29	1.9	
pyrazophos	C ₁₄ H ₂₀ N ₃ O ₅ PS	373.37	36.60	221	232 (35.0)	373 (24.8)	328 (4.9)	268 (10.5)	37.55	232→204	10	232→124	15	29	15	
pyridaphenthion	C ₁₄ H ₁₇ N ₂ O ₄ PS	340.34	34.23	340	188 (45.1)	199 (52.1)	77 (39.0)	204 (28.9)	35.48	340→91	30	340→124	35	27	28	
quinalphos	C ₁₂ H ₁₅ N ₂ O ₃ PS	298.32	26.58	298	146 (367.5)	157 (241.9)	270 (42.5)		27.98	146→118	15	156→103	20	18	8.0	
quintozene	C ₆ Cl ₅ NO ₂	295.33	19.34	295	265 (68.9)	249 (60.3)	237 (139.5)		20.23	237→141	20	237→167	20	8	4.3	
resmethrin	C ₂₂ H ₂₆ O ₃	338.45	33.64	123	143 (32.5)	171 (60.4)	128 (43.7)		34.97	171→128	10	123→81	5	26	1.4	
simazine	C ₇ H ₁₂ ClN ₅	201.64	18.68	201	173 (43.9)	186 (63.3)	203 (33.8)		20.06	186→91	5	186→104	10	8	1.2	
sulfotep-ethyl	C ₈ H ₂₀ O ₅ P ₂ S ₂	322.32	17.56	322	97 (34.7)	202 (40.7)	238 (24.0)	266 (28.0)	18.28	322→146	20	322→202	10	6	2	
sulprofos	C ₁₂ H ₁₉ O ₂ PS ₃	322.45	31.40	322	156 (55.3)	140 (71.6)	125 (24.3)	280 (9.6)	33.06	322→97	30	322→156	15	24	1.5	
tebupirimfos	C ₁₃ H ₂₃ N ₂ O ₃ PS	318.37	21.21	318	261 (94.7)	234 (77.5)	276 (48.1)		22.31	318→152	10	318→123	40	11	1.2	
tecnazene (TCNB)	C ₆ HCl ₄ NO ₂	260.89	15.43	261	203 (127.1)	215 (103.3)	217 (57.2)	231 (68.5)	16.10	261→203	20	261→143	35	5	6.5	
tefluthrin	C ₁₇ H ₁₄ ClF ₇ O ₂	418.74	20.86	177	197 (27.2)	199 (8.5)	178 (10.5)		21.99	177→127	15	177→87	25	10	3.4	
temephos	C ₁₆ H ₂₀ O ₆ P ₂ S ₃	466.48	43.62	466	467 (20.1)	171 (6.3)	203 (11.4)									
terbufos	C ₉ H ₂₁ O ₂ PS ₃	288.44	19.60	231	153 (22.8)	186 (16.1)	203 (9.0)	288 (9.6)								
terbuthylazine	C ₉ H ₁₆ ClN ₅	229.70	19.56	214	229 (29.7)	173 (43.3)	216 (39.6)		20.92	229→172	20	229→138	20	9	2.5	
2,3,5,6-tetrachloroaniline	C ₆ H ₃ Cl ₄ N	230.91	15.92	231	158 (19.0)	169 (6.7)	229 (83.5)	233 (51.5)	16.98	231→158	20			5	NA	
tetrachlorvinphos	C ₁₀ H ₉ Cl ₄ O ₄ P	365.96	27.68	331	329 (103.5)	333 (36.7)	109 (71.6)	240 (11.0)	29.04	331→127	10	331→126	25	19	77	
tetramethrin	C ₁₉ H ₂₅ NO ₄	331.41	34.72	164	123 (30.2)	165 (10.8)	135 (3.3)	107 (7.0)	35.88	164→77	20	164→107	10	27	1.5	
thiometon	C ₆ H ₁₅ O ₂ PS ₃	246.36	18.04	88	246 (7.9)	158 (7.8)	125 (41.4)									
tolclofos-methyl	C ₉ H ₁₃ Cl ₂ O ₂ PS	301.13	22.45	265	267 (37.3)	125 (18.1)	250 (11.0)		23.69	265→250	15	265→109	35	13	1.6	
tolylfluaniid	C ₁₀ H ₁₃ Cl ₂ FN ₂ O ₂ S ₂	347.25	26.12	137	238 (37.7)	240 (26.9)	181 (29.7)		27.59	240→137	20	237→137	10	17	2.7	
triallate	C ₁₀ H ₁₆ Cl ₃ NOS	304.67	20.62	268	270 (69.3)	145 (29.6)	86 (170.5)		21.98	268→184	25	270→186	20	10	1.1	
triazophos	C ₁₂ H ₁₆ N ₃ O ₃ PS	313.32	31.55	161	285 (24.5)	313 (12.5)	257 (34.2)		33.16	257→162	10	161→106	15	24	1.4	
trifluralin	C ₁₃ H ₁₆ F ₃ N ₃ O ₄	335.26	17.39	306	264 (61.5)	290 (12.2)	335 (9.3)		18.13	306→264	5	306→148	20	6	1.9	
triphenyl phosphate	C ₁₈ H ₁₅ O ₄ P	326.28	33.12	326	325 (84.4)	215 (18.7)	170 (16.0)		34.71	326→226	30	326→141	40	26	2.8	
tris(1,3-dichloroisopropyl) phosphate	C ₉ H ₁₅ Cl ₆ O ₄ P	430.91	31.96	381	383 (65.0)	321 (35.9)	303 (26.9)		33.31	379→159	20	379→123	20	24	2.1	
vinclozolin	C ₁₂ H ₉ Cl ₂ NO ₃	286.11	22.28	285	212 (103.4)	187 (80.6)	198 (95.1)		23.59	285→212	10	285→172	25	13	1.4	

^a RT, retention time; SIM, selective ion monitoring; LOQ, limit of quantitation; T, target ion; Q₁ = qualifier ion 1; Q₂, qualifier ion 2; Q₃, qualifier ion 3; Q₄, qualifier ion 4; %Q_{*n*}/T, percent qualifier-to-target ratio where *n* = 1, 2, 3, and 4; CE 1, collision energy of primary transition; CE 2, collision energy of secondary transition; MRM, multiple reaction monitoring.

rotary evaporation, which also decreases solvent disposal wastes and costs. The use of toluene is essential to desorb planar, aromatic pesticides (e.g., hexachlorobenzene and pentachlorobenzene) from GCB. Toluene has other unique properties essential for this analysis including its insolubility to water and polar coextractives, lower volume expansion compared to acetonitrile, and compatibility with splitless injection, making it an ideal GC solvent (21, 39, 42).

Sample chromatograms from bell pepper extracts using the modified QuEChERS procedure are shown in Figures 2 and 3. These chromatograms illustrate that GCs equipped with single- and triple-quadrupole mass spectrometers are compatible for the

analysis of these sample extracts. GC-MS/SIM and GC-MS/MS chromatograms of extracts from a bell pepper blank, matrix (bell pepper)-matched calibration standard at 167 ng/mL, bell pepper blank fortified at 25 µg/kg, and incurred bell pepper sample are revealed. Previous studies have shown that these sample extracts can also be injected and analyzed by gas chromatographs equipped with element selective detectors such as flame photometric and halogen selective detectors (34–36). A comparison of the GC-MS/SIM and GC-MS/MS chromatograms (Figures 2 and 3) of the bell pepper reveals fewer extraneous peaks in the blanks and fortified samples at both concentration levels when analyzed by GC-MS/MS. The incurred pepper extracts show

differences with the pepper blank, which could have resulted from differences of pepper species or breakdown of the pepper matrix

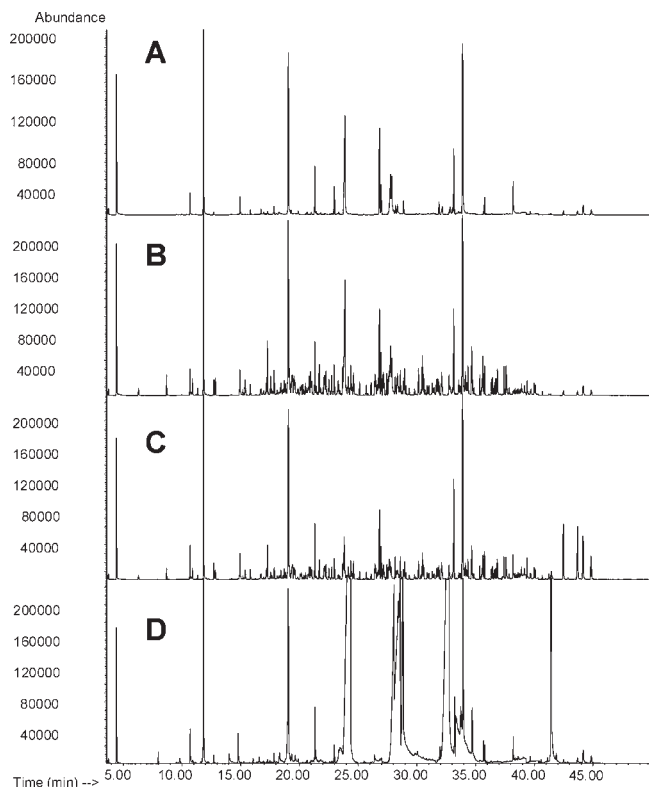


Figure 2. Reconstructed GC-MS/SIM chromatograms of a bell pepper extract prepared from the proposed method: (A) bell pepper blank; (B) matrix (bell pepper)-matched calibration standard at 167 ng/mL of pesticide standards; (C) extract of bell pepper blank fortified at 25 µg/kg; (D) incurred bell pepper extract. See Materials and Methods for details on preparation of the extract.

due to a longer storage time of the incurred sample in the -40°C freezer.

Method Validation. The modified QuEChERS procedure was evaluated for 167 organohalogen, organophosphorus, and pyrethroid pesticides, isomers, and metabolites listed **Table 1** using GC-MS/SIM and GC-MS/MS. Standard mixes in toluene were used to determine retention times, mass spectra and ion abundances, and acquisition time segments for both GC-MS/SIM and GC-MS/MS. Percentages of qualifier ion to target ion ratios (% Q/T) for GC-MS/SIM and precursor to product ion transitions, collision energies, and ion ratios (ratio between the primary and secondary transitions) used for pesticide identification are also provided in **Table 1**. Matrix-matched standards, ranging from 0.0033 to 6.67 µg/mL (depending on the pesticide) with $r^2 > 0.99$ ($n = 6$), established linear ranges for each pesticide and the minimum limits of quantitation (LOQs) expected for the method. Target and three qualifier ions preselected by full-scan MS and two transitions resulting from collision-induced dissociation of the precursor ion into product fragments characteristic of the precursor were used for GC-MS/SIM and GC-MS/MS, respectively. The LOQs were defined as the amount of pesticide that would produce a 3:1 signal/noise in the matrix-matched standard for all qualifying ions (SIM) or qualifying (secondary) transition (MS/MS) and 10:1 signal/noise for the target ion (SIM) or quantitating (or primary) transition (MS/MS). The LOQs listed in **Table 2** were averages of LOQs determined from 10 produce commodities (bell pepper, broccoli, cantaloupe, carrot, onion, orange, peach, potato, spinach, and tomato). The geometric mean LOQ, based on the average LOQs of 167 and 162 pesticides, metabolites, and isomers, were 8.4 and 3.4 µg/kg for GC-MS/SIM and GC-MS/MS, respectively. These data indicate that a majority of the pesticides could be detected at the 10 µg/kg level: 98 of 167 and 160 of 162 pesticides had LOQs of 10 µg/kg or lower for GC-MS/SIM and GC-MS/MS, respectively. A majority of these pesticides were organochlorine and nonpolar pesticides. The remaining 67 of the 69 pesticides for the GC-MS/SIM LOQs

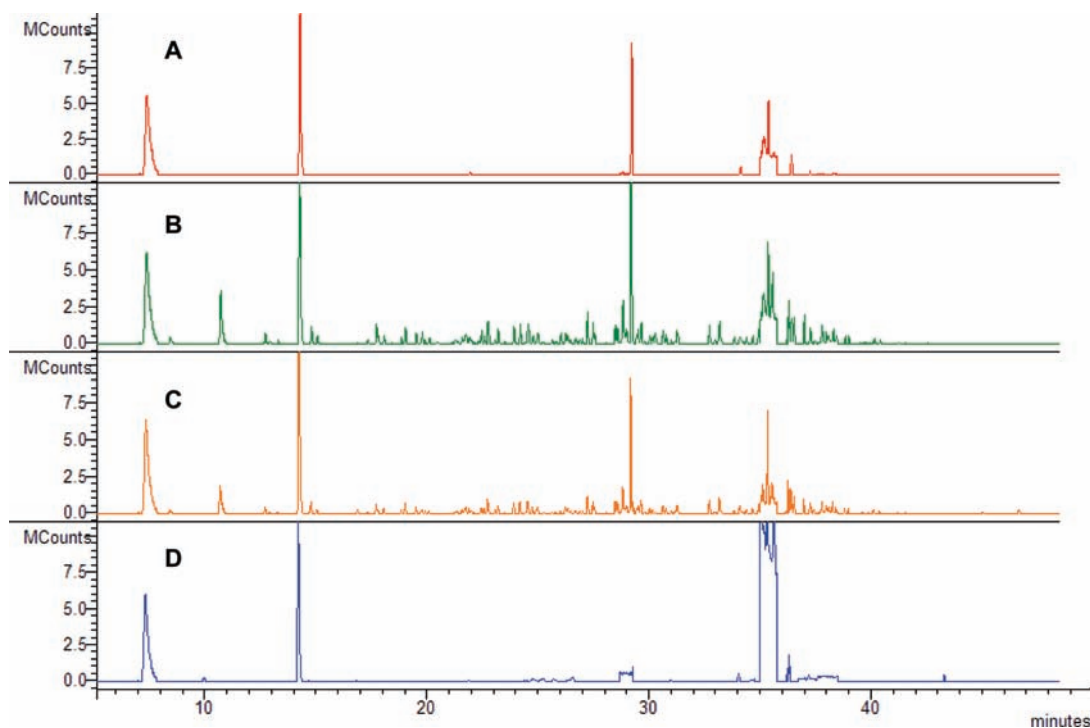


Figure 3. Reconstructed GC-MS/MS chromatograms of the same bell pepper extract used in **Figure 2** prepared from the proposed method: (A) bell pepper blank; (B) matrix (bell pepper)-matched calibration standard at 167 ng/mL; (C) extract from a bell pepper blank fortified at 25 µg/kg; (D) incurred bell pepper extract. See Materials and Methods for details on preparation of the extract.

Table 2. Recoveries and Average Limits of Quantitation (LOQs) of Pesticides Extracted from 10 Produce Commodities (Bell Pepper, Broccoli, Cantaloupe, Carrot, Onion, Orange, Peach, Potato, Spinach, and Tomato) Fortified at 10, 25, 100, and 500 $\mu\text{g}/\text{kg}$ Levels Using the Proposed Sample Preparation Procedures and Analyzed by GC-MS/SIM and GC-MS/MS^a

pesticide	GC-MS/SIM					GC-MS/MS				
	LOQ ($\mu\text{g}/\text{kg}$)	10 $\mu\text{g}/\text{kg}$ (n)	25 $\mu\text{g}/\text{kg}$ (n)	100 $\mu\text{g}/\text{kg}$ (n)	500 $\mu\text{g}/\text{kg}$ (n)	LOQ ($\mu\text{g}/\text{kg}$)	10 $\mu\text{g}/\text{kg}$ (n = 40)	25 $\mu\text{g}/\text{kg}$ (n = 40)	100 $\mu\text{g}/\text{kg}$ (n = 40)	500 $\mu\text{g}/\text{kg}$ (n = 40)
acrinathrin	15	89 ± 12 (40)	90 ± 10 (40)	91 ± 10 (40)	97 ± 6 (40)	10	91 ± 10	94 ± 8	99 ± 11	105 ± 10
akton	1	98 ± 5 (39)	93 ± 5 (40)	96 ± 5 (40)	96 ± 4 (40)	1	98 ± 11	97 ± 9	96 ± 8	100 ± 8
alachlor	10	90 ± 20 (40)	87 ± 21 (40)	90 ± 12 (40)	99 ± 4 (40)	5	101 ± 12	97 ± 10	98 ± 8	103 ± 9
aldrin	5	88 ± 8 (40)	83 ± 9 (40)	84 ± 8 (40)	88 ± 5 (40)	5	70 ± 17	58 ± 11	53 ± 10	54 ± 7
allethrin	15	99 ± 8 (32)	94 ± 11 (36)	98 ± 6 (40)	98 ± 7 (40)	5	100 ± 10	99 ± 9	100 ± 8	103 ± 8
atrazine	10	99 ± 10 (40)	94 ± 8 (40)	98 ± 4 (40)	100 ± 4 (40)	10	99 ± 11	97 ± 12	98 ± 10	104 ± 10
azamethidaphos	20	nd	87 ± 16 (32)	89 ± 18 (36)	90 ± 19 (40)	10	95 ± 10	94 ± 11	91 ± 8	97 ± 12
azinphos-ethyl	10	94 ± 8 (40)	92 ± 8 (40)	94 ± 6 (40)	96 ± 3 (40)	2	98 ± 10	98 ± 10	98 ± 7	100 ± 8
azinphos-methyl	15	89 ± 13 (36)	84 ± 13 (40)	87 ± 13 (40)	92 ± 14 (40)	2	99 ± 11	97 ± 11	95 ± 7	99 ± 10
BHC, α -	5	88 ± 10 (40)	82 ± 8 (40)	86 ± 11 (40)	88 ± 7 (40)	1	86 ± 8	85 ± 13	87 ± 10	89 ± 8
BHC, β -	20	nd	91 ± 15 (36)	96 ± 17 (40)	102 ± 6 (40)	5	94 ± 10	88 ± 25	97 ± 15	104 ± 14
BHC, δ -	10	94 ± 7 (32)	94 ± 5 (32)	85 ± 22 (40)	98 ± 7 (40)	1	97 ± 12	92 ± 20	100 ± 9	107 ± 9
BHC, γ -	15	nd	87 ± 15 (32)	95 ± 9 (40)	94 ± 5 (40)	2	93 ± 9	93 ± 17	95 ± 9	97 ± 10
bifenthrin	5	98 ± 5 (40)	93 ± 6 (40)	96 ± 6 (40)	97 ± 5 (40)	1	97 ± 8	96 ± 7	95 ± 9	99 ± 8
bromophos	2	87 ± 16 (39)	85 ± 5 (40)	87 ± 5 (40)	88 ± 4 (40)	1	83 ± 11	83 ± 7	81 ± 7	83 ± 8
bromophos-ethyl	2	82 ± 14 (40)	80 ± 5 (40)	82 ± 5 (40)	82 ± 3 (40)	1	89 ± 9	89 ± 9	86 ± 7	90 ± 5
bromopropylate	10	100 ± 6 (40)	94 ± 9 (40)	98 ± 4 (40)	100 ± 4 (40)	1	97 ± 8	97 ± 6	96 ± 7	98 ± 7
captafol	30	nd	nd	75 ± 17 (20)	80 ± 18 (40)	55	nd	nd	nd	nd
captan	50	nd	nd	75 ± 26 (40)	94 ± 29 (40)	40	nd	nd	nd	nd
carbophenothion	15	nd	94 ± 10 (40)	98 ± 6 (40)	100 ± 3 (40)	5	98 ± 11	101 ± 10	100 ± 7	105 ± 9
chlorbenzilate	2	103 ± 5 (40)	97 ± 4 (40)	100 ± 4 (40)	101 ± 4 (40)	1	103 ± 7	101 ± 7	98 ± 7	103 ± 7
chlordane, <i>cis</i> -	1	98 ± 7 (40)	93 ± 6 (40)	93 ± 5 (40)	95 ± 3 (40)	2	92 ± 12	90 ± 13	89 ± 10	94 ± 13
chlordane, <i>trans</i> -	1	78 ± 8 (40)	75 ± 7 (40)	75 ± 5 (40)	76 ± 5 (40)	2	91 ± 10	87 ± 12	84 ± 13	86 ± 8
chlordene, α -	2	96 ± 12 (40)	90 ± 10 (40)	95 ± 7 (40)	98 ± 5 (40)	2	100 ± 10	99 ± 12	98 ± 11	102 ± 8
chlordene, β -	2	100 ± 5 (40)	95 ± 5 (40)	97 ± 5 (40)	99 ± 3 (40)	5	95 ± 11	95 ± 10	97 ± 13	95 ± 10
chlordene, γ -	2	90 ± 13 (28)	87 ± 8 (36)	93 ± 7 (40)	99 ± 6 (40)	5	97 ± 10	99 ± 12	98 ± 12	96 ± 10
chlorfenvinphos, β -	2	117 ± 9 (40)	114 ± 10 (40)	119 ± 7 (40)	120 ± 5 (40)	5	114 ± 20	121 ± 18	115 ± 12	118 ± 16
chloroneb	5	136 ± 80 (24)	80 ± 22 (28)	84 ± 20 (40)	83 ± 15 (40)	1	83 ± 13	79 ± 19	46 ± 15	86 ± 11
chlorothalonil	10	41 ± 14 (20)	43 ± 26 (28)	40 ± 18 (40)	59 ± 14 (40)	10	48 ± 26	35 ± 20	46 ± 23	58 ± 18
chlorpyrifos	5	92 ± 17 (40)	85 ± 15 (40)	92 ± 6 (40)	93 ± 3 (40)	2	94 ± 9	95 ± 7	89 ± 13	97 ± 7
chlorpyrifos-methyl	10	92 ± 17 (40)	89 ± 6 (40)	91 ± 6 (40)	93 ± 4 (40)	2	93 ± 12	93 ± 12	91 ± 8	96 ± 7
chlorthiophos	5	92 ± 7 (40)	88 ± 5 (40)	90 ± 5 (40)	91 ± 4 (40)	5	91 ± 10	92 ± 9	90 ± 7	93 ± 5
coumaphos	10	81 ± 10 (40)	78 ± 8 (40)	79 ± 8 (40)	81 ± 6 (40)	5	86 ± 13	84 ± 12	88 ± 13	90 ± 9
cyanazine	20	nd	88 ± 12 (28)	94 ± 12 (36)	101 ± 6 (40)	10	93 ± 9	93 ± 8	97 ± 9	99 ± 8
cyanophos	20	nd	92 ± 7 (36)	95 ± 6 (40)	96 ± 4 (40)	2	97 ± 9	95 ± 10	95 ± 8	99 ± 9
cyfluthrin 1	15	nd	94 ± 6 (36)	96 ± 6 (40)	97 ± 5 (40)	5	96 ± 9	96 ± 11	103 ± 10	102 ± 9
cyfluthrin 2	15	nd	94 ± 10 (36)	96 ± 7 (40)	96 ± 5 (40)	5	89 ± 15	93 ± 10	100 ± 8	101 ± 7
cyfluthrin 3	15	nd	93 ± 6 (36)	95 ± 6 (40)	96 ± 4 (40)	10	92 ± 19	92 ± 11	97 ± 12	102 ± 9
cyfluthrin 4	15	nd	92 ± 11 (36)	94 ± 7 (40)	98 ± 4 (40)	10	90 ± 23	94 ± 13	104 ± 11	104 ± 9
cyhalothrin, λ -	10	93 ± 8 (40)	93 ± 9 (40)	97 ± 6 (40)	100 ± 5 (40)					
cypermethrin 1	25	nd	94 ± 8 (32)	95 ± 7 (36)	99 ± 11 (40)	5	97 ± 13	94 ± 9	100 ± 10	104 ± 10
cypermethrin 2	25	nd	97 ± 8 (32)	95 ± 8 (40)	95 ± 9 (40)	5	95 ± 13	99 ± 10	98 ± 18	104 ± 9
cypermethrin 3	25	nd	96 ± 8 (32)	95 ± 8 (40)	96 ± 7 (40)	10	92 ± 17	87 ± 11	98 ± 12	101 ± 11
cypermethrin 4	25	nd	92 ± 8 (32)	94 ± 5 (40)	97 ± 7 (40)	10	94 ± 16	96 ± 10	99 ± 13	102 ± 10
dacthal	1	101 ± 6 (40)	94 ± 5 (40)	97 ± 5 (40)	100 ± 3 (40)	2	100 ± 12	98 ± 11	98 ± 9	101 ± 9
DDD, <i>o,p'</i> -	2	98 ± 5 (40)	93 ± 4 (40)	96 ± 5 (40)	98 ± 4 (40)	2	98 ± 5	97 ± 7	95 ± 6	99 ± 8
DDD, <i>p,p'</i> -	2	102 ± 9 (40)	96 ± 5 (40)	96 ± 5 (40)	98 ± 4 (40)	2	98 ± 5	97 ± 7	95 ± 6	99 ± 7
DDE, <i>o,p'</i> -	2	96 ± 7 (40)	92 ± 7 (40)	93 ± 5 (40)	95 ± 4 (40)	1	96 ± 9	95 ± 8	94 ± 8	97 ± 7
DDE, <i>p,p'</i> -	1	120 ± 13 (40)	113 ± 13 (40)	117 ± 9 (40)	114 ± 14 (40)	2	122 ± 12	125 ± 14	124 ± 11	132 ± 11
DDT, <i>o,p'</i> -	2	94 ± 7 (36)	92 ± 4 (36)	93 ± 5 (40)	95 ± 7 (40)	2	98 ± 5	97 ± 7	95 ± 6	100 ± 7
DDT, <i>p,p'</i> -	2	93 ± 13 (40)	90 ± 13 (40)	92 ± 9 (40)	94 ± 7 (40)	2	97 ± 6	96 ± 8	93 ± 7	100 ± 10
deltamethrin	20	nd	97 ± 12 (36)	93 ± 12 (40)	98 ± 8 (40)	10	105 ± 34	105 ± 37	105 ± 14	107 ± 11
demeton S-methyl	20	nd	83 ± 12 (40)	79 ± 19 (40)	86 ± 15 (40)	2	91 ± 14	89 ± 15	90 ± 12	93 ± 12
demeton-S	15	nd	77 ± 16 (40)	76 ± 21 (40)	83 ± 17 (40)					
dialifor	10	93 ± 6 (40)	94 ± 7 (40)	95 ± 5 (40)	99 ± 4 (40)	5	104 ± 12	100 ± 8	103 ± 14	103 ± 13
diallate 1	10	83 ± 16 (40)	79 ± 12 (40)	86 ± 13 (40)	89 ± 8 (40)	1	91 ± 11	90 ± 14	90 ± 11	95 ± 10
diallate 2	10	88 ± 12 (40)	82 ± 10 (40)	86 ± 12 (40)	89 ± 8 (40)	1	93 ± 11	89 ± 15	91 ± 10	94 ± 8
diazinon	5	98 ± 10 (39)	93 ± 7 (40)	96 ± 7 (40)	97 ± 4 (40)	2	97 ± 10	97 ± 11	97 ± 10	101 ± 7
dicapthos	15	nd	83 ± 10 (40)	83 ± 9 (40)	87 ± 6 (40)	2	89 ± 8	90 ± 11	89 ± 8	92 ± 7
dichlofluanid	5	30 ± 23 (16)	55 ± 30 (28)	48 ± 22 (40)	69 ± 23 (40)	10	22 ± 22	49 ± 20	49 ± 21	73 ± 20
dichlorfenthion	20	nd	88 ± 10 (40)	93 ± 7 (40)	95 ± 4 (40)	1	93 ± 9	92 ± 10	90 ± 8	96 ± 8
dichloroaniline, 3,4'-	5	54 ± 15 (19)	64 ± 17 (32)	62 ± 16 (36)	59 ± 22 (40)	5	70 ± 12	61 ± 16	69 ± 18	72 ± 18
dichlorobenzophenone, 4,4'-	15	nd	87 ± 11 (36)	95 ± 5 (40)	99 ± 8 (40)	1	135 ± 118	108 ± 42	101 ± 13	104 ± 9

Table 2. Continued

pesticide	GC-MS/SIM					GC-MS/MS				
	LOQ ($\mu\text{g}/\text{kg}$)	10 $\mu\text{g}/\text{kg}$ (n)	25 $\mu\text{g}/\text{kg}$ (n)	100 $\mu\text{g}/\text{kg}$ (n)	500 $\mu\text{g}/\text{kg}$ (n)	LOQ ($\mu\text{g}/\text{kg}$)	10 $\mu\text{g}/\text{kg}$ (n = 40)	25 $\mu\text{g}/\text{kg}$ (n = 40)	100 $\mu\text{g}/\text{kg}$ (n = 40)	500 $\mu\text{g}/\text{kg}$ (n = 40)
dichlorvos	10	71 ± 25 (35)	64 ± 22 (40)	63 ± 28 (40)	66 ± 24 (40)	10	74 ± 12	72 ± 21	84 ± 8	76 ± 20
diclobenil	10	69 ± 23 (40)	60 ± 22 (40)	61 ± 29 (40)	63 ± 24 (40)	5	75 ± 15	75 ± 24	82 ± 7	83 ± 9
dicloran	10	94 ± 16 (36)	89 ± 15 (40)	89 ± 5 (40)	91 ± 5 (40)	5	92 ± 7	92 ± 6	93 ± 8	90 ± 5
dieldrin	20	nd	94 ± 7 (40)	95 ± 5 (40)	99 ± 5 (40)	10	94 ± 11	94 ± 9	96 ± 8	95 ± 6
dimethachlor	5	97 ± 17 (36)	87 ± 21 (40)	94 ± 11 (40)	100 ± 4 (40)	1	99 ± 10	98 ± 9	97 ± 9	103 ± 9
dioxathion	15	nd	89 ± 11 (40)	94 ± 10 (40)	97 ± 6 (40)	5	106 ± 15	99 ± 11	101 ± 11	102 ± 10
disulfoton	10	62 ± 22 (40)	65 ± 16 (40)	72 ± 17 (40)	81 ± 14 (40)	10	91 ± 9	86 ± 16	88 ± 10	93 ± 7
ditalimfos	25	nd	41 ± 12 (32)	42 ± 16 (40)	51 ± 19 (40)	2	46 ± 18	49 ± 19	50 ± 20	63 ± 26
edifenphos	15	nd	94 ± 9 (40)	95 ± 6 (40)	97 ± 4 (40)	5	98 ± 8	99 ± 6	97 ± 6	101 ± 6
endosulfan ether	15	nd	91 ± 10 (40)	90 ± 8 (40)	95 ± 6 (40)	10	94 ± 12	93 ± 12	96 ± 11	100 ± 8
endosulfan sulfate	15	nd	92 ± 11 (32)	79 ± 37 (40)	94 ± 15 (40)	10	98 ± 12	99 ± 14	100 ± 8	102 ± 6
endosulfan, α -	15	nd	93 ± 7 (40)	93 ± 4 (40)	96 ± 3 (40)	10	100 ± 15	92 ± 11	95 ± 10	100 ± 10
endosulfan, β -	15	nd	95 ± 6 (40)	97 ± 4 (40)	99 ± 5 (40)	10	101 ± 22	91 ± 15	100 ± 14	99 ± 12
endrin	20	nd	93 ± 6 (40)	93 ± 5 (40)	95 ± 4 (40)	10	102 ± 36	112 ± 28	105 ± 15	106 ± 12
endrin aldehyde	15	nd	23 ± 14 (20)	14 ± 7 (36)	13 ± 8 (40)	10	82 ± 24	87 ± 17	80 ± 32	83 ± 28
endrin ketone	15	nd	95 ± 8 (36)	97 ± 6 (40)	100 ± 5 (40)	5	90 ± 28	96 ± 11	101 ± 7	102 ± 8
EPN	20	nd	95 ± 9 (36)	94 ± 8 (40)	98 ± 4 (40)	10	101 ± 10	98 ± 11	95 ± 9	101 ± 7
ethalfuralin	5	89 ± 20 (40)	89 ± 12 (40)	91 ± 13 (40)	94 ± 7 (40)	5	89 ± 12	92 ± 14	92 ± 13	99 ± 12
ethion	10	96 ± 8 (40)	95 ± 7 (40)	100 ± 5 (40)	102 ± 3 (40)	1	92 ± 12	90 ± 14	90 ± 10	96 ± 9
ethoprop	10	90 ± 18 (40)	90 ± 8 (40)	92 ± 9 (40)	95 ± 6 (40)	1	97 ± 13	97 ± 13	97 ± 11	101 ± 11
etridazole	5	73 ± 22 (40)	67 ± 18 (40)	65 ± 28 (40)	68 ± 22 (40)	10	85 ± 13	78 ± 25	82 ± 20	90 ± 9
famphur	15	nd	96 ± 9 (40)	91 ± 14 (40)	99 ± 10 (40)	10	101 ± 11	99 ± 10	98 ± 10	101 ± 10
fenamiphos	5	96 ± 9 (36)	93 ± 11 (40)	93 ± 9 (40)	95 ± 7 (40)	1	98 ± 10	91 ± 21	93 ± 9	98 ± 10
fenarimol	10	96 ± 9 (36)	92 ± 6 (40)	97 ± 5 (40)	100 ± 4 (40)	2	110 ± 17	99 ± 8	98 ± 9	100 ± 6
fenchlorphos	5	94 ± 7 (39)	89 ± 5 (40)	91 ± 6 (40)	93 ± 4 (40)	1	94 ± 9	93 ± 9	89 ± 8	96 ± 7
fenitrothion	15	nd	99 ± 16 (40)	90 ± 21 (40)	100 ± 4 (40)	5	98 ± 9	103 ± 13	101 ± 11	106 ± 14
fensulfotthion	15	nd	105 ± 14 (40)	103 ± 17 (40)	97 ± 12 (40)	5	109 ± 16	106 ± 19	109 ± 10	115 ± 8
fenthion	10	98 ± 7 (39)	94 ± 5 (40)	94 ± 7 (40)	97 ± 5 (40)	2	95 ± 11	97 ± 10	94 ± 7	101 ± 9
fenvalerate 1	20	nd	84 ± 15 (40)	89 ± 11 (40)	93 ± 5 (40)	10	101 ± 22	98 ± 23	101 ± 12	99 ± 9
fenvalerate 2	20	nd	91 ± 13 (40)	92 ± 10 (40)	100 ± 6 (40)	10	107 ± 22	107 ± 26	108 ± 13	107 ± 11
fluchloralin	20	nd	90 ± 19 (40)	97 ± 10 (40)	98 ± 6 (40)	1	92 ± 11	95 ± 14	95 ± 10	104 ± 8
flucythrinate 1	15	nd	100 ± 11 (36)	104 ± 11 (40)	113 ± 10 (40)	1	120 ± 20	121 ± 22	123 ± 15	122 ± 18
flucythrinate 2	15	nd	89 ± 16 (36)	89 ± 9 (40)	89 ± 6 (40)	1	94 ± 15	92 ± 18	92 ± 10	93 ± 9
fluridone	20	nd	138 ± 18 (40)	144 ± 13 (40)	146 ± 17 (40)	5	322 ± 227	180 ± 60	173 ± 27	181 ± 38
fluvalinate τ -1	10	99 ± 9 (28)	96 ± 14 (40)	100 ± 14 (40)	101 ± 11 (40)	10	97 ± 12	95 ± 12	102 ± 11	106 ± 12
fluvalinate τ -2	10	97 ± 7 (28)	95 ± 9 (40)	97 ± 8 (40)	99 ± 6 (40)	10	99 ± 10	96 ± 13	104 ± 12	105 ± 11
folpet	45	nd	nd	63 ± 19 (40)	71 ± 21 (40)	10	40 ± 41	70 ± 26	72 ± 16	85 ± 17
fonophos	20	nd	86 ± 8 (40)	90 ± 8 (40)	93 ± 6 (40)	2	96 ± 11	93 ± 11	92 ± 10	96 ± 10
heptachlor	20	nd	79 ± 20 (36)	93 ± 13 (40)	100 ± 7 (40)	1	105 ± 13	103 ± 14	103 ± 11	109 ± 10
hexachlorobenzene	1	50 ± 9 (40)	45 ± 8 (40)	47 ± 10 (40)	48 ± 6 (40)	1	58 ± 10	53 ± 13	52 ± 13	57 ± 10
iprobenfos	20	nd	91 ± 6 (40)	94 ± 5 (40)	94 ± 8 (40)	2	91 ± 11	95 ± 14	89 ± 10	96 ± 9
iprodione	15	nd	96 ± 6 (40)	96 ± 4 (40)	99 ± 4 (40)	5	99 ± 12	102 ± 13	99 ± 9	102 ± 7
isazophos	20	nd	71 ± 21 (36)	88 ± 10 (40)	92 ± 10 (40)	5	98 ± 12	93 ± 9	95 ± 11	100 ± 7
isofenphos	15	nd	98 ± 5 (40)	101 ± 5 (40)	102 ± 4 (40)	5	102 ± 7	103 ± 9	101 ± 7	107 ± 7
jodfenphos	5	95 ± 7 (40)	91 ± 5 (40)	93 ± 6 (40)	95 ± 5 (40)	2	95 ± 11	96 ± 8	95 ± 8	98 ± 7
leptophos	10	79 ± 7 (40)	74 ± 6 (40)	76 ± 6 (40)	76 ± 5 (40)	5	80 ± 6	79 ± 5	79 ± 6	80 ± 7
malathion	25	nd	96 ± 5 (36)	100 ± 5 (40)	101 ± 4 (40)	2	101 ± 9	101 ± 10	104 ± 9	108 ± 7
methidathion	20	nd	96 ± 10 (40)	98 ± 8 (40)	99 ± 5 (40)	1	99 ± 8	100 ± 8	100 ± 7	104 ± 8
methoxychlor, <i>o,p'</i> -	10	96 ± 7 (36)	92 ± 9 (40)	94 ± 6 (40)	96 ± 4 (40)	1	102 ± 10	101 ± 11	96 ± 13	104 ± 20
methoxychlor, <i>p,p'</i> -	10	97 ± 9 (40)	92 ± 10 (40)	96 ± 8 (40)	99 ± 6 (40)	1	100 ± 7	99 ± 6	101 ± 21	99 ± 8
metolachlor	5	100 ± 6 (40)	96 ± 5 (40)	100 ± 5 (40)	102 ± 4 (40)	2	100 ± 12	100 ± 16	98 ± 12	102 ± 10
mevinphos	10	90 ± 13 (39)	87 ± 7 (40)	88 ± 11 (40)	91 ± 9 (40)	5	88 ± 12	90 ± 13	92 ± 8	94 ± 10
mirex	10	85 ± 8 (40)	81 ± 11 (40)	86 ± 8 (40)	85 ± 7 (40)	5	89 ± 8	88 ± 10	86 ± 8	86 ± 10
nonachlor, <i>cis</i> -	1	95 ± 5 (40)	90 ± 5 (40)	92 ± 5 (40)	93 ± 4 (40)	2	95 ± 12	94 ± 11	95 ± 10	99 ± 8
nonachlor, <i>trans</i> -	1	97 ± 8 (40)	90 ± 6 (40)	93 ± 5 (40)	95 ± 4 (40)	2	94 ± 10	93 ± 8	93 ± 6	95 ± 7
oxadiazon	5	103 ± 6 (40)	99 ± 5 (40)	101 ± 5 (40)	103 ± 4 (40)	10	106 ± 9	104 ± 9	103 ± 7	105 ± 7
parathion	10	99 ± 12 (40)	93 ± 10 (40)	95 ± 8 (40)	100 ± 3 (40)	5	98 ± 13	99 ± 10	98 ± 7	106 ± 9
parathion-methyl	20	nd	93 ± 11 (36)	92 ± 8 (40)	97 ± 4 (40)	5	94 ± 9	95 ± 10	95 ± 8	99 ± 8
pentachloroaniline	1	72 ± 10 (40)	66 ± 7 (40)	66 ± 5 (40)	67 ± 4 (40)	5	68 ± 9	68 ± 9	68 ± 6	69 ± 5
pentachlorobenzene	1	63 ± 20 (40)	58 ± 14 (36)	54 ± 23 (40)	56 ± 18 (40)	2	71 ± 12	69 ± 10	68 ± 10	70 ± 10
pentachlorobenzonitrile	2	64 ± 11 (40)	59 ± 7 (40)	59 ± 6 (40)	60 ± 4 (40)	1	64 ± 8	62 ± 7	62 ± 8	62 ± 7
pentachlorophenyl methyl ester	1	75 ± 12 (40)	68 ± 10 (40)	71 ± 13 (40)	73 ± 9 (40)	2	79 ± 11	75 ± 13	77 ± 11	77 ± 8
pentachlorothioanisole	1	54 ± 7 (40)	50 ± 5 (40)	51 ± 6 (40)	52 ± 4 (40)	5	62 ± 17	56 ± 11	58 ± 8	55 ± 10
permethrin, <i>cis</i> -	10	94 ± 6 (36)	90 ± 8 (40)	94 ± 5 (40)	95 ± 4 (40)	5	100 ± 12	99 ± 11	97 ± 7	101 ± 10
permethrin, <i>trans</i> -	10	98 ± 6 (36)	93 ± 6 (40)	95 ± 6 (40)	96 ± 5 (40)	5	95 ± 9	92 ± 7	96 ± 9	97 ± 8

Table 2. Continued

pesticide	GC-MS/SIM					GC-MS/MS				
	LOQ ($\mu\text{g/kg}$)	10 $\mu\text{g/kg}$ (<i>n</i>)	25 $\mu\text{g/kg}$ (<i>n</i>)	100 $\mu\text{g/kg}$ (<i>n</i>)	500 $\mu\text{g/kg}$ (<i>n</i>)	LOQ ($\mu\text{g/kg}$)	10 $\mu\text{g/kg}$ (<i>n</i> = 40)	25 $\mu\text{g/kg}$ (<i>n</i> = 40)	100 $\mu\text{g/kg}$ (<i>n</i> = 40)	500 $\mu\text{g/kg}$ (<i>n</i> = 40)
phenothrin	10	97 ± 7 (40)	92 ± 7 (40)	95 ± 5 (40)	98 ± 4 (40)	10	101 ± 77	84 ± 15	105 ± 23	101 ± 10
phenthoate	15	nd	95 ± 6 (40)	100 ± 5 (40)	100 ± 5 (40)					
phorate	20	nd	82 ± 12 (40)	85 ± 13 (40)	88 ± 10 (40)	10	90 ± 12	88 ± 17	84 ± 23	92 ± 9
phosalone	10	92 ± 8 (40)	89 ± 7 (40)	92 ± 7 (40)	95 ± 4 (40)	5	89 ± 18	88 ± 5	94 ± 6	102 ± 6
phosmet	10	91 ± 11 (40)	90 ± 9 (40)	91 ± 9 (40)	95 ± 9 (40)	2	98 ± 10	97 ± 8	97 ± 6	101 ± 9
pirimphos-ethyl	2	96 ± 17 (40)	94 ± 5 (40)	96 ± 5 (40)	97 ± 3 (40)	5	98 ± 11	97 ± 11	96 ± 7	101 ± 7
pirimphos-methyl	2	97 ± 10 (40)	91 ± 14 (40)	99 ± 6 (40)	99 ± 3 (40)	1	97 ± 11	100 ± 10	98 ± 10	103 ± 9
procymidone	5	102 ± 5 (40)	98 ± 6 (40)	99 ± 4 (40)	101 ± 3 (40)	5	102 ± 9	100 ± 9	100 ± 7	103 ± 8
profenophos	10	94 ± 7 (40)	91 ± 6 (40)	94 ± 5 (40)	95 ± 4 (40)	2	92 ± 11	95 ± 9	94 ± 6	95 ± 8
propachlor	10	93 ± 10 (24)	88 ± 7 (40)	91 ± 9 (40)	94 ± 7 (40)	5	92 ± 11	93 ± 13	93 ± 12	97 ± 10
propazine	15	nd	89 ± 13 (28)	96 ± 16 (40)	97 ± 9 (40)	10	93 ± 14	99 ± 8	99 ± 7	103 ± 7
propetamphos	15	nd	95 ± 5 (36)	98 ± 5 (40)	100 ± 4 (40)	5	95 ± 9	94 ± 11	98 ± 8	103 ± 9
propyzamide	20	nd	91 ± 7 (32)	87 ± 17 (40)	99 ± 5 (40)	5	99 ± 11	99 ± 10	100 ± 9	104 ± 9
prothiophos	15	nd	96 ± 16 (36)	86 ± 30 (36)	92 ± 9 (40)	1	96 ± 13	95 ± 15	96 ± 13	98 ± 10
pyraclofos	5	95 ± 11 (40)	92 ± 11 (40)	94 ± 7 (40)	97 ± 4 (40)	10	106 ± 12	100 ± 10	99 ± 7	106 ± 7
pyrazophos	10	82 ± 7 (40)	79 ± 8 (40)	82 ± 7 (40)	83 ± 5 (40)	10	86 ± 12	88 ± 13	85 ± 8	94 ± 18
pyridaphenthion	10	97 ± 9 (40)	96 ± 9 (40)	97 ± 7 (40)	100 ± 4 (40)	10	94 ± 12	91 ± 17	100 ± 7	98 ± 19
quinalphos	15	nd	94 ± 5 (40)	97 ± 4 (40)	98 ± 3 (40)	1	96 ± 7	96 ± 8	98 ± 7	101 ± 7
quintozene	5	82 ± 12 (40)	73 ± 8 (40)	76 ± 9 (40)	80 ± 6 (40)	5	78 ± 9	75 ± 10	79 ± 11	84 ± 8
resmethrin	10	88 ± 17 (36)	81 ± 15 (40)	81 ± 18 (40)	83 ± 16 (40)	5	90 ± 12	89 ± 11	83 ± 18	83 ± 19
simazine	15	nd	95 ± 6 (40)	98 ± 5 (40)	99 ± 3 (40)	5	98 ± 10	96 ± 10	101 ± 11	99 ± 9
sulfotep-ethyl	5	87 ± 19 (39)	84 ± 9 (40)	88 ± 10 (40)	92 ± 7 (40)	1	93 ± 13	90 ± 16	89 ± 11	97 ± 10
sulprofos	10	92 ± 8 (36)	87 ± 15 (40)	91 ± 8 (40)	95 ± 5 (40)	2	94 ± 8	95 ± 8	94 ± 8	98 ± 7
tebupirimphos	2	96 ± 18 (39)	93 ± 5 (40)	96 ± 7 (40)	98 ± 4 (40)	1	94 ± 10	95 ± 10	93 ± 8	100 ± 10
tecnazene	2	80 ± 15 (40)	71 ± 15 (40)	75 ± 17 (40)	79 ± 13 (40)	2	82 ± 15	78 ± 16	81 ± 14	86 ± 10
tefluthrin	10	89 ± 11 (40)	87 ± 8 (40)	90 ± 7 (40)	93 ± 5 (40)	1	93 ± 9	91 ± 10	89 ± 9	96 ± 8
temephos	30	nd	nd	84 ± 34 (24)	88 ± 51 (28)		na	na	na	na
terbufos	20	nd	81 ± 11 (40)	89 ± 10 (40)	93 ± 7 (40)		na	na	na	na
terbutylazine	20	nd	94 ± 5 (36)	96 ± 6 (40)	100 ± 4 (40)	5	93 ± 13	97 ± 11	99 ± 8	102 ± 8
tetrachloroaniline, 2,3,5,6-	5	83 ± 11 (40)	75 ± 8 (40)	78 ± 12 (40)	80 ± 10 (40)	2	82 ± 12	79 ± 13	80 ± 11	82 ± 8
tetrachlorvinphos	5	101 ± 6 (40)	95 ± 8 (40)	97 ± 6 (40)	100 ± 4 (40)	10	100 ± 18	95 ± 14	96 ± 9	101 ± 11
tetramethrin	10	99 ± 6 (40)	94 ± 6 (40)	98 ± 5 (40)	99 ± 4 (40)	5	98 ± 18	100 ± 11	98 ± 6	101 ± 5
tolclofos-methyl	10	97 ± 8 (39)	92 ± 6 (40)	94 ± 6 (40)	95 ± 4 (40)	1	94 ± 8	93 ± 10	90 ± 8	97 ± 8
tolyfluanid	15	nd	53 ± 14 (28)	59 ± 23 (40)	79 ± 24 (40)	10	85 ± 52	96 ± 43	92 ± 36	109 ± 39
triallate	20	nd	82 ± 8 (40)	85 ± 9 (40)	88 ± 7 (40)	2	91 ± 11	89 ± 12	89 ± 11	93 ± 7
triazophos	10	102 ± 7 (36)	101 ± 6 (40)	105 ± 7 (40)	105 ± 5 (40)	5	103 ± 11	108 ± 25	107 ± 32	104 ± 9
tribufos (DEF)	10	93 ± 8 (36)	90 ± 9 (40)	92 ± 6 (40)	92 ± 5 (40)	2	97 ± 10	98 ± 9	97 ± 6	98 ± 6
trifluralin	5	90 ± 13 (39)	86 ± 11 (40)	89 ± 11 (40)	92 ± 6 (40)	5	89 ± 10	88 ± 11	91 ± 10	98 ± 9
vinclozolin	10	100 ± 8 (40)	96 ± 6 (40)	97 ± 4 (40)	100 ± 4 (40)	2	100 ± 8	97 ± 8	95 ± 7	102 ± 10

^a Quantitation of the recoveries is described under Materials and Methods. Samples are expressed as average ± standard deviation, *n* = total number of replicates. Each commodity was analyzed four times at each fortification level. The average LOQs were determined by the averages of the individual LOQs of the 10 commodities combined. nd, not detected; na, not analyzed.

were 15–25 $\mu\text{g/kg}$. Captafol and captan were the two pesticides that had the highest LOQ for both MS detection methods.

Fortification studies were conducted by fortifying 10 raw produce commodities at concentrations of 10, 25, 100, and 500 $\mu\text{g/kg}$. The 10 commodities (bell pepper, broccoli, cantaloupe, carrot, onion, orange, peach, potato, spinach, and tomato) were chosen on the basis of consumer consumption, variety, and product characteristics and analyzed at each fortification level in quadruplicates. **Table 2** lists the mean recoveries and standard deviations for 167 pesticides at 10, 25, 100, and 500 $\mu\text{g/kg}$ for all 10 produce commodities. The mean percent recoveries were 90 ± 14, 87 ± 14, 89 ± 14, and 92 ± 14% for GC-MS/SIM and 95 ± 22, 93 ± 14, 93 ± 13, and 97 ± 13% for GC-MS/MS at 10, 25, 100, and 500 $\mu\text{g/kg}$, respectively. The numbers of pesticides in which > 70% recovery was observed at the 10, 25, 100, and 500 $\mu\text{g/kg}$ levels were 91, 146, 151, and 153 for GC-MS/SIM (167 total pesticides measured) and 149, 149, 147, and 150 for GC-MS/MS (160 total pesticides measured). These results indicate recoveries using the proposed method for most of the pesticides in a wide variety of fresh produce matrices were generally in the acceptable range of 70–120%. Pesticides that have low

(< 70%) recoveries or large variances (*SD* > 20%) were early-eluting analytes or those that tended to be sensitive to pH changes, more prone to volatility loss (i.e., 3,4'-dichloroaniline, dichlorvos, diclobenil, and etridazole), strongly adsorbed by the PSA or GCB sorbents (i.e., chlorothalonil, endrin aldehyde, hexachlorobenzene, pentachlorobenzene, pentachlorobenzonitrile, and pentachloroethoxyanisole), or more difficult to ionize by mass spectrometric detection (i.e., captafol, captan, dichlofluanid, folpet, and tolyfluanid). Highly nonpolar or late-eluting pesticides such as temephos and fluridone were also problematic.

Statistical analysis using a two-tailed Student's *t* test at the 95% confidence level and PCA were used to evaluate the performance of both SIM and MS/MS analysis modes using recovery results. Results from Student's *t* test analysis of the data in **Table 2** reveal that the two detection methods were similar for most of the analytes at the 25, 100, and 500 $\mu\text{g/kg}$ fortification concentrations. For all concentrations, differences in recoveries were observed for aldrin and endrin aldehyde. Six pesticides, including demeton-S, dioxabenzofos, heptachlor epoxide, phorate, temephos, and terbufos, were excluded from Student's *t* test and

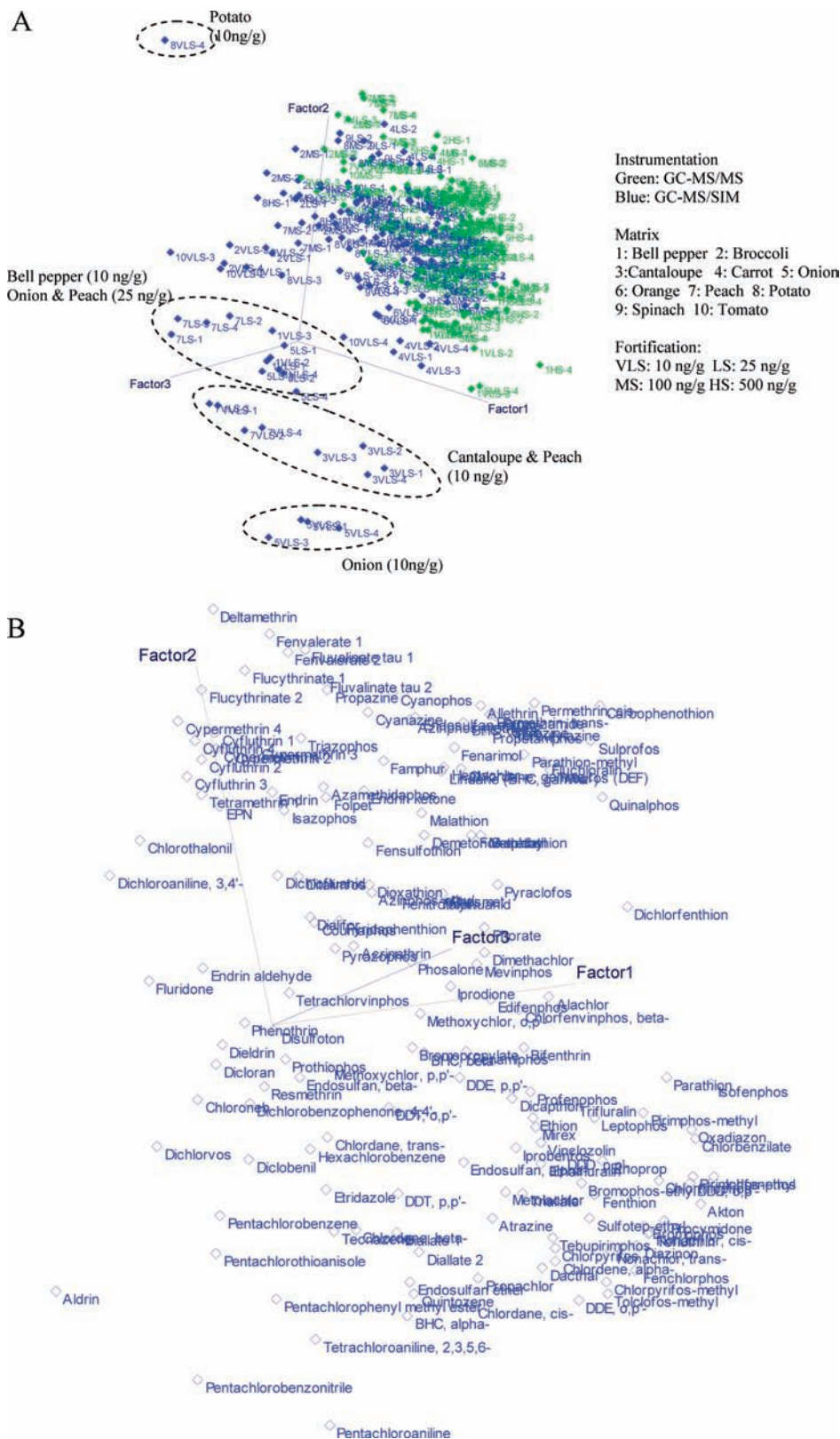


Figure 4. Principal component analysis of the first 3 factors for 160 pesticides analyzed in 10 produce commodities (bell pepper, broccoli, cantaloupe, carrot, onion, orange, peach, potato, spinach, and tomato) and 4 fortification concentrations (10, 25, 100, and 500 ng/g ($\mu\text{g}/\text{kg}$)) using GC-MS/SIM and GC-MS/MS detection: **(A)** scores (fortified samples); **(B)** loadings (pesticides).

PCA analyses because these pesticides were not detected by both GC-MS/SIM and GC-MS/MS.

A comprehensive comparative analysis of the two detection techniques for 10 produce samples containing 160 pesticides at 4 concentrations (12800 data points) is quite difficult without the

use of computer processing techniques. PCA is ideally suited for this type of analysis. Results from PCA are shown in **Figure 4**, panels **A** (scores) and **B** (loadings), which illustrates the variance of 160 pesticides at 4 concentrations detected by GC-MS/SIM and GC-MS/MS. The PCA found that 81% of the data are

Table 3. Results of Incurred Residues in Produce Samples (Bell Pepper, Carrot, Peach, Spinach, and Tomato)^a

pesticide	concentration ($\mu\text{g}/\text{kg}$)									
	carrot ($n = 4$)		bell pepper ($n = 4$)		spinach ($n = 4$)		tomato ($n = 3$)		peach ($n = 3$)	
	GC-MS/SIM	GC-MS/MS	GC-MS/SIM	GC-MS/MS	GC-MS/SIM	GC-MS/MS	GC-MS/SIM	GC-MS/MS	GC-MS/SIM	GC-MS/MS
bifenthrin			45 \pm 2	50 \pm 2						
chlorothalonil							153 \pm 26	180 \pm 5		
chlorpyrifos	8 \pm 1	7 \pm 1								
DDE, <i>o,p'</i> -	2 \pm 1	8 \pm 1			nd	10 \pm 2				
DDE, <i>p,p'</i> -	56 \pm 2	54 \pm 3			31 \pm 2	25 \pm 1				
DDD, <i>p,p'</i> -	14 \pm 1	13 \pm 1			nd	7 \pm 1				
DDT, <i>p,p'</i> -	39 \pm 1	37 \pm 2			6 \pm 1	5 \pm 1				
α -endosulfan			nd	6 \pm 2			26 \pm 4	24 \pm 2		
β -endosulfan							63 \pm 3	63 \pm 12		
endosulfan sulfate			10 \pm 1	13 \pm 3			21 \pm 6	15 \pm 2		
phosmet									51 \pm 8	57 \pm 4

^aThe samples were subjected to the proposed sample preparation procedures and analyzed by GC-MS/SIM and GC-MS/MS as described under Materials and Methods. Samples are expressed as average \pm standard deviation ($n = 3$ or 4) $\mu\text{g}/\text{kg}$. nd, not detected.

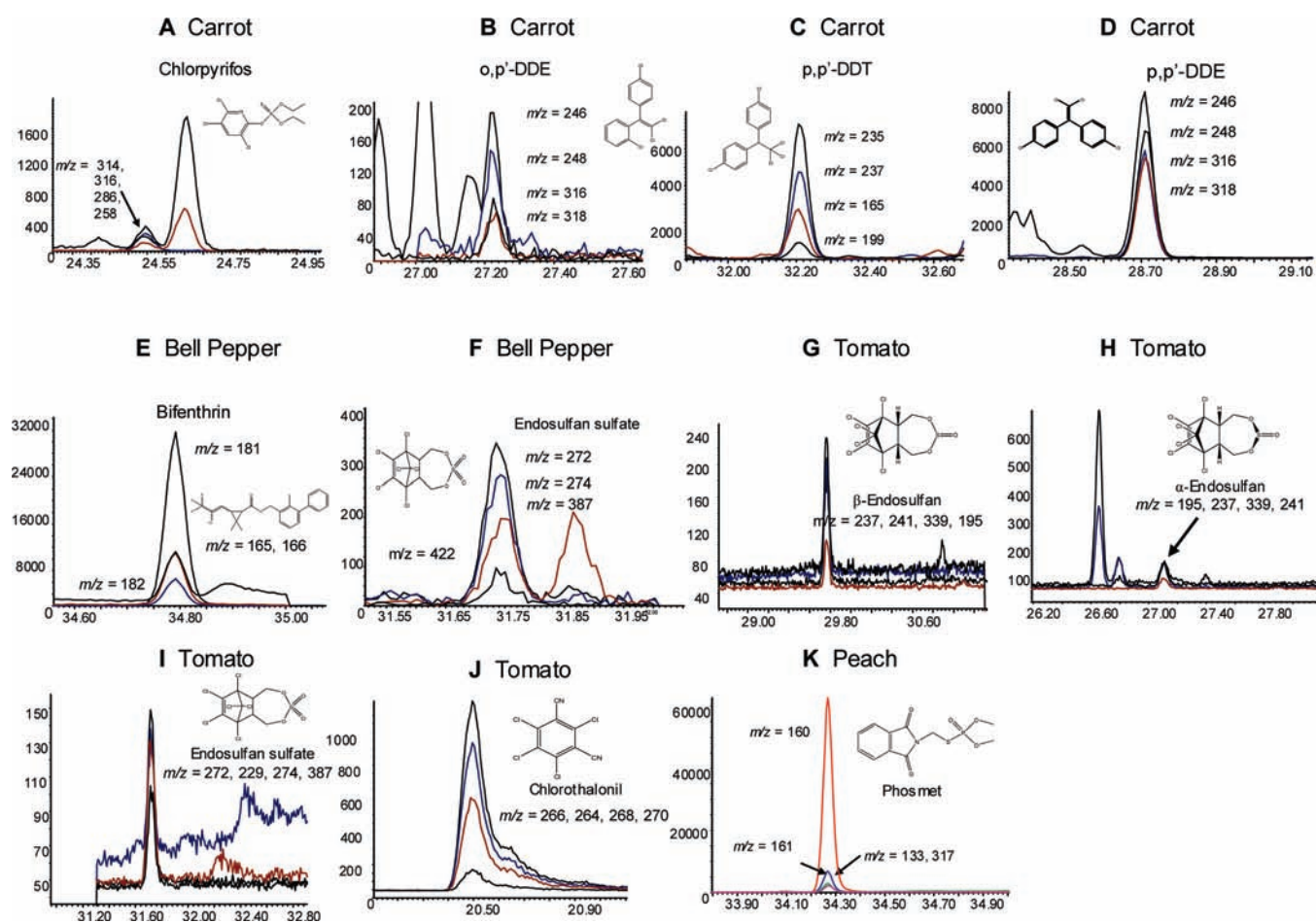


Figure 5. Reconstructed GC-MS/SIM chromatograms of the incurred produce commodities containing various pesticides including (A) chlorpyrifos, (B) *o,p'*-DDE, (C) *p,p'*-DDT, and (D) *p,p'*-DDE present in carrot; (E) bifenthrin and (F) endosulfan sulfate present in bell pepper; (G) β - and (H) α -endosulfan, (I) chlorothalonil, and (J) endosulfan sulfate present in carrot; and (K) phosmet in peach. Included are the target and three qualifier ions used for pesticide identification.

represented by the first 20 factors; the first 3 factors are illustrated in Figure 4. Although the PCA shows the majority of the recovery data for the 161 pesticides are similar, PCA easily highlights the outlier groups (circled). These outliers are all used the GC-MS/SIM detection in the 10 $\mu\text{g}/\text{kg}$ fortification concentration range for the bell pepper, cantaloupe, onion, peach, and potato products and for the onion and peach products at the 25 $\mu\text{g}/\text{kg}$ fortification. These outliers could be attributed to the produce

matrix, which may have interfered with the analysis of pesticides at the 10 $\mu\text{g}/\text{kg}$ level by GC-MS/SIM.

Overall, the 10 sample matrices and the two instrumentation detection techniques (GC-MS/MS and GC-MS/SIM) have no effect on the pesticide recovery results at the 25, 100, and 500 $\mu\text{g}/\text{kg}$ fortification concentrations. Generally, one major clustering group based on the recovery data was produced, most of the blue and green data points

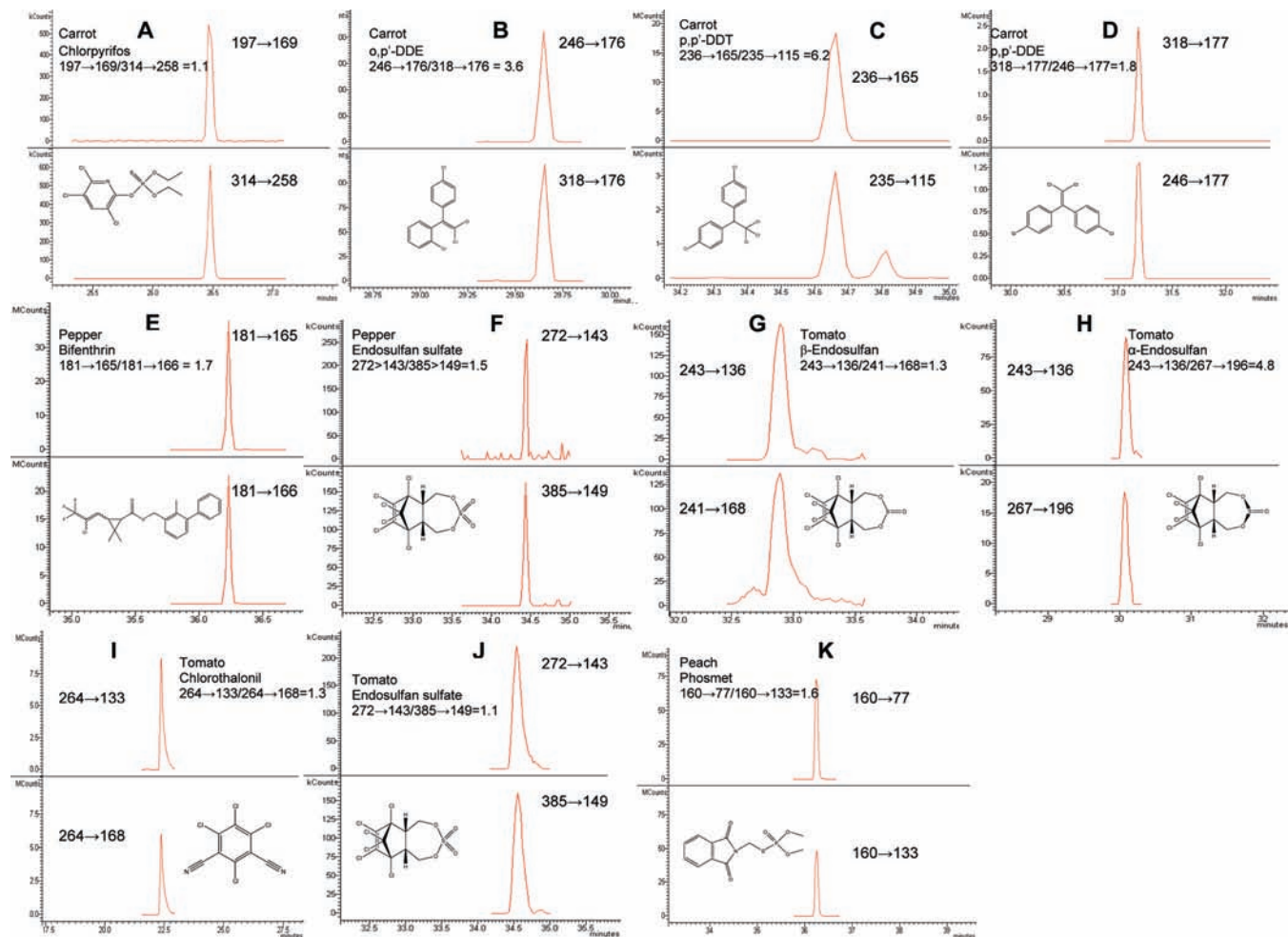


Figure 6. Reconstructed GC-MS/MS chromatograms of the same incurred produce commodities as analyzed by GC-MS/SIM in **Figure 5** containing various pesticides including chlorpyrifos (**A**), *o,p'*-DDE (**B**), *p,p'*-DDT (**C**), and *p,p'*-DDE (**D**) present in carrot; bifenthrin (**E**) and endosulfan sulfate (**F**) present in bell pepper; β - (**G**) and α - (**H**) endosulfan, endosulfan sulfate (**I**) and chlorothalonil (**J**) present in tomato; and phosmet (**K**) in peach. Included are the transitions from precursor to product ions and the relative ion ratios between the two transitions, primary (top) and secondary (bottom), which are used for pesticide identification.

in **Figure 4A** overlap, indicating the GC-MS/SIM detection (blue) and GC-MS/MS detection (green) will produce similar results in the 10 produce samples. However, in the lowest concentration range, GC-MS/SIM is more susceptible to matrix effects. The results from statistical analysis and PCA suggest the method is robust for produce samples containing pesticides in the 25–500 $\mu\text{g}/\text{kg}$ concentration range by either GC-MS/SIM or GC-MS/MS. The ruggedness of the method is further improved with GC-MS/MS analysis because the results indicate that even at the lowest fortified concentration of 10 $\mu\text{g}/\text{kg}$, GC-MS/MS is still sensitive enough to detect the pesticides and selective enough so that the matrix did not effect the detection and identification of the pesticides.

Analysis of Incurred Samples and Comparison by GC-MS/SIM and GC-MS/MS. Examples of incurred produce samples, including bell pepper, carrot, peach, spinach, and tomato, were provided by the FDA field laboratories (Southeast Regional Laboratory, Atlanta, GA, and Northwest Regional Laboratory, Bothell, WA), prepared in replicates ($n = 3$ or 4 for each sample), and analyzed using the procedure described above. Results for the analysis of pesticides found in the produce samples and their concentrations are given in **Table 3**. GC-MS/SIM and GC-MS/MS chromatograms of these detected pesticides in these matrices are shown in

Figures 5 and 6. We found organochlorine, organophosphorus, and pyrethroid pesticides in these samples with concentrations ranging from $2 \pm 1 \mu\text{g}/\text{kg}$ (*o,p'*-DDE in carrot) to $153 \pm 26 \mu\text{g}/\text{kg}$ (chlorothalonil in tomato) by GC-MS/SIM and from $5 \pm 1 \mu\text{g}/\text{kg}$ (*p,p'*-DDT in spinach) to $180 \pm 5 \mu\text{g}/\text{kg}$ (chlorothalonil in tomato) by GC-MS/MS analysis. All pesticides were identified in the produce samples on the basis of the criteria established by the Comité Européen de Normalization (European Committee for Standardization (CEN)) using qualifier-to-target (MS/SIM) and primary ion transition/secondary ion transition ratios (MS/MS) (19). In summary, the carrot and spinach samples were found to contain primarily *p,p'*-DDE and other metabolites of the parent compound, *p,p'*-DDT. Tomato and bell pepper samples were found to contain endosulfan and its metabolite, endosulfan sulfate, in addition to the pyrethroid insecticide bifenthrin (bell pepper) and the aromatic fungicide chlorothalonil (tomato). Two organophosphorus pesticides, chlorpyrifos and phosmet, were present in carrot and peach samples. With the exception of the chlorothalonil in tomato, the concentrations of all other detectable pesticides in these produce sample were $< 63 \mu\text{g}/\text{kg}$ (β -endosulfan in tomato).

GC-MS/SIM and GC-MS/MS chromatograms for extracts from produce are illustrated in **Figures 5 and 6**, respectively.

These figures indicate significantly more background and matrix contributions to the GC-MS/SIM chromatograms, especially for carrot (*o,p'*-DDE) and tomato (endosulfan sulfate). The presence of *o,p'*-DDE in carrot (**Figure 5B**) could not be properly verified by GC-MS/SIM according to CEN criteria (29), because of the interference with the *m/z* 246 ion. In contrast, the same carrot extract was analyzed by GC-MS/MS, and the resulting chromatogram (**Figure 6B**) reveals two distinct ion transitions (246→176, 318→176) unaffected by the carrot matrix. Other incurred pesticides in the produce samples also showed more background in the GC-MS/SIM chromatograms when compared to GC-MS/MS. The LOQ values listed in **Table 2** and the GC-MS/MS chromatograms in **Figure 6** indicate the higher specificity and sensitivity of GC-MS/MS, which suggests extracts can be further diluted to allow for a smaller mass of sample to be introduced into the GC system. This can extend the use of the GC linear and column, resulting in less instrument maintenance.

The pesticide concentrations found in the five produce commodities and analyzed by GC-MS/SIM or GC-MS/MS listed in **Table 3** are in agreement. The GC-MS/SIM nondetects in the bell pepper and spinach extracts were probably due to interferences from coextractives in the plant matrices. Previously we have also validated the method for the effective analysis of pesticides in hundreds of produce samples using gas chromatography with element selective detection (ESD), such as the pulsed flame photometric (PFPD), flame photometric (FPD), and halogen-selective detectors (XSD, ELCD), along with GC-MS/SIM (36, 37). Identification can then be based on retention times of GC-ESD in combination with both retention times and product confirmation with GC-MS/SIM. Another technique worth evaluating is the use of GC equipped with negative chemical ionization—mass spectrometry for these classes of pesticides. This past and current work indicates the procedure is efficient, rugged, and effective in screening, identifying, and quantitating pesticides in various produce samples using GC-MS/SIM or GC-MS/MS. These features make the procedure fit for routine screening and surveillance.

In conclusion, a method was developed for the multiresidue analysis of pesticides in fresh produce based on modified versions of the Canadian procedure and QuEChERS. The method uses smaller sample sizes and less solvent than standard multiresidue procedures, and the solid-phase dispersive steps involving GCB/PSA provide a sufficient cleanup for GC-MS analysis. The modified QuEChERS procedure used for GC-MS/SIM and GC-MS/MS analysis is an improvement over the traditional QuEChERS procedure because the sample extracts are much cleaner due to the additional cleanup procedures. This requires less maintenance of the instrument.

The method has been validated for organohalogen, organophosphorus, and pyrethroid pesticides in a variety of fresh fruits and vegetables using both GC-MS/SIM and GC-MS/MS. Although a triple-quadrupole mass spectrometer is generally more expensive than a single quadrupole, its specificity makes it more reliable for pesticide identification and measurements, especially at the low micrograms per kilogram concentrations in fresh produce samples.

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Supporting Information Available: Additional information regarding the GC-MS/SIM and GC-MS/MS programs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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