DOI:10.1021/jf903851h

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

Multiresidue Pesticide Analysis of Ginseng Powders Using Acetonitrile- or Acetone-Based Extraction, Solid-Phase Extraction Cleanup, and Gas Chromatography−Mass Spectrometry/Selective Ion Monitoring (GC-MS/SIM) or −Tandem Mass Spectrometry (GC-MS/MS)†

Jon W. Wong,*[,§] Kai Zhang,[§] Katherine Tech,[#] Douglas G. Hayward,[§] Alexander J. Krynitsky,[§] Irene Cassias,[⊥] Frank J. Schenck,[⊗] Kaushik Banerjee,[△] Soma Dasgupta,[△] and Don Brown[◇]

[§]Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, HFS-706, 5100 Paint Branch Parkway, College Park, Maryland 20740-3835, [#]Joint Institute for Food Safety and Applied Nutrition, 1122 Patapsco Building, University of Maryland, College Park, Maryland 20742-6730, [⊥]Office of Regulatory Affairs, Pacific Regional Laboratory Southwest, U.S. Food and Drug Administration, HFR-PA260, 19701 Fairchild, Irvine, California 92612-2506, [⊗]Office of Regulatory Affairs, Southeast Regional Laboratory, U.S. Food and Drug Administration, HFR-SE660, 60 Eighth Street N.E., Atlanta, Georgia 30309-3959, [△]National Research Centre for Grapes, P.O. Manjri Farm, Pune, Maharashtra 412 307, India, and [◇]Exova U.K., 121 Shady Lane, Great Barr, Birmingham B44 9ET, United Kingdom

A multiresidue method for the analysis of 168 pesticides in dried powdered ginseng has been developed using acetonitrile or acetone mixture (acetone/cyclohexane/ethyl acetate, 2:1:1 v/v/v) extraction, solid-phase extraction (SPE) cleanup with octyl-bonded silica (C_8), graphitized carbon black/primary−secondary amine (GCB/PSA) sorbents and toluene, and capillary gas chromatography−mass spectrometry/selective ion monitoring (GC-MS/SIM) or −tandem mass spectrometry (GC-MS/MS). The geometric mean limits of quantitation (LOQs) were 53 and 6 μg/kg for the acetonitrile extraction and 48 and 7 μg/kg for the acetone-based extraction for GC-MS/SIM and GC-MS/MS, respectively. Mean percent recoveries and standard deviations from the ginseng fortified at 25, 100, and 500 μg/kg using GC-MS/SIM were 87 ± 10, 88 ± 8, and 86 ± 10% from acetonitrile extracts and 88 ± 13, 88 ± 12, and 88 ± 14% from acetone mixture extracts, respectively. The mean percent recoveries from the ginseng at the 25, 100, and 500 μg/kg levels using GC-MS/MS were 83 ± 19, 90 ± 13, and 89 ± 11% from acetonitrile extracts and 98 ± 20, 91 ± 13, and 88 ± 14% from acetone extracts, respectively. Twelve dried ginseng products were found to contain one or more of the following pesticides and their metabolites: BHCs (benzene hexachlorides, α-, β-, γ-, and δ-), chlorothalonil, chlorpyrifos, DDT (dichlorodiphenyl trichloroethane), dacthal, diazinon, iprodione, quintozene, and procymidone ranging from <1 to >4000 μg/kg. No significant differences were found between the two extraction solvents, and GC-MS/MS was found to be more specific and sensitive than GC-MS/SIM. The procedures described were shown to be effective in screening, identifying, confirming, and quantitating pesticides in commercial ginseng products.

KEYWORDS: Multiresidue methods; organohalogen pesticides; GC-MS/SIM; GC-MS/MS; acetonitrile; acetone/cyclohexane/ethyl acetate; ginseng

INTRODUCTION

Panax quinquefolius and *Panax ginseng* commonly known as American and Asian ginseng, respectively, are botanical dietary supplements widely used for health purposes. Due to its potential health benefits, ginseng root is widely regarded as a valuable agricultural crop, and to prevent economic losses, pesticides may be used against pests such as mold and insects that may damage the plants and the highly valued roots. Despite the usefulness of pesticides in agricultural practices, there are concerns about their excessive use, presence, and levels in plant commodities. Ginseng roots can accumulate pesticides during the growing stage or postharvest treatment, and previous studies have shown that many organochlorine and organophosphorus pesticides have been detected in dried ginseng root products (*1*−*8*). Therefore, the presence of pesticides in ginseng root and other botanical products requires validated analytical procedures for effective

†Part of the Florida Pesticide Residue Workshop 2009.

*Author to whom correspondence should be addressed [telephone (301) 436-2172; fax (301) 436-2332; e-mail jon.wong@fda.hhs.gov].

 Published on Web 03/15/2010

and efficient screening and enforcement. An interlaboratory comparison study conducted by Kong et al. (*7*) revealed the difficulties and the many different procedures of analyzing pesticides in ginseng products.

There are numerous methods (*1*−*16*) that describe pesticide screening in dried botanical dietary supplements, spices, medicinal plants, herbals, teas, and phytomedicines, which are based on procedures for fresh plant-derived foods (*17*−*28*). These analytical methods usually involve organic solvent extraction of the pesticides and cleanup procedures to remove coextractives and interfering components from the matrix; these are followed by instrumental analysis such as capillary gas chromatography or high-performance liquid chromatography with element-selective, spectrophotometric, and/or mass spectrometric detectors. Although these methods work well with fresh produce, there are unique challenges with dried botanicals because of the concentrated levels of the matrix and lower limits of detection due to the concentrated sample sizes. This often complicates the detection, identification, and quantification of pesticide residues in dried botanicals. We recently evaluated methods for the analysis of pesticides in ginseng utilizing acetonitrile salt-out extraction, solid-phase dispersive techniques, gas chromatography with flame photometric detection (GC-FPD) and single-quadrupole mass spectrometry (GC-MS) (*5*) and gel permeation chromatography/solid-phase extraction (GPC/SPE) cleanup procedures and GC-high resolution time-of-flight mass spectrometry (GC-HR-TOF-MS) (*6*). This study describes a method that uses aspects and improvements of these existing procedures and technologies for the multiresidue analysis of pesticides in ginseng.

Organohalogen, organophosphorus, and pyrethroid pesticides in this study were measured using two different GC-MS techniques. One instrument used was a GC-MS operated in selective ion monitoring (SIM) mode (GC-MS/SIM). This approach has been widely used for the targeted determination of pesticides in ginseng and other plant products (*5*−*8*, *11*, *14*−*17*, *21*, *23*−*28*) because of its reliability, effectiveness, and low cost. Although GC-MS/SIM provides qualitative and quantitative information on pesticide residues in foods, there are potential difficulties with this approach. Common pesticide identification using GC-MS/SIM requires criteria that call for four ions at the proper ion ratios in combination with correct GC retention time and other quality assurance protocols to take regulatory action (*29*). These ions may not be uniquely specific to the pesticide or analyte of interest, and the ion abundances may result from coextractives in the plant matrix that may skew the ratios between the identifying ions.

A second procedure is to use GC-triple-quadrupole or tandem mass spectrometry (GC-MS/MS), which is now being used by some pesticide laboratories for multiresidue targeted screening of pesticides in food samples due to commercial availability (*30*−*35*). In MS/MS, target masses are selected in the first quadrupole and fragmented in a collision chamber. Depending on the analyte, unique product ions are generated from the collision chamber, and only selected product ions are allowed to pass through the second quadrupole to be monitored and detected. The fragmentation pattern and resulting product ions are dependent on the chemical structures of the target analytes so that MS/MS is more specific than the SIM mode commonly used in the single-quadrupole detectors. The tandem or triple-quadrupole mass analyzer can operate in multiple reaction monitoring (MRM) mode, which can monitor specific product ions from a large number of analytes, but the number of product ions screened in MS/MS is limited by the scan speed of the instrument. A recent paper by Okihashi et al. (*31*) showed lower limits of detection at the 0.01 μg/g concentration and improved selectivity for the identification and confirmation of 260 pesticides in fresh produce by MS/MS over GC-element selective detection (i.e., flame photometric detection) and GC-MS/SIM.

This study employs and compares both GC-MS/SIM and GC-MS/MS for the multiresidue screening of 168 pesticides in dried ginseng root powders using conventional multiresidue procedures (*21*, *23*, *24*, *26*, *27*, *31*). The methods utilize a salt-out organic solvent extraction step, followed by primary−secondary amine/graphitized carbon black (PSA/GCB) solid-phase extraction column cleanup. Due to recent shortages of acetonitrile (*36*), we also investigated the use of acetone-based extraction procedure using an acetone/ethyl acetate/cyclohexane (2:1:1, v/v/v) mixture employed by Sannino et al. (*24*), both as an alternative extraction solvent and for comparative studies. Finally, the methods will be used to screen and analyze pesticides in dried, powdered ginseng roots from different commercial sources.

MATERIALS AND METHODS

Materials and Standards Preparation. The majority of pesticide standards were obtained from the U.S. Environmental Protection Agency (U.S. EPA) National Pesticide Standard Repository (Ft. Meade, MD). Other pesticides were purchased from Sigma Aldrich (Fluka, Milwaukee, WI) and Chem Service Inc. (West Chester, PA). Pesticide-grade acetonitrile and toluene, HPLC-grade water, and certified-grade anhydrous sodium 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 quality control standards, naphthalene-d_8, acenaphthlene-d_{10}, pheneanthrene-d_{10}, and chrysene-d_{12} were purchased by Sigma Aldrich. Solid-phase extraction cartridges consisting of 250 mg of graphitized carbon black (top layer) and 500 mg of primary−secondary amine bonded to silica (bottom layer) containing a Teflon frit were purchased from United Chemical Technologies (Bristol, PA) and Supelco Co. (Bellefonte, PA), respectively. Ginseng (*P. quinquefolius*) used to prepare ginseng blanks, and matrix-matched standards was generously provided by the Wisconsin Ginseng Board (Wausau, WI). Incurred ginseng products of different varieties (*P. quinquefolius*, *P. ginseng*, Red Korean, American, etc.) containing pesticide residues were obtained from commercial sources.

Stock solutions of individual pesticide standards were prepared by dissolving 25−100 mg of pesticides in 25 mL of acetonitrile for fortification standards and 25 mL of toluene for calibration standards. The working standards used for quantitation were prepared by mixing 2−5 mL of each standard using a 250 mL volumetric flask to prepare a 20 μg/mL working standard. The fortification solutions were prepared by diluting the 20 μg/mL acetonitrile working standard into 0.167, 167, and 6.67 μg/mL fortification solution with acetonitrile. Successive dilutions of the stock pesticide standards were used to prepare 5.0, 2.5, 1.0, 0.50, 0.25, 0.10, 0.05, 0.025, 0.010, 0.005, 0.0025, and 0.001 μg/mL standards in toluene (each 50 mL standards). 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 from a 1000 μg/mL stock solution. Care must be taken to ensure that tris(1,3-dichloroisopropyl)phosphate is not an incurred residue by prescreening the ginseng samples without the addition of the standard.

Ginseng Extraction Preparation. A schematic of the extraction and cleanup procedure is shown in **Figure 1**. Dried ground ginseng powder (2.00 ± 0.05 g), 10 mL of water, and a steel ball bearing were placed in a disposable centrifuge tube and shaken in a 2000 GenoGrinder mechanical shaker (SPEX SamplePrep, Metuchen, NJ) for 1 min at 1000 strokes/min. An internal standard (200 μL of a 3.4 μg/mL solution of tris(1,3-dichloroisopropyl) phosphate, 20 mL of solvent (acetonitrile or 2:1:1 acetone/cyclohexane/ethyl acetate), and NaCl (2.0 g of NaCl for acetonitrile extraction or 3.5 g of NaCl for the acetone mixture extraction) were added to the ginseng/water mixture. The sample was extracted in the GenoGrinder for 1 min at 1000 strokes/min and centrifuged at 4500 rpm × 5 min using a centrifuge (ThermoElectron Corp., Milford, MA).

C-8 Dispersive Cleanup. The centrifuged organic extract (∼18−19 mL) was transferred to a centrifuge tube containing 0.5 g of C-8 sorbent (United Chemical Technologies) and shaken for 1 min at 500 strokes/min using the GenoGrinder. The tube was centrifuged at 4500 rpm × 5 min,

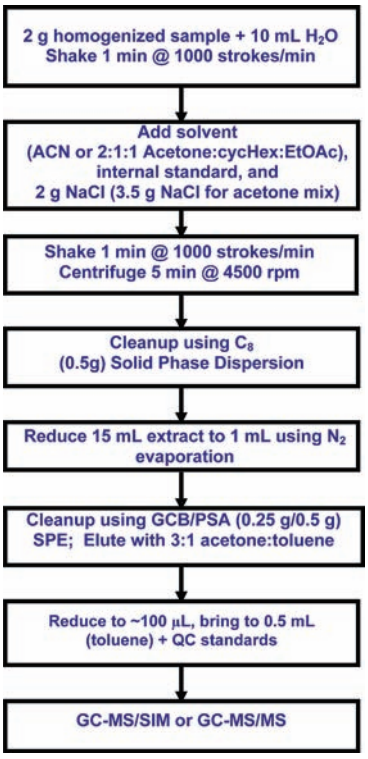

Figure 1. Flowchart of the multiresidue analysis of pesticides in dried ginseng powders.

and 15 mL (1.5 g sample equivalent) was transferred to a clean glass centrifuge tube and reduced to ~1 mL under a gentle stream of nitrogen using a nitrogen evaporator (N-Evap, Organomation Associates, Berlin, MA).

Solid-Phase Extraction (SPE) Cleanup. The concentrated extract was loaded onto an acetone-conditioned (3 column volumes of acetone) tandem SPE cartridge (United Chemical Technologies) containing 250 mg of graphitized carbon black (GCB, top) and 500 mg of primary−secondary amine (PSA, bottom) sorbents topped with anhydrous sodium sulfate. The cartridges were eluted and collected with 12 mL of 3:1 acetone/toluene. The GC extract was reduced (~100 μL) and brought to 0.5 mL of toluene, and 25 μL of QC standards (the mixture of deuterated polycyclic aromatic hydrocarbons, 20 μg/mL) was added. Fifty milligrams of magnesium sulfate was added, and the extracts were centrifuged at 2500 rpm × 5 min to remove any cloudiness or fine precipitates that may be present in the extracts. The toluene extracts were divided into two portions and transferred to GC vials with vial inserts for GC-MS/SIM and GC-MS/MS analysis.

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 105 °C (1 min hold) to 130 °C at a rate of 10 °C/min, increased to 230 at 4 °C/min, followed by a final ramp to 290 at 20 °C/min (7 min hold) using He as the carrier gas at 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 ginseng extracts, standards, and blanks were injected (1 μL) 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 of the Supporting Information. Identification by mass spectrometry was established by the retention time of the target ion and the agreement of three qualifier-to-target ion ratios established by the European Commission (*29*). The SIM program was separated into 27 time segments and could be populated up to 60 ions as shown in Table 2 of the Supporting Information. 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 the ChemStation G1701DA rev D.03.00 software.

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 using GC-MS/MS. Analytes were separated with a Varian 30 m × 0.25 mm × 0.25 μm, VF-5 fused silica capillary column preceded by a deactivated guard column (5 m × 0.25 mm i.d., Restek Corp., Bellefonte, PA). 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 at 10 °C/min, ramped to 230 at 4 °C/min and to 290 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 μL 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. Two ion transitions for each pesticide were determined via collision tests. Determined precursor ions, daughter ions, and corresponding collision energies for all analytes were determined and are provided in Table 1 of the Supporting Information. 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 the pesticide in the ginseng matrix was based on criteria by the ratio of the primary ion transition to the secondary ion transition and the acceptable tolerances of the ratio established by the European Commission (*29*).

Fortification Studies. For fortification studies, 2.0 g of ginseng powder was fortified with 250 μL of the internal standard solution (tris(1,3-dichloroisopropyl) phosphate) and 300, 120, and 150 μL of the appropriate fortification solution (0.167, 1.67, and 6.67 μg/mL standards prepared in acetonitrile) to a final concentration of 25, 100, or 500 μg/kg, respectively, and the centrifuge tube was vigorously vortexed to distribute the pesticides and allowed to rest for 30 min so that the solvent could evaporate. Extraction and cleanup are described in the previous sections. Quantitation was performed by using the peak area ratio responses of the analyte to that of the internal standard, tris(1,3-dichloroisopropyl) phosphate, and calculating the concentration by preparing a calibration curve using the peak area ratios of matrix-matched calibration standards to that of the same internal standard. Matrix-matched standards were prepared by extracting ginseng blanks (as described above) and fortifying the ginseng extracts with standards dissolved in the toluene. Standards were prepared at concentration levels of 0.005, 0.010, 0.025, 0.05, 0.10, 0.25, 0.50, 1.0, 2.5, and 5.0 μg/mL.

Statistics Analysis and Calculations. Averages and standard deviations from fortification and sample studies and linear regressions and correlation coefficients for calibration curves were determined using Microsoft Excel 2003. Pesticide concentrations from GC-MS/SIM and GC-MS/MS analysis were determined by using ChemStation G1701DA rev. D.03.00 and Varian Workstation, version 6.9, software, respectively. These software programs were also used to develop calibration curves using the peak area response ratios of the primary ion transitions of the pesticide analyte to the internal standard (tris(1,3-dichloroisopropyl) phosphate) versus pesticide calibration standards. The recovery data from each fortification level were analyzed by a two-tailed Student's t test at 95% confidence level. Recovery samples using two different solvents, namely, acetone/cyclohexane/ethyl acetate and acetonitrile, were considered independent of each other for comparison of solvent extraction performance. The data were grouped in six sets, namely, three fortification levels each for MS/MS and SIM analysis modes. The data set for each set was tested for homogeneity of variance using an F test at 95% confidence level. Similar tests for comparison of the performance in SIM versus

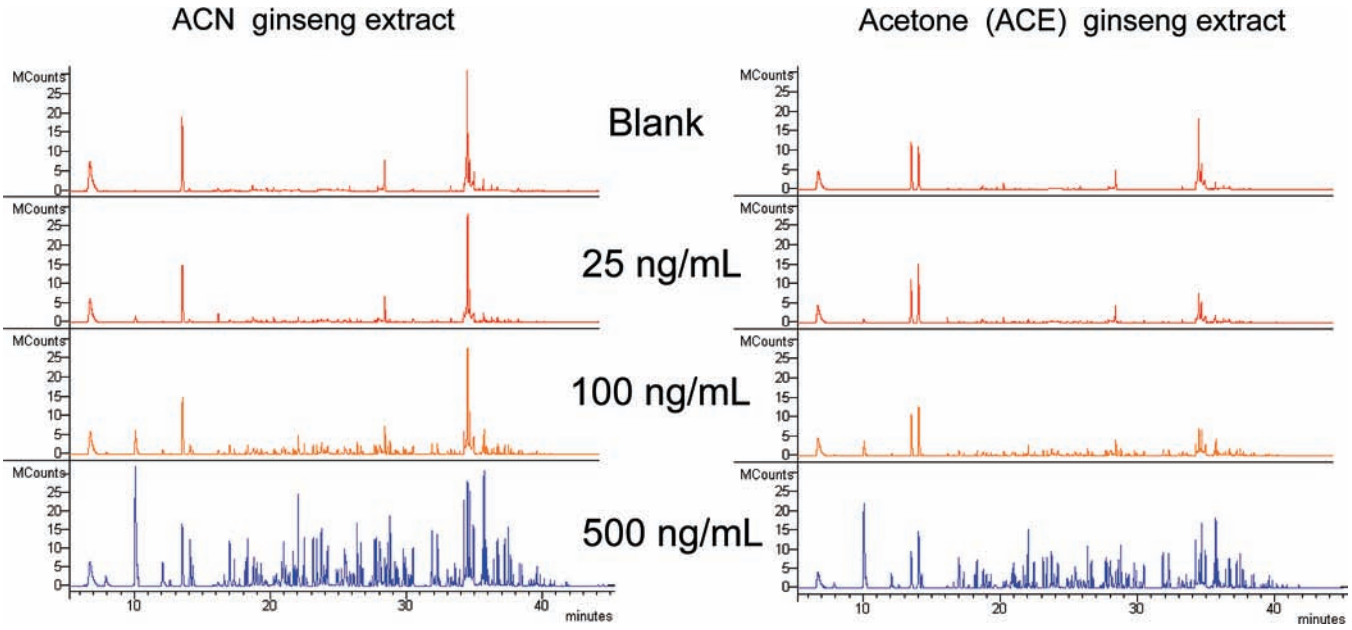

Figure 2. Reconstructed GC-MS/MS chromatograms of ginseng powder extracts prepared by acetonitrile (left) and 2:1:1 acetone/cyclohexane/ethyl acetate extraction (right) procedures. Shown are blank and fortified extracts at 25, 100, and 500 ng/mL. Refer to Materials and Methods for sample preparation details and GC-MS/MS conditions. See Table 1 and Figure 1 of the Supporting Information for details on GC-MS/MS conditions.

MS/MS mode were also conducted. Recovery data were therefore arranged in six sets, namely, three levels each for acetone and acetonitrile. All calculations were performed using Microsoft Excel 2003.

RESULTS AND DISCUSSION

Ginseng Extraction and Cleanup. Salt-out organic solvent extraction is a common procedure used to extract and partition nonpolar pesticides from a plant material into an organic solvent, such as acetonitrile or acetone (*19*−*24*). The addition of water has also been shown to aid in the extraction of pesticides from dehydrated plant materials (*37*). Acetonitrile, which was originally used by Mills et al. (*38*), has been shown to be an effective extraction solvent in many multiresidue procedures (*19*−*21*, *23*, *26*−*28*) and is also used in the *Qu*ick, *E*asy, *Ch*eap, *E*ffective, *R*ugged, and *S*afe (QuEChERS) procedure (*25*). Sannino et al. (*24*) modified a procedure based on that of Specht et al. (*39*) which involved acetone extraction of pesticides in fresh produce samples, followed by a partitioning step involving a 1:1 (v/v) mixture of cyclohexane/ethyl acetate. The solvent mixture of a 2:1:1 acetone/cyclohexane/ethyl acetate was shown to be effective for the extraction of a variety of pesticides analyzed by GC and GC-MS (*24*). In this work, an organic solvent extraction/partitioning procedure was aided by the addition of NaCl and the GenoGrinder, which blended the dried powder with water and provided consistent shaking and uniform extraction of the hydrated powdered ginseng roots. The GenoGrinder turned out to be a useful apparatus because multiple simultaneous individual extractions of the 2 g samples are performed in disposable centrifuge tubes instead of stainless steel blenders or a homogenizer or tissuemizer. Although a blender, homogenizer, or tissuemizer can be used to macerate the ginseng with water and blend the hydrated sample with the organic solvent, the blender containers and homogenizer or tissuemizer rotors must be rinsed thoroughly if multiple samples are to be analyzed to avoid any possibility of contamination. One advantage of the 2:1:1 acetone/ethyl acetate/cyclohexane solvent mixture was that the solvent mixture was easily reduced in volume with a gentle N_2 stream, which was much faster than reducing the volume of acetonitrile. The resulting concentrated extract, containing primarily ethyl acetate and cyclohexane, could either be loaded for gel permeation chromatography cleanup as described by Specht et al. (*39*) or subjected to solid-phase extraction cleanup.

The cleanup procedures in this work employ C-8 solid-phase dispersive cleanup, followed by solid-phase extraction using tandem GCB/PSA cartridges. C-8 or C-18 sorbents have been used by Fillion et al. (*21*, *23*) and Pang et al. (*27*) to remove fats, lipids, and other nonspecific components from the plant matrix. In this study, we employed a dispersive solid-phase cleanup step using C-8 for the ginseng extract due to speed and convenience compared to solid-phase extraction procedures. The combination of the three sorbent cleanup of C-8 or C-18 and tandem GCB/PSA SPE columns is shown to be effective for the removal of a variety of matrix components. PSA has been shown to remove organic acids and other components, which may potentially contribute to matrix enhancement effects during capillary GC detection (*25*, *28*, *40*). These matrix enhancement effects may lead to erroneous results. GCB is effectively used to remove plant pigments such as chlorophyll and carotenoids, as well as polyphenols and sterols, which are all commonly present in plant foods (*28*, *40*). However, GCB can also retain structurally planar and aromatic pesticides and metabolites such as hexachlorobenzene, chlorothalonil, and pentachlorobenzene and requires toluene to elute all bound pesticides from the graphitized carbon layers (*40*). When GCB sorbents are used, a 25% toluene solution (v/v) is typically used to elute any bound pesticides from the GCB layer. A 25% toluene in acetone solution was utilized instead of ethyl acetate or acetonitrile because the acetone can be quickly removed by N_2 evaporation. We considered employing a dispersive or QuEChERS type application utilizing GCB and PSA sorbents and later adding toluene, but results (data not shown) have shown that the hexachlorobenzene and pentachlorobenzene recoveries were low (typically ~50%), whereas extraction and cleanup using GCB/PSA SPE led to better (> 70%) recoveries. The resulting SPE method, as outlined in **Figure 1**, was then subjected to validation.

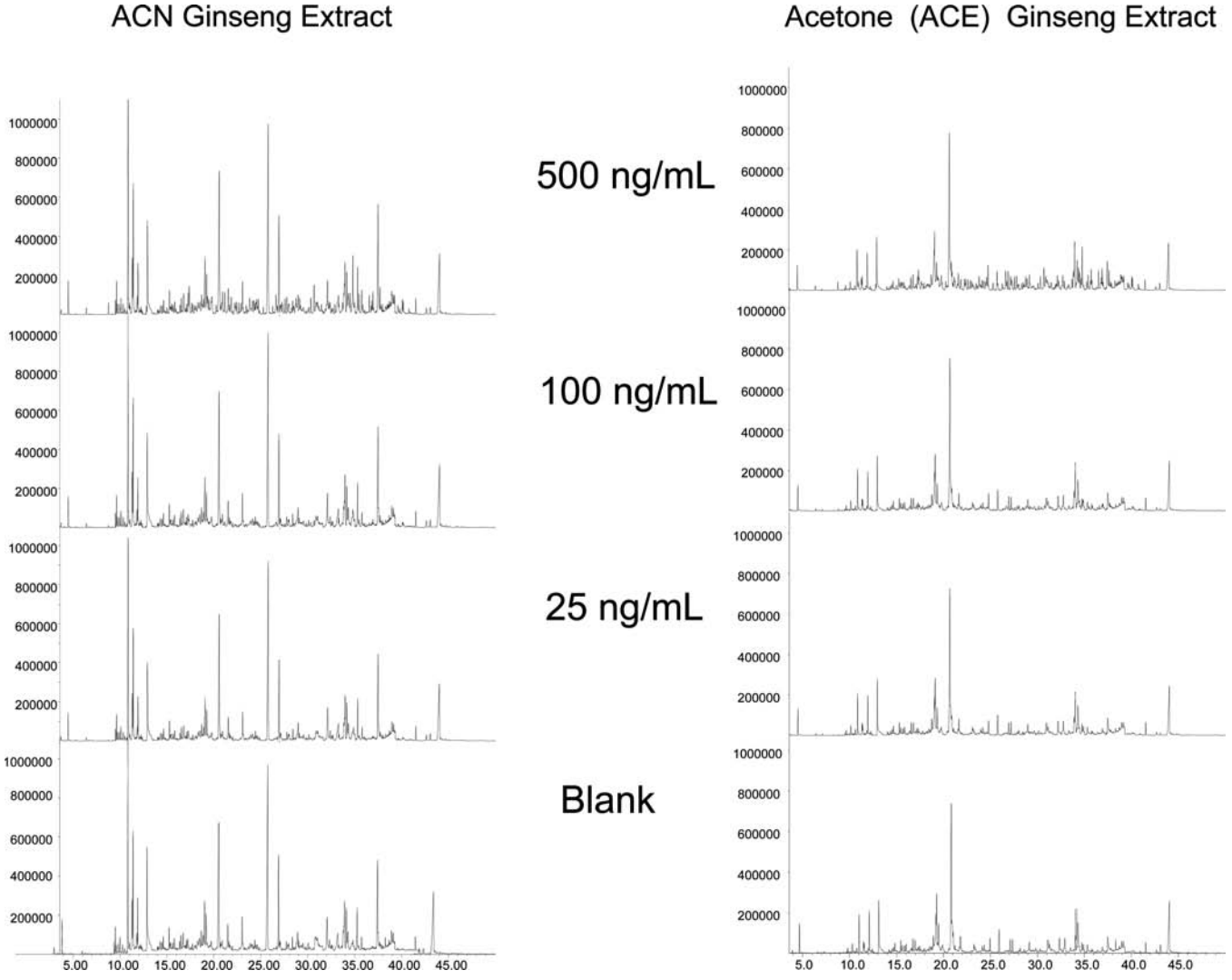

Figure 3. Reconstructed GC-MS/SIM chromatograms of ginseng powder extracts prepared by acetonitrile (left) and 2:1:1 acetone/cyclohexane/ethyl acetate extraction (right) procedures. Shown are blank and fortified extracts at 25, 100, and 500 ng/mL. Refer to Methods and Materials for sample preparation details and GC-MS/SIM conditions. See Tables 1 and 2 of the Supporting Information for details on GC-MS/SIM conditions.

Method Validation. Standard mixes of 168 organohalogen, organophosphorus, and pyrethroid pesticides, including isomers and metabolites in solvent, were initially used to determine retention times, mass spectra, and acquisition time segments for both GC-MS/SIM and GC-MS/MS are provided in Table 1 of the Supporting Information. Typical mass spectrometry parameters such as percentages of qualifier to target ratios (% Q/T) for GC-MS/SIM and transitions from precursor to product ions, collision energies, and ion ratios (abundances of the precursor to the product ion) for GC-MS/MS are also listed in Table 1 of the Supporting Information. The GC-MS/SIM and GC-MS/MS results listed were obtained from pesticide standards dissolved in toluene in these studies. Matrix-matched standards, ranging in concentration from 0.005 to 5.0 μg/mL, established the linear ranges and the minimum limits of quantitation (LOQs) expected for the method. Most of the pesticides could be determined in the 0.005−5.0 μg/mL and $r^2 > 0.99$ range when analyzed by GC-MS/MS. Linear ranges for pesticides analyzed by GC-MS/SIM varied by pesticide due to different LOQs (range from 5 to 333 μg/kg from matrix interferences in the ginseng). Using GC-MS/SIM, one target and three qualifier ions preselected by full-scan MS were used for detection, whereas for GC-MS/MS detection, two transitions resulting from the collision-induced dissociation of the precursor ion into product fragments characteristic of the precursor were used. The EC directives (*29*) for method performance were used for pesticide identification and detection using GC-MS/SIM and GC-MS/MS. This required using qualifier-to-target ratios and ion ratios of the primary to secondary ion transitions for confirmation.

The LOQ for each pesticide analyzed by GC-MS/SIM and GC-MS/MS was defined as the amount of pesticide that would produce at least 3:1 signal/noise in the matrix-matched standards for all qualifying ions (SIM) or qualifying (or secondary) transition (MS/MS) and 10:1 for the target ion (SIM) or quantitating (or primary) transition (MS/MS). The geometric mean LOQ based on the LOQs of 168 pesticides, metabolites, and isomers listed in Table 1 of the Supporting Information and analyzed by GC-MS/SIM were 53 and 48 μg/kg for extraction by acetonitrile and acetone/cyclohexane/ethyl acetate solvents, respectively. In contrast, the geometric mean LOQs from GC-MS/MS analysis were approximately 7−9 times lower, with values of 6 and 7 μg/kg, respectively, for both solvents. Most of the LOQ values for GC-MS/MS were typically in the 1−20 μg/kg range, compared to 83−167 μg/kg for GC-MS/SIM for both solvent extraction methods, indicating that GC-MS/MS is a more sensitive technique than GC-MS/SIM.

Table 1. Average Recoveries (av) and Relative Standard Deviations (RSD) of Pesticides Extracted from Dried Ginseng Powder Fortified at 25, 100, and 500 μg/kg Levels ($n = 4$) Using Acetonitrile and Acetone/Cyclohexane/Ethyl Acetate (2:1:1) Extraction, Cleaned up by C8 Solid-Phase Dispersion and GCB/PSA Solid-Phase Extraction and Analyzed by GC-MS/SIM and GC-MS/MS Using Matrix (Ginseng)-Matched Standards[a]

	25 μg/kg								100 μg/kg								500 μg/kg							
	acetone extraction				acetonitrile extraction				acetone extraction				acetonitrile extraction				acetone extraction				acetonitrile extraction			
	SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS	
pesticide	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD
acrinathrin	ND		85	4	ND		87	10	90	4	79	7	85	1	89	1	87	3	79	5	90	2	90	4
akton	80	3	91	4	84	3	83	8	81	4	85	5	80	3	90	3	81	3	79	3	84	3	85	2
alachlor	ND		117	5	ND		86	7	102	3	100	7	89	4	95	4	100	3	93	2	89	3	90	2
aldrin	85	4	106	9	88	12	78	7	85	6	82	4	83	3	81	4	83	1	76	2	84	2	75	2
allethrin	ND		83	10	ND		78	7	81	4	82	5	77	5	88	3	83	3	74	3	81	5	83	2
atrazine	ND		120	3	ND		87	12	106	5	103	8	92	4	99	6	102	3	97	2	95	3	96	2
azamethidaphos	ND		100	7	ND		102	8	104	5	103	3	ND		98	2	101	2	106	4	78	13	99	5
azinphos-ethyl	ND		108	2	ND		87	10	92	3	98	3	87	3	89	2	96	3	102	7	89	4	89	3
azinphos-methyl	ND		104	6	ND		86	14	100	3	94	6	ND		88	2	100	2	106	8	92	2	88	3
α-BHC	85	6	97	3	87	6	76	9	86	2	89	6	79	4	86	4	86	2	81	2	80	3	84	3
β-BHC	ND		104	7	ND		91	10	ND		97	10	ND		97	1	101	21	87	4	81	10	94	2
δ-BHC	94	10	106	17	86	9	71	13	94	7	109	6	86	3	109	1	92	2	89	2	86	3	90	2
bifenthrin	82	6	83	3	96	5	83	9	78	3	77	3	86	3	91	1	79	2	90	4	88	2	96	2
bromophos	84	2	95	2	83	2	79	8	77	2	80	6	78	3	83	2	84	3	76	3	80	2	82	3
bromophos-ethyl	77	3	86	5	80	3	84	6	84	3	87	5	76	3	87	2	77	3	82	3	78	2	79	3
bromopropylate	84	3	89	2	92	6	86	10	84	2	86	4	85	2	91	1	84	4	95	4	89	2	94	2
captafol	ND		ND		ND		ND		ND		ND		ND		ND		ND		ND		76	7	ND	
captan	ND		ND		ND		ND		ND		ND		ND		ND		112	3	104	4	98	2	97	2
carbophenothion	ND		83	11	ND		89	8	85	3	83	5	87	3	88	2	86	2	77	4	90	2	83	2
chlorbenzilate	83	3	75	2	91	3	66	11	87	4	93	4	83	2	74	3	89	3	66	3	87	2	71	2
cis-chlordane	67	3	95	3	93	8	91	8	83	4	71	5	85	3	91	2	83	2	80	3	86	3	86	1
trans-chlordane	91	2	111	3	73	4	90	8	66	5	87	4	67	2	98	4	66	2	87	2	67	2	94	3
α-chlordene	81	9	95	8	94	2	76	5	90	4	95	6	90	3	91	3	90	3	80	4	91	3	86	2
β-chlordene	89	9	96	3	90	7	81	7	74	5	87	6	83	3	92	5	82	1	80	1	87	2	85	2
γ-chlordene	116	2	137	3	89	5	108	9	86	5	90	6	86	3	112	3	85	3	113	3	85	3	108	2
β-chlorfenvinphos	ND		99	3	115	2	85	10	117	3	119	5	103	3	92	3	120	2	94	3	108	3	92	2
chloroneb	ND		77	13	ND		74	10	ND		101	7	84	2	102	2	129	24	87	5	90	6	89	3
chlorothalonil	ND		24	20	22	17	15	24	52	4	58	7	45	11	54	4	72	6	70	4	64	9	67	9
chlorpyrifos	85	5	94	4	86	6	82	8	82	1	89	7	80	2	87	4	83	3	81	2	83	2	86	2
chlorpyrifos-methyl	ND		107	5	ND		90	7	90	3	92	6	81	5	88	3	90	3	84	2	82	2	85	2
chlorthiophos	89	10	95	2	87	8	84	8	86	3	90	4	82	5	92	2	85	3	83	1	86	2	92	2
coumaphos	90	4	87	7	ND		100	16	86	1	91	8	82	5	87	5	87	8	108	5	87	3	91	6
cyanazine	ND		95	5	ND		83	9	107	5	91	7	95	4	90	5	101	1	86	5	109	10	87	3
cyanophos	98	3	113	6	92	2	81	8	99	4	104	6	88	3	94	5	99	2	93	3	87	3	87	2
cyfluthrin 1	ND		71	14	ND		82	19	ND		79	10	88	3	84	15	70	4	87	8	90	2	94	7
cyfluthrin 2	ND		63	2	ND		82	9	ND		80	10	89	6	104	5	59	16	89	10	92	4	96	7
cyfluthrin 3	ND		79	19	ND		ND		ND		77	16	88	3	65	17	87	16	89	10	94	3	92	4
cyfluthrin 4	ND		98	10	ND		ND		ND		98	10	88	3	38	13	69	2	91	5	95	5	88	7
λ-cyhalothrin	77	5	ND		78	9	ND		75	7	ND		83	10	ND		77	3	ND		86	4	ND	
cypermethrin 1	ND		85	9	ND		85	9	ND		79	6	ND		93	7	81	2	89	8	93	4	93	4
cypermethrin 2	ND		ND		ND		ND		ND		78	9	ND		90	3	76	3	86	8	93	3	94	6
cypermethrin 3	ND		ND		ND		ND		ND		77	8	ND		62	2	77	3	86	9	91	4	93	5
cypermethrin 4	ND		ND		ND		ND		ND		75	7	ND		81	6	60	5	88	9	90	4	88	7
dacthal	82	23	161	10	89	3	83	6	97	6	102	7	85	3	91	4	96	2	94	4	87	3	88	3
o,p′-DDD	87	2	95	2	94	6	85	7	86	4	88	3	85	2	93	2	85	2	86	2	86	3	90	1
p,p′-DDD	81	6	95	2	86	4	85	7	82	7	88	4	85	3	92	2	85	3	86	2	90	3	89	2
o,p′-DDE	84	1	97	2	90	6	85	6	85	3	88	6	83	3	93	3	85	2	83	2	86	2	88	2
p,p′-DDE	84	1	129	3	90	6	111	5	85	3	116	5	83	3	124	2	85	2	108	2	86	2	119	2
o,p′-DDT	106	13	95	2	88	8	85	7	104	13	88	4	84	4	93	3	84	4	86	2	78	4	89	1
p,p′-DDT	87	2	92	2	92	7	85	8	82	4	88	4	85	3	91	1	84	3	83	2	89	2	90	2
DEF (tribufos)	ND		104	3	ND		82	10	80	6	87	5	ND		92	4	90	10	82	4	98	3	89	2
deltamethrin	75	7	79	9	ND		97	9	75	4	76	8	92	5	91	6	79	2	98	4	91	3	97	7
demeton S	ND		ND		ND		ND		71	3	ND		72	6	ND		76	2	ND		73	3	ND	
demeton *S*-methyl	ND		104	5	ND		87	7	83	4	90	7	ND		96	2	90	7	84	1	91	4	93	2
dialifor	ND		96	5	ND		88	10	82	4	89	3	82	2	84	7	84	3	91	6	88	3	86	5
diallate 1	ND		98	2	ND		80	9	97	6	93	7	85	5	88	4	86	2	83	4	77	4	83	3
diallate 2	ND		100	4	ND		80	10	88	5	92	7	85	4	89	2	81	3	82	4	82	3	84	3
diazinon	95	4	110	5	90	8	82	7	96	3	97	8	84	5	91	4	95	3	89	3	85	3	88	3
dicapthon	80	4	96	5	81	1	79	8	83	2	91	5	76	4	84	3	87	3	84	3	78	3	80	3
dichlofluanid	ND		ND		ND		5	22	61	6	64	8	ND		59	3	63	61	79	3	77	2	78	3
dichlorfenthion	85	3	96	5	89	4	92	4	85	4	91	8	82	2	89	4	85	2	84	2	83	3	89	4
3,4′-dichloroaniline	ND		28	10	ND		8	4	ND		30	4	ND		7	10	36	4	25	6	ND		25	6
4,4′-dichlorobenzophenone	ND		105	4	ND		80	7	93	3	95	4	85	2	90	1	94	2	93	3	87	3	89	3
dichlorvos	ND		94	9	ND		80	9	85	6	93	8	88	5	96	2	78	8	71	4	87	3	88	3
diclobenil	88	3	101	4	ND		75	8	90	6	91	7	83	4	90	1	81	9	71	6	82	3	83	3

Table 1. Continued

	25 μg/kg								100 μg/kg								500 μg/kg							
	acetone extraction				acetonitrile extraction				acetone extraction				acetonitrile extraction				acetone extraction				acetonitrile extraction			
	SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS	
pesticide	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD
dicloran	ND		118	13	ND		90	5	109	8	104	6	92	8	98	1	99	4	95	1	97	3	92	1
dieldrin	ND		97	7	ND		82	10	92	3	89	5	84	4	87	1	89	2	81	3	89	4	89	2
dimethachlor	104	7	86	16	91	5	79	9	104	3	96	17	96	1	108	1	104	3	96	2	97	3	94	1
dioxathion	ND		ND		ND		92	4	107	15	77	9	86	7	116	6	82	7	86	9	90	3	107	30
disulfoton	ND		93	4	ND		89	2	62	8	79	17	69	5	69	7	68	3	69	7	70	3	92	4
ditalimfos	ND		93	8	ND		77	11	79	5	84	5	76	10	85	3	80	11	83	3	79	6	82	6
edifenphos	ND		104	4	ND		86	8	95	5	100	2	ND		91	2	99	3	96	3	90	3	90	2
α-endosulfan	ND		79	17	93	6	84	16	85	3	93	15	85	1	107	8	84	3	88	2	82	4	89	1
β-endosulfan	ND		93	5	ND		124	19	92	7	93	3	85	2	96	2	91	3	89	4	89	3	90	2
endosulfan ether	ND		103	6	ND		92	9	93	7	94	7	89	3	93	7	91	2	86	3	86	5	89	3
endosulfan sulfate	93	5	ND		99	4	83	8	91	7	80	18	83	5	89	5	90	4	87	4	87	2	90	2
endrin	83	10	121	15	ND		113	8	90	10	119	8	81	4	128	3	89	2	109	3	88	4	123	1
endrin aldehyde	ND		ND		ND		ND		ND		ND		ND		ND		3	25	ND		9	25	ND	
endrin ketone	ND		99	10	ND		92	3	94	4	97	4	87	3	101	4	95	3	102	7	91	5	96	5
EPN	ND		89	3	ND		90	8	80	3	85	1	ND		90	2	86	4	88	6	90	3	87	3
ethalfluralin	78	8	89	5	91	3	76	14	77	5	81	8	82	6	90	3	76	1	72	2	83	3	86	4
ethion	ND		91	4	ND		79	10	ND		86	7	ND		88	3	88	3	78	3	88	2	84	2
ethoprop	ND		116	6	ND		88	8	104	5	105	6	93	1	98	3	104	2	97	2	90	4	97	2
etridazole	87	8	106	3	79	3	78	7	91	4	97	7	83	6	90	1	84	8	77	3	81	4	84	4
famphur	ND		104	2	ND		87	9	100	4	101	4	79	4	91	4	102	2	99	4	91	3	89	4
fenamiphos	ND		109	4	ND		76	18	95	3	95	2	87	3	96	7	97	3	91	2	89	3	88	2
fenarimol	ND		101	5	ND		86	9	96	3	101	6	96	2	95	1	98	1	107	6	95	3	96	5
fenchlorphos	ND		102	3	ND		82	7	90	3	93	6	84	3	91	1	89	2	84	2	85	3	87	2
fenitrothion	ND		108	5	ND		88	9	97	4	111	6	87	3	95	2	98	3	93	2	88	3	89	2
fensulfothion	ND		132	4	ND		125	6	110	3	119	4	ND		118	2	115	2	120	4	109	2	116	3
fenthion	83	3	96	2	86	3	81	9	87	3	89	6	81	3	87	4	90	2	84	4	82	3	84	2
fenvalerate 1	ND		79	10	ND		83	16	76	4	74	8	90	4	81	3	76	3	94	4	90	4	89	7
fenvalerate 2	ND		87	6	ND		93	17	80	5	74	8	86	5	89	4	81	3	102	3	94	5	97	6
fluchloralin	ND		83	5	ND		81	7	73	4	80	6	ND		87	3	76	3	73	2	82	3	86	4
flucythrinate 1	ND		95	3	ND		105	13	90	3	93	8	94	4	103	1	89	4	109	9	99	2	111	5
flucythrinate 2	ND		73	1	ND		82	14	69	8	68	9	88	10	76	1	70	3	87	5	85	3	84	7
fluridone	ND		216	33	ND		198	45	150	3	157	10	136	2	149	5	153	1	188	12	145	4	158	14
fluvalinate T-1	76	4	82	4	90	7	83	3	74	2	75	12	88	2	85	3	77	4	95	6	92	3	96	6
fluvalinate T-2	80	6	82	4	86	11	83	3	76	1	76	13	85	3	85	3	78	3	95	6	91	3	96	6
folpet	ND		2	10	ND		9	12	77	4	87	7	77	5	85	3	87	2	89	2	86	2	88	4
fonophos	ND		100	8	ND		79	16	90	4	90	7	82	2	86	9	91	2	82	3	82	2	80	3
heptachlor	ND		109	2	ND		96	6	96	4	100	6	94	3	107	2	95	2	92	3	96	3	103	2
hexachlorobenzene	81	5	93	8	73	7	71	10	81	5	84	6	73	8	81	5	73	12	71	3	72	2	74	4
iprobenfos	ND		114	3	ND		79	7	98	4	99	6	84	4	89	2	97	2	92	3	86	3	84	2
iprodione	82	10	90	9	92	5	101	16	95	4	95	12	85	4	98	6	97	2	99	5	88	3	93	3
isazophos	100	5	103	11	ND		88	14	97	3	93	7	79	5	82	4	93	3	89	3	83	4	85	3
isofenphos	89	4	101	3	87	6	80	8	87	6	91	5	80	3	88	3	88	3	84	3	86	3	83	2
jodfenphos	92	1	90	18	92	3	81	16	90	3	86	16	86	3	103	1	93	4	88	3	90	2	96	2
leptophos	84	3	86	5	90	6	83	12	82	2	83	3	81	5	87	2	81	6	81	7	85	2	85	4
lindane (γ-BHC)	ND		83	9	ND		80	3	ND		97	8	ND		90	3	104	10	88	4	97	2	86	3
malathion	ND		118	11	ND		78	11	98	3	99	8	ND		91	1	99	2	94	3	84	3	85	3
methidathion	ND		111	2	ND		85	7	101	4	99	4	ND		93	0	101	1	97	3	92	3	88	2
o,p′-methoxychlor	ND		93	2	ND		89	10	83	3	89	1	ND		92	3	84	3	91	4	84	2	90	3
p,p′-methoxychlor	86	5	92	2	ND		81	8	84	4	90	3	83	2	89	3	87	3	109	3	89	2	99	2
metolachlor	100	1	114	3	ND		89	8	104	4	103	6	ND		96	4	104	2	96	2	93	3	90	2
mevinphos	ND		114	1	ND		88	5	92	9	103	7	98	1	103	1	97	1	91	4	97	4	96	1
mirex	95	4	93	2	91	4	85	9	84	6	87	3	85	1	92	1	85	2	85	3	86	3	91	2
cis-nonachlor	80	2	101	3	86	3	84	8	79	3	86	5	83	3	91	3	81	2	83	3	86	2	90	2
trans-nonachlor	82	4	102	3	90	3	86	4	81	4	95	3	84	2	89	3	82	3	82	3	86	3	91	2
oxadiazon	83	5	94	3	91	3	84	8	86	4	91	4	87	5	89	3	86	3	83	2	86	3	91	2
parathion	ND		100	3	ND		87	7	89	3	92	6	84	2	92	2	93	3	85	3	87	3	87	4
parathion methyl	ND		108	4	ND		86	6	94	2	98	6	85	4	93	2	97	3	91	3	87	4	88	3
pentachloroaniline	81	8	94	7	79	4	81	8	83	3	87	5	75	7	84	5	81	10	77	7	77	2	80	4
pentachloroanisole	85	2	104	4	89	8	79	7	88	3	92	6	81	5	91	1	86	2	81	3	81	3	85	3
pentachlorobenzene	85	3	97	3	78	5	72	9	86	6	91	7	77	5	84	2	79	4	75	7	76	3	79	4
pentachlorobenzonitrile	81	6	97	6	76	7	65	20	82	4	87	4	73	9	87	4	78	10	74	8	75	2	78	4
pentachlorothioanisole	79	6	91	7	75	5	72	10	82	5	85	6	71	7	81	6	74	15	75	2	73	2	75	4
cis-permethrin	ND		82	9	ND		79	10	77	2	78	5	85	1	92	4	81	5	87	6	96	4	91	4
trans-permethrin	ND		95	8	ND		83	8	77	4	84	6	84	1	88	3	80	3	86	7	92	4	90	4
phenothrin	ND		ND		ND		ND		81	5	59	20	85	6	85	14	79	2	79	7	88	3	65	3
phenthoate	91	4	ND		90	8	ND		89	4	ND		81	4	ND		92	3	ND		86	4	ND	
phorate	ND		93	3	ND		75	8	84	6	87	6	ND		89	3	83	2	78	4	80	5	81	4

Table 1. Continued

	25 μg/kg								100 μg/kg								500 μg/kg							
	acetone extraction				acetonitrile extraction				acetone extraction				acetonitrile extraction				acetone extraction				acetonitrile extraction			
	SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS		SIM		MS/MS	
pesticide	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD	av	RSD
phosalone	ND		98	5	ND		90	10	92	4	107	6	84	2	100	2	87	4	95	7	87	4	88	3
phosmet	ND		110	4	ND		88	10	101	2	99	3	ND		89	3	101	2	103	6	92	2	90	4
pirimphos-ethyl	85	3	103	3	89	4	80	9	84	3	86	6	82	3	88	3	85	4	79	4	84	3	83	3
pirimphos-methyl	91	4	105	2	85	5	84	8	92	5	95	7	84	3	90	4	94	3	88	3	84	3	87	3
procymidone	97	6	108	4	87	6	84	6	98	4	98	4	87	3	92	3	98	2	92	2	89	3	89	2
profenofos	ND		101	4	ND		65	9	90	6	95	4	81	11	91	12	90	3	93	3	85	3	86	3
propachlor	ND		110	10	ND		91	11	106	7	99	8	93	4	101	7	102	2	92	2	92	3	97	2
propazine	ND		130	8	ND		91	7	ND		105	10	ND		97	2	98	1	97	3	93	4	93	3
propetamphos	ND		96	6	ND		83	9	95	3	95	7	82	6	87	2	96	4	93	3	85	3	87	3
propyzamide	ND		111	7	ND		85	3	100	4	101	8	88	4	94	2	100	3	94	1	90	3	92	2
prothiophos	ND		101	6	ND		90	11	95	3	107	16	ND		84	5	97	3	79	4	89	3	96	8
pyraclofos	ND		103	5	ND		94	9	94	3	99	7	85	2	92	3	97	3	106	9	93	3	92	5
pyrazophos	ND		91	4	ND		83	19	86	4	91	7	86	7	86	4	88	6	92	8	85	3	85	5
pyridaphenthion	101	2	123	4	ND		100	4	99	3	106	7	88	3	98	7	102	2	107	6	89	6	95	4
quinalphos	ND		102	3	ND		83	8	97	5	95	5	85	4	89	2	96	3	93	4	88	3	88	2
quintozene	89	5	97	5	82	5	79	14	89	1	89	5	81	6	95	2	86	2	82	3	81	5	88	5
resmethrin	ND		52	12	ND	ND	ND		80	8	69	8	71	6	73	8	63	3	64	4	78	11	68	8
simazine	ND		111	7	ND		83	10	105	4	108	7	ND		102	1	106	3	96	3	98	4	99	1
sulfotep-ethyl	86	3	99	2	86	1	80	7	85	3	90	7	79	3	87	4	85	2	80	2	80	4	82	3
sulprofos	75	4	79	6	85	4	82	9	75	2	81	2	79	2	88	2	79	2	77	3	83	2	86	2
tebupirimphos	83	3	93	6	91	8	80	8	83	3	84	8	84	3	87	0	83	3	76	3	84	3	85	3
tecnazene	89	4	101	4	87	7	83	10	90	4	96	7	86	3	91	4	88	2	85	5	83	3	88	3
tefluthrin	ND		85	3	ND		78	7	72	2	78	7	77	3	85	2	76	4	73	2	82	3	84	2
temephos	ND		ND		ND		ND		86	1	ND		ND		ND		82	2	ND		69	2	ND	
terbufos	ND		ND		ND		ND		81	4	ND		81	2	ND		81	3	ND		81	2	ND	
terbutylazine	102	4	116	6	100	8	89	11	101	3	106	8	90	4	99	3	101	2	97	1	91	3	92	2
2,3,5,6-tetrachloroaniline	94	2	109	1	87	3	82	8	95	5	99	7	85	4	93	2	93	2	88	3	85	2	87	3
tetrachlorvinphos	99	2	104	7	94	6	87	6	99	3	94	4	85	4	90	1	100	3	91	5	90	2	87	4
tetramethrin 1	ND		89	5	ND		77	12	81	5	84	3	79	6	87	2	83	3	83	4	84	3	85	3
tetramethrin 2	ND		ND		ND		ND		84	4	ND		82	2	ND		85	2	ND		85	2	ND	
tolclofos-methyl	91	1	103	4	86	2	81	8	91	3	95	6	82	4	89	3	91	3	86	3	83	3	86	2
tolylfluanid	ND		ND		ND		8	2	67	5	71	5	63	3	67	4	84	3	82	4	81	3	83	2
triallate	85	1	95	4	ND		80	8	86	5	90	7	80	4	87	2	84	2	80	3	82	4	85	3
triazophos	ND		110	7	ND		89	7	102	6	104	4	87	6	98	1	105	4	104	2	97	1	95	3
trifluralin	72	4	82	11	84	4	76	6	72	3	81	14	80	3	88	1	75	2	72	2	81	3	87	3
vinclozolin	ND		102	4	ND		85	8	93	4	96	6	ND		91	5	93	2	87	2	86	3	87	4

[a] ND = not detected. NA = not analyzed.

Reconstructed GC-MS/MS and GC-MS/SIM chromatograms of ginseng blank extracts and extracts fortified to concentrations of 25, 100, and 500 ng/mL prepared from both the acetonitrile and acetone/cyclohexane/ethyl acetate procedures are shown in **Figures 2** and **3**, respectively. The GC-MS/MS chromatograms in **Figure 2** show the presence of increasing peak heights of pesticides as a result of increasing pesticide concentrations and minimal background contribution from the ginseng matrix. However, the GC-MS/SIM chromatograms in **Figure 3** reveal no significant difference between the ginseng blank and the levels at 25 and 100 ng/mL, but additional peaks due to the higher concentration of the pesticides were noticeable at 500 ng/mL. Comparison of the two GC-MS chromatograms indicates the desired specificity by selecting the two precursor-to-product ion transitions used in GC-MS/MS over the nonspecific qualifier and target ions used in GC-MS/SIM to analyze the targeted pesticides for quantitation and identification purposes from the ginseng extracts.

Table 1 lists the mean recoveries and relative standard deviations for 168 pesticides fortified at 25, 100, and 500 μg/kg of dry weight of ginseng using both solvent mixtures and measured by both GC-MS/SIM and GC-MS/MS. The fortified ginseng was extracted by both solvent mixtures and cleaned up using dispersive C8 and tandem GCB/PSA SPE. Recoveries for most of the pesticides were in the 70−120% range using either solvent or mass spectrometric method. The mean recoveries at the 25, 100, and 500 μg/kg fortification concentrations for GC-MS/SIM analysis by using the two different solvent extraction procedures (acetonitrile and acetone) were 87 ± 10 and 87 ± 8%, 84 ± 8 and 88 ± 12%, and 86 ± 10 and 88 ± 14%, respectively. The mean recoveries for GC-MS/MS were similar to the GC-MS/SIM results: 83 ± 19 and 98 ± 20%, 90 ± 13 and 91 ± 13%, and 89 ± 11 and 88 ± 14% at 25, 100, and 500 μg/kg for acetonitrile and acetone extractions, respectively.

The performances of both solvents were similar for most pesticides at all three fortification concentrations when analyzed by GC-MS/MS. In the case of GC-MS/SIM analysis, the solvent performances were different for most analytes, showing higher recoveries in the acetone mixture compared to acetonitrile. This could possibly be due to the higher selectivity in the analysis by MS/MS compared to SIM. Comparison of the analysis modes for both solvents, namely, acetone mixture and acetonitrile using a two-tailed Student's t test ($p = 0.05$), indicates that the performances of both analysis modes (i.e., MS/MS and SIM) were equivalent for most of the pesticides. However, using GC-MS/SIM, at the lower fortification concentration of 25 μg/kg, only 66 (acetonitrile) and 73 (acetone) pesticides (of a total of 168 pesticides) could be detected at this concentration, whereas most of the pesticides (153 and 151) could be identified by GC-MS/MS for

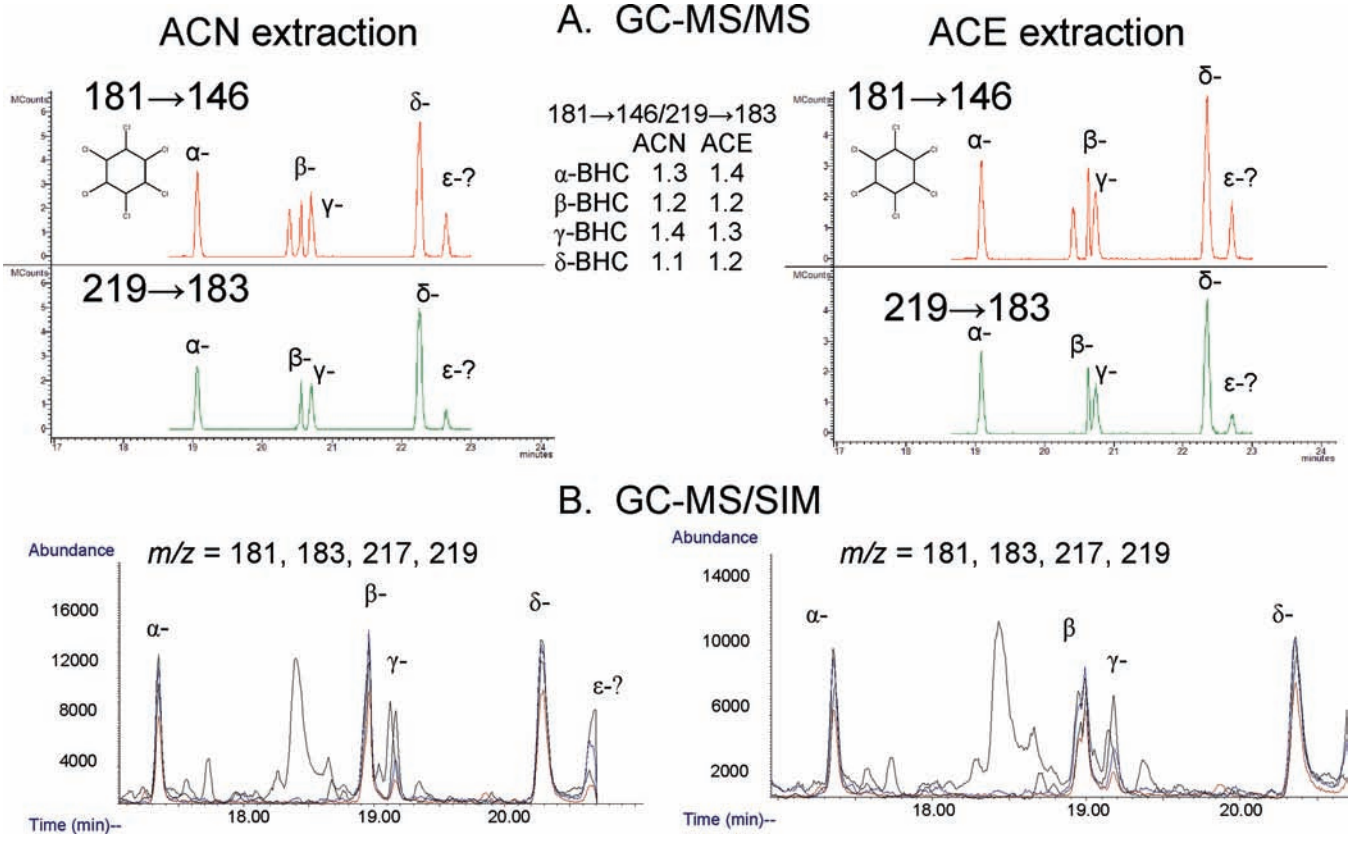

Figure 4. Presence of incurred BHC residues in dried ginseng powder (*Panax quinquefolius*) determined by the two extraction (acetonitrile, ACN, and 2:1:1 acetone/cyclohexane/ethyl acetate, ACE) methods and GC-MS/MS (**A**) or GC-MS/SIM (**B**). (**A**) GC-MS/MS shows the presence and separation of α-, β-, γ-, δ-, ε-BHC isomers by the two transitions, 181 → 146 (primary, quantitation) and 219 → 183 (secondary, qualifier). Transition ratios 181 → 146/219 → 183 of the two extraction procedures showed that the two procedures are similar. (**B**) GC-MS/SIM indicates interferences in the screening and identification of the β- and γ-BHC isomers using *m/z* 181, 183, 217, 219. Concentrations (μg/kg) of BHC isomers are listed in **Table 3** of the Supporting Information. Values of 181 → 146/219 → 183 are provided to show that the ratios of the four isomers resulting from the two extraction solvents are similar.

both solvent extraction procedures. This indicates a significant difference between the two instruments independent of the two extraction solvent procedures. At higher fortification concentration (100 μg/kg) the 2:1:1 acetone/cyclohexane/ethyl acetate extraction resulted in the detection and identification of a few more pesticides (151 pesticides) than the acetonitrile extraction procedure (137 pesticides) by GC-MS/SIM, but the same number of pesticides (153) by both extraction procedures was detected by GC-MS/MS. Both solvent extraction and instrumental procedures were found to be equivalent at the highest fortification level of 500 μg/kg.

Pesticides that were difficult (recoveries < 70% or > 120%) to analyze across the fortification concentrations, different solvent extraction, and either GC-MS/SIM or GC-MS/MS analysis were captan, captafol, chlorothalonil, dichlofluanid, folpet, fluridone, and endrin aldehyde. These particular pesticides have been found to be thermally labile and unstable or difficult to analyze by GC-MS procedures because of pH, thermal lability, poor ionization, or fragmentation. Chlorothalonil has been shown to adsorb onto the PSA sorbent (*40*). Captan, captafol, dichlofluanid, folpet, and tolylfluanid have been shown to be better stabilized in an acidic solvent, but we did not pursue this because the presence of the acid in acetonitrile will protonate the amine groups and possibly diminish the activity of the PSA sorbent. The pyrethroids, cypermethrin, cyfluthrin, and resmethrin, were difficult to analyze by both GC-MS and GC-MS/MS due to interferences in the SIM analysis and the difficulty in finding stable transitions in the MS/MS mode.

Incurred Residues in Ginseng. Table 3 of the Supporting Information provides the results for triplicate determination of 12 commercial ginseng products. The ginseng extracts were prepared by both acetonitrile and acetone/cyclohexane/ethyl acetate extraction procedures, cleaned up by C-8 dispersive and GCB/PSA SPE, and measured by GC-MS/SIM and GC-MS/MS. Typical GC-MS/SIM and GC-MS/MS chromatograms of a *P. quinquefolius* sample, ginseng sample 2, are shown in **Figures 4** and **5**. **Figure 4** shows GC-MS/SIM and GC-MS/MS chromatograms of the α-, β-, γ-, and δ-forms of BHC. The use of *m/z* 181, 183, 217, and 219 as target and qualifier ions for the GC-MS/SIM chromatograms clearly indicates that components from the ginseng matrix interfere with the identification of β- and γ-BHC. GC-MS/MS shows separation of all forms of BHC as well as a fifth peak consisting of the 181 → 146 and 219 → 183 transitions, corresponding to the nonconfirmed presence of the ε-BHC isomer. **Figure 4** also lists the similar values of the transition ion ratios between the primary (181 → 146) and secondary (219 → 183) transitions of the two extraction solvents, acetonitrile (ACN) and 2:1:1 acetone/cyclohexane/ethyl acetate (ACE).

In addition to the recovery results, particularly at the 25 μg/kg fortification level presented in **Table 1**, the separation of the BHC isomers illustrated in the chromatograms in **Figure 4** indicates the difference in specificity of MS/MS over SIM in ginseng matrices. The concentrations of the BHC isomers ranged from 82 ± 9 μg/kg (α-BHC by GC-MS/SIM) to 567 ± 5 μg/kg (δ-BHC by GC-MS/MS). Other pesticides found in the ginseng samples were quintozene and its metabolites, pentachloroaniline, pentachlorobenzene, and pentachlorothioanisole and other contaminants found in technical-grade quintozene, such as hexachlorobenzene, tecnazene, and 2,3,5,6-tetrachloroaniline. The presence of *p,p′*-DDE in the ginseng sample is most likely due to the persistence

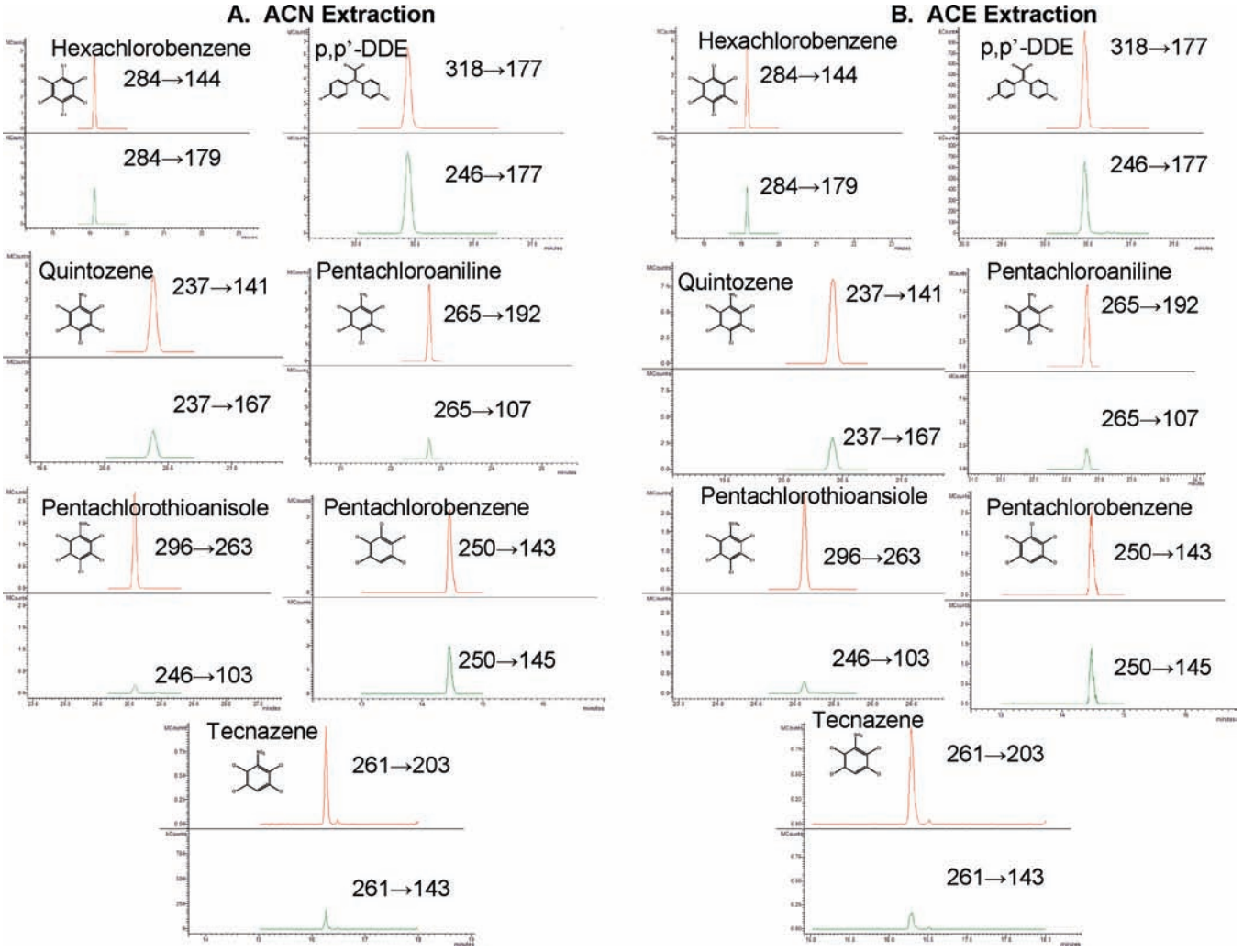

Figure 5. Presence of seven incurred pesticides and metabolites in the same dried ginseng powder (*Panax quinquefolius*) as in **Figure 4**, extracted by acetonitrile (ACN, **A**, left) and 2:1:1 acetone/cyclohexane/ethyl acetate (ACE, **B**, right) and analyzed by GC-MS/MS. Incurred pesticides present in the ginseng sample are hexachlorobenzene (284 → 144, 284 → 179), *p,p′*-DDT (318 → 177, 246 → 177), quintozene (237 → 141, 237 → 167), pentachloroaniline (265 → 192, 265 → 107), pentachlorothioanisole (296 → 263, 246 → 103), pentachlorobenzene (250 → 143, 250 → 145), and tecnazene (261 → 203, 261 → 143). Concentrations (μg/kg) of all compounds are listed in Table 3 of the Supporting Information.

and breakdown of *p,p′*-DDT in the environment. All of these compounds extracted from both the acetonitrile and acetone/cyclohexane/ethyl acetate methods can be detected by GC-MS/MS and GC-MS/SIM as shown in **Figures 5** and **6**, respectively. Concentrations range from 42 ± 4 μg/kg *p,p′*-DDE (as determined by acetone/cyclohexane/ethyl acetate extraction and GC-MS/SIM) to 1689 ± 60 μg/kg quintozene (as determined by acetonitrile extraction and GC-MS/SIM). The pesticide values obtained from both extraction methods using either the acetonitrile or the 2:1:1 acetone/cyclohexane/ethyl acetate solvents, and MS techniques were shown to be consistent and similar.

Other ginseng samples were analyzed, and the results are listed in Table 3 of the Supporting Information. Many of these samples contained organochlorine fungicides and insecticides, such as quintozene and its metabolites and contaminants, DDT and its metabolites, and the various isomers of BHC, chlordane, procymidone, iprodione, chlorothalonil, and dacthal. In addition, two organophosphorus insecticides, chlorpyrifos and diazinon, were present in the same ginseng sample. The concentrations of these compounds range from low microgram per kilogram concentrations (< 1 μg/kg hexachlorobenzene, pentachlorobenzonitrile, chlordane) to concentrations as high as > 4000 μg/kg quintozene. Both GC-MS/SIM and GC-MS/MS were able to detect, quantitate, and identify all of these compounds. The comparable results in **Table 3** of the Supporting Information also reveal that both acetonitrile and 2:1:1 acetone/cyclohexane/ethyl acetate were suitable for the salt-out solvent extraction of the pesticides from the ginseng matrix. The values are consistent with other studies that have shown the presence and levels of these same pesticides listed in Table 3 of the Supporting Information (*1*−*4*). The presence of banned organochlorine insecticides, such as *p,p′*-DDT and its metabolites and BHC isomers, is probably due to the persistence of these pesticides in the environment that these ginseng roots were cultivated in. The presence of procymidone, iprodione, quintozene, and quintozene byproducts indicates the effectiveness, popularity, and technical quality of these fungicides in controlling mold growth of these valued roots.

GC-MS/SIM versus GC-MS/MS. One advantage of GC-MS/MS over GC-MS/SIM is instrument specificity and sensitivity. Lower LOQs were achieved by GC-MS/MS, and this can have an effect in sample preparation. Although extensive SPE cleanup procedures were used, the ginseng matrix was so complex and concentrated that many of the pesticides, particularly organophosphorus pesticides and early eluting pesticides, were still very difficult to detect and identify by GC-MS/SIM. Matrix interferences can contribute to the pesticide target and qualifier ion abundances that affected the qualifier-to-target percentage ratios

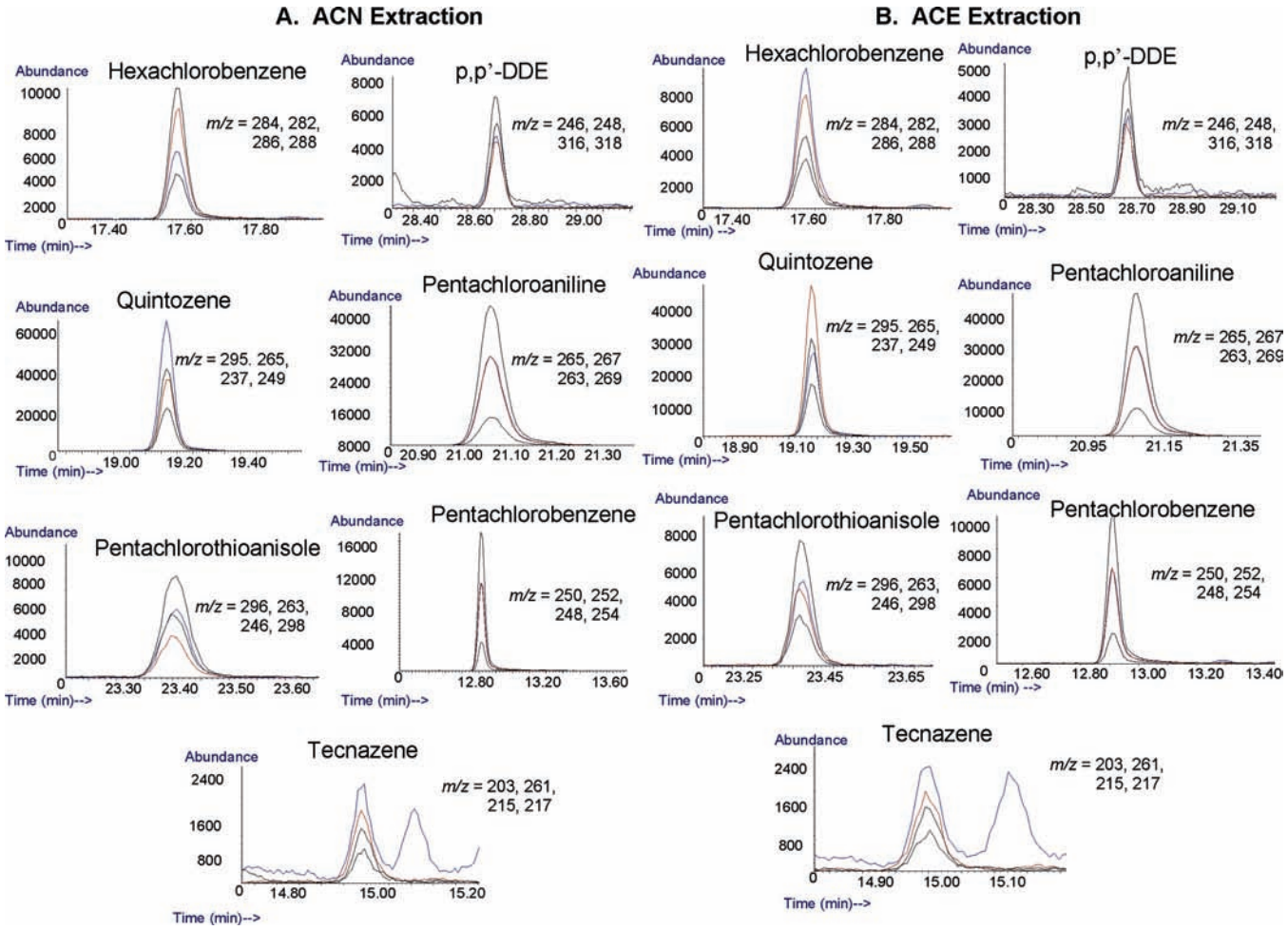

Figure 6. Presence of seven incurred pesticides and metabolites in the same dried ginseng powder (*Panax quinquefolius*) as in **Figure 4**, extracted by acetonitrile (ACN, **A**, left) and 2:1:1 acetone/cyclohexane/ethyl acetate (ACE, **B**, right) and analyzed by GC-MS/SIM. Incurred pesticides present in the ginseng sample are hexachlorobenzene (*m/z* 284, 282, 286, 288), *p,p'*-DDE (*m/z* 246, 248, 316, 318), quintozene (*m/z* 295, 265, 237, 249), pentachloroaniline (*m/z* 265, 267, 263, 269), pentachlorothioanisole (*m/z* 296, 263, 246, 298), pentachlorobenzene (*m/z* 250, 252, 248, 254), and tecnazene (*m/z* 203, 261, 215, 217). Concentrations (μg/kg) of all compounds are listed in Table 3 of the Supporting Information.

used for identification in GC-MS/SIM. Previous work required the use of additional cleanup using gel permeation chromatography, which was found to be necessary for better detection by GC-MS/SIM (*6*). The specificity of GC-MS/MS, on the other hand, provided transition ions that were only specific to the pesticide even in the presence of the complex ginseng matrix. The specificity of MS/MS results in an improvement of the signal-to-noise, allowing for improved sensitivity over MS/SIM and resulting in higher numbers of pesticides detected and identified at the 25 μg/kg fortification concentration for both extraction solvent methods. With the exception of β- and γ-BHC, most of the pesticides listed in Table 3 of the Supporting Information that were found in the ginseng samples could easily be identified and quantitated by both GC-MS/SIM and GC-MS/MS methods. These pesticides tend to be persistent organochlorine pesticides, such as DDT, hexachlorobenzene, endosulfan, and endrin. The results show that GC-MS/SIM can be used in screening for a limited number of pesticides, many of which happened to be present in the ginseng roots. Further confirmation of the pesticides present in the sample by GC-MS/SIM could come from other element-selective GC detectors, such as flame photometric or electrolytic conductivity detectors for screening organophosphorus and organochlorine pesticides, respectively (*4*, *5*). However, GC-MS/MS requires only one injection, rather than multiple injections for multiple instruments, for the screening, identification, and quantitation of pesticides in the sample. Due to the improved sensitivity of GC-MS/MS, extracts can be further diluted to allow for a smaller sample size to be introduced into the GC system. This extends the use of the GC liner and column and requires less instrument maintenance, which will be effective for high-throughput screening.

In conclusion, a method was developed for the multiresidue analysis of pesticides in dried, powdered ginseng. Using 168 pesticides, the method was evaluated and validated using two extraction solvents and two different instruments, GC-MS/SIM and GC-MS/MS. Although a triple-quadrupole mass spectrometer is generally more expensive than a single quadrupole, its specificity and sensitivity make it one of the more reliable instruments for pesticide identification and measurements in ginseng and for future applications to the multiresidue analysis of other plant-based supplements.

ACKNOWLEDGMENT

We thank the U.S. Environmental Protection Agency National Pesticide Standard Repository (Ft. Meade, MD) and especially Theresa Cole for providing pesticide standards used in this study. We also thank Butch Weege of the Ginseng Board of Wisconsin (Wausau, WI) for providing ground ginseng roots for blanks used to prepare the matrix-matched standards. This work was inspired by a Washington Chromatography Discussion Group seminar

presented by Jacques Gagnon of Health Canada on October 18, 2005, at the U.S. Pharmacopeia (Rockville, MD).

Supporting Information Available: Additional information regarding the pesticides studied, GG-MS/SIM and GC-MS/MS parameters, limits of quantitation, and incurred residue levels in ginseng samples are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

LITERATURE CITED

(1) Huggett, D. B.; Block, D. S.; Khan, I. A.; Allgood, J. C.; Benson, W. H. Environmental contaminants in the botanical dietary supplement ginseng and potential human risk. *Hum. Ecol. Risk Assessment* **2000**, *6*, 767–776.

(2) Huggett, D. B.; Khan, I. A.; Allgood, J. C.; Blosck, D. S.; Schlenk, D. Organochlorine pesticides and metals in select botanical dietary supplements. *Bull. Environ. Contam. Toxicol.* **2001**, *66*, 150–155.

(3) Khan, I. A.; Allgood, J.; Walker, L. A.; Abourashed, E. A.; Schlenk, D.; Benson, W. H. Determination of heavy metals and pesticides in ginseng products. *J. AOAC Int.* **2001**, *84*, 936–939.

(4) Durgnat, J.-M.; Heuser, J.; Andrey, D.; Perrin, C. Quality and safety assessment of ginseng extracts by determination of the contents of pesticides and metals. *Food Addit. Contam.* **2005**, *22* (12), 1224–1230.

(5) Wong, J. W.; Hennessy, M. K.; Hayward, D. G.; Krynitsky, A. J.; Cassias, I.; Schenck, F. J. Analysis of organophosphorus pesticides in dried ground ginseng root by capillary gas chromatography-mass spectrometry and -flame photometric detection. *J. Agric. Food Chem.* **2007**, *55* (4), 1117–1128.

(6) Hayward, D. G.; Wong, J. W. Organohalogen and organophosphorous pesticide method for ginseng root − a comparison of gas chromatography-single quadrupole mass spectrometry with high resolution time-of-flight mass spectrometry. *Anal. Chem.* **2009**, *81* (14), 5716–23.

(7) Kong, M.-F.; Chan, S.; Wong, Y.-C.; Wong, S.-K.; Sin, D. W.-M. Interlaboratory comparison for the determination of five residual organochlorine pesticides in ginseng root samples by gas chromatography. *J. AOAC Int.* **2007**, *90* (4), 1133–1141.

(8) Chan, S.; Kong, M. F.; Wong, Y. C.; Wong, S. K.; Sin, D. W. Application of isotope dilution gas chromatography-mass spectrometry in analysis of organochlorine pesticide residues in ginseng root. *J. Agric. Food Chem.* **2007**, *55* (9), 3339–3345.

(9) U.S. Pharmacopeia 24. Articles of Botanical Origin, Pesticide Residue Testing. Sec. 561.

(10) Moltó, J. C.; Lejeune, B.; Prognon, P.; Pradeau, D. GC-MS determination of organochlorine pesticides in five medicinal plants. *Int. J. Environ. Anal. Chem.* **1994**, *54*, 81–91.

(11) Manirakiza, P.; Covaci, A.; Schepens, P. Single step clean-up and GC-MS quantification of organochlorine pesticide residues in spice powders. *Chromatographia* **2000**, *52* (11−12), 787–790.

(12) Zuin, V. G.; Vilegas, J. H. Y. Pesticide residues in medicinal plants and phytomedicines. *Phytother. Res.* **2000**, *14*, 73–88.

(13) Ahmed, M. T.; Loutfy, N.; Yousef, Y. Contamination of medicinal herbs with organophosphorus insecticides. *Bull. Environ. Contam. Toxicol.* **2001**, *66*, 421–426.

(14) Leung, K. S.-Y.; Chan, K.; Chan, C.-L.; Lu, G.-H. Systematic evaluation of organochlorine pesticide residues in Chinese Materia Medica. *Phytother. Res.* **2005**, *19*, 514–518.

(15) Tagami, T.; Kajimura, K.; Satsuki, Y.; Nakamura, A.; Okihashi, M.; Takatori, S.; Kakimoto, K.; Obana, H.; Kitagawa, M. Rapid analysis of 56 pesticide residues in natural medicines by GC/MS with negative chemical ionization. *J. Nat. Med.* **2008**, *62*, 126–129.

(16) Huang, Z.; Li, Y.; Chen, B.; Yao, S. Simultaneous determination of 102 pesticide residues in Chinese teas by gas chromatography−mass spectrometry. *J. Chromatogr., B* **2007**, *853* (1−2), 154–162.

(17) Luke, M. A.; Froberg, J. E.; Masumoto, H. T. Extraction and cleanup of organochlorine, organophosphate, organonitrogen, and hydrocarbon pesticides in produce for determination by gas−liquid chromatography. *J. Assoc. Off. Anal. Chem.* **1975**, *58* (5), 1020–1026.

(18) Luke, M. A.; Froberg, J. E.; Doose, G. M.; Masumoto, H. T. Improved multiresidue gas chromatographic determination of organophosphorus, organonitrogen, and organohalogen pesticides in produce, using flame photometric and electrolytic conductivity detectors. *J. Assoc. Off. Anal. Chem.* **1981**, *64* (5), 1187–1195.

(19) Lee, S. M.; Papathakis, M. L.; Feng, H. C.; Hunter, G. F.; Carr, J. E. Multipesticide residue method for fruits and vegetables: California Department of Food and Agriculture. *Fresenius' J. Anal. Chem.* **1991**, *339*, 376–383.

(20) Nakamura, Y.; Tonogai, Y.; Sekiguchi, Y.; Tsumura, Y.; Nishida, N.; Takakura, K.; Isechi, M.; Yuasa, K.; Nakamura, M.; Kifune, N.; Yamamoto, K.; Terasawa, S.; Oshima, T.; Miyata, M.; Kamakura, K.; Ito, Y. Multiresidue analysis of 48 pesticides in agricultural products by capillary gas chromatography. *J. Agric. Food Chem.* **1994**, *42*, 2508–2518.

(21) Fillion, J.; Hindle, R.; Lacroix, M.; Selwyn, J. Multiresidue determination of pesticides in fruit and vegetables by gas chromatography-mass selective detection and liquid chromatography with fluorescence detection. *J. AOAC Int.* **1995**, *78*, 1252–1266.

(22) U.S. Food and Drug Administration. *Pesticide Analytical Manual*, 3rd ed.; U.S. Department of Health and Human Services, Public Health Service: Rockville, MD, 1999; Vol. 1.

(23) Fillion, J.; Sauve, F.; Selwyn, J. Multiresidue method for the determination of residues of 251 pesticides in fruits and vegetables by gas chromatography/mass spectrometry and liquid chromatography with fluorescence detection: chromatographic pesticide residue analysis. *J. AOAC Int.* **2000**, *83*, 698–713.

(24) Sannino, A.; Bandini, M.; Bolzoni, L. Determination of pyrethroid pesticide residues in processed fruits and vegetables by gas chromatography with electron capture and mass spectrometric detection. *J. AOAC Int.* **2003**, *86*, 101–108.

(25) Anastassiades, M.; Lehotay, S. J.; Štajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *J. AOAC Int.* **2003**, *86*, 412–431.

(26) Okihashi, M.; Kitagawa, Y.; Akutsu, K.; Obana, H.; Tanaka, Y. Rapid method for the determination of 180 pesticide residues in foods by gas chromatography/mass spectrometry and flame photometric detection. *J. Pestic. Sci.* **2005**, *30*, 368–377.

(27) Pang, G. F.; Fan, C. L.; Liu, Y. M.; Cao, Y. Z.; Zhang, J. J.; Li, X. M.; Li, Z. Y.; Wu, Y. P.; Guo, T. T. Determination of residues of 446 pesticides in fruits and vegetables by three-cartridge solid-phase extraction−gas chromatography−mass spectrometry and liquid chromatography−tandem mass spectrometry. *J. AOAC Int.* **2006**, *89*, 740–771.

(28) Shimelis, O.; Yang, Y.; Stenerson, K.; Kaneko, T.; Ye, M. Evaluation of a solid-phase extraction dual-layer carbon/primary secondary amine for clean-up of fatty acid matrix components from food extracts in multiresidue pesticide analysis. *J. Chromatogr., A* **2007**, *1165*, 18–25.

(29) EC Council Directive 2002/657/EC of 12 August, 1990 on implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. *Off. J. Eur. Communities* **2002**, *L221*, 8.

(30) Walorczyk, S.; Gnusowski, B. Fast and sensitive determination of pesticide residues in vegetables using low pressure gas chromatography with a triple quadrupole mass spectrometer. *J. Chromatogr., A* **2006**, *1128* (1−2), 236–243.

(31) Okihashi, M.; Takatori, S.; Kitagawa, Y.; Tanaka, Y. Simultaneous analysis of 260 pesticide residues in agricultural products by gas chromatography/triple quadrupole mass spectrometry. *J. AOAC Int.* **2007**, *90* (4), 1165–1179.

(32) Paýa, P.; Anastassiades, M.; Mack, D.; Sigalova, I.; Tasdelen, B.; Oliva, J.; Barba, A. Analysis of pesticide residues using the Quick Easy Cheap Effective Rugged and Safe (QuEChERS) pesticide multiresidue method in combination with gas and liquid chromatography and tandem mass spectrometric detection. *Anal. Bioanal. Chem.* **2007**, *389* (6), 1697–1714.

(33) Pihlström, T.; Blomkvist, G.; Friman, P.; Pagard, U.; Osterdahl, B. G. Analysis of pesticide residues in fruit and vegetables with ethyl acetate extraction using gas and liquid chromatography with tandem mass spectrometric detection. *Anal. Bioanal. Chem.* **2007**, *389* (6), 1773–1789.

(34) Fernández Moreno, J. L.; Garrido Frenich, A.; Plaza Bolaños, P.; Martinez Vidal, J. L. Multiresidue method for the analysis of more than 140 pesticide residues in fruits and vegetables by gas chromatography coupled to triple quadrupole mass spectrometry. *J. Mass Spectrom.* **2008**, *43* (9), 1235–54.
(35) Walorczyk, S. Application of gas chromatography/tandem quadrupole mass spectrometry to the multi-residue analysis of pesticides in green leafy vegetables. *Rapid Commun. Mass Spectrom.* **2008**, *22* (23), 3791–3801.
(36) Tullo, A. A solvent dries up. *Chem. Eng. News* **2008**, *86* (47), 27.
(37) Luke, M. A.; Doose, G. M. A modification of the Luke multiresidue procedure for low moisture, nonfatty products. *Bull. Environm. Contam. Toxicol.* **1983**, *30*, 110–116.
(38) Mills, P. A.; Onley, J. H.; Gaither, R. A. Rapid method for chlorinated pesticide residues in non fatty foods. *J. Assoc. Off. Anal. Chem.* **1963**, *46*, 186.
(39) Specht, W.; Pelz, S.; Gilsbach, W. Gas chromatographic determination of pesticide residues after clean-up by gel permeation chromatography and mini-silica gel-column chromatography. Replacement of dichloromethane by ethyl acetate/cyclohexane in liquid−liquid partition and simplified conditions for extraction and liquid−liquid partitioning. *Anal. Bioanal. Chem.* **1995**, *353* (2), 183–190.
(40) Mol, H. G.; Rosseboom, A.; van Dam, R.; Roding, M.; Arondeus, K.; Sunarto, S. Modification and re-validation of the ethyl acetate based multi-residue method for pesticides in produce. *Anal. Bioanal. Chem.* **2007**, *389* (6), 1715–1754.

Received for review November 2, 2009. Revised manuscript received January 22, 2010. Accepted February 1, 2010. This work was supported by National Institutes of Health, Office of Dietary Supplements (NIH, ODS) through an Interagency Agreement, Y1-OD-6412-01.