JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Analysis of Organophosphorus Pesticides in Dried Ground Ginseng Root by Capillary Gas Chromatography−Mass Spectrometry and −Flame Photometric Detection

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A method was developed to determine organophosphorus pesticides (OPs) in dried ground ginseng root. Pesticides were extracted from the sample using acetonitrile/water saturated with salts, followed by solid-phase dispersive cleanup, and analyzed by capillary gas chromatography with electron ionization mass spectrometry in selective ion monitoring mode (GC-MS/SIM) and flame photometric detection (GC-FPD) in phosphorus mode. The detection limits for most of the pesticides were 0.025−0.05 μg/g using GC-FPD but were analyte-dependent for GC-MS/SIM, ranging from 0.005 to 0.50 μg/g. Quantitation was determined from 0.050 to 5.0 μg/g with $r^2 > 0.99$ for a majority of the pesticides using both detectors. Recovery studies were performed by fortifying the dried ground ginseng root samples to concentrations of 0.025, 0.1, and 1.0 μg/g, resulting in recoveries of >90% for most pesticides by GC-FPD. Lower (<70%) and higher (>120%) recoveries were most likely from complications of pesticide lability or volatility, matrix interference, or inefficient desorption from the solid-phase sorbents. There was difficulty in analyzing the ginseng samples for the OPs using GC-MS at the lower fortification levels for some of the OPs due to lack of confirmation. GC-FPD and GC-MS/SIM complement each other in detecting the OPs in dried ground ginseng root samples. This procedure was shown to be effective and was applied to the analysis of OPs in ginseng root samples. One particular sample, a ground and dried American ginseng (*Panax quinquefolius*) root sample, was found to contain diazinon quantified at approximately 25 μg/kg by external calibration using matrix-matched standards or standard addition using both detectors. The advantage of using both detectors is that confirmation can be achieved using GC-MS, whereas the use of a megabore column in GC-FPD can be used to quantitate some of the nonpolar OPs without the use of matrix-matched standards or standard addition.

KEYWORDS: ***Panax quinquefolius*** **(American ginseng);** ***Panax ginseng*** **(Asian ginseng); ginseng root; capillary gas chromatography−mass spectrometry (GC-MS); gas chromatography−flame photometric detection (GC-FPD); organophosphorus pesticides (OPs); solid-phase dispersive cleanup**

INTRODUCTION

The root of *Panax quinquefolius* (American ginseng) or *Panax ginseng* (Asian ginseng) is an important botanical dietary supplement primarily used by consumers to improve energy and vitality. In addition to the postharvest treatment against pests, the root generally takes 4−6 years to grow and mature for harvest, a long enough time for the root to accumulate chemical contaminants, such as pesticides. There are numerous reports of organochlorine pesticides such as quintozene and dichlorodiphenyltrichloroethane (DDT) and their metabolites, lindane and other hexachlorocyclohexanes, and endosulfan present in ginseng root, but few on organophosphorus pesticides (OPs) (*1*−*6*). Although OPs are generally less persistent than organochlorines, they are still frequently used on agricultural crops and are extremely toxic to animals and humans (*4*). There are studies that involve the screening of individual components such as chlorpyrifos, but there are not any reports of multiresidue screening for OPs in ginseng products (*5*). To improve the detection of pesticide contaminants in dietary supplements to

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10.1021/jf062774q This article not subject to U.S. Copyright. Published 2007 by the American Chemical Society
Published on Web 01/24/2007

ensure their safety and quality, validated pesticide analytical methods are needed.

There are reported methods that have been developed for screening pesticides in dried botanical dietary supplements, dried spices, medicinal plants, herbals, and phytomedicines based on procedures primarily for fresh plant-derived foods (*1*−*14*). These methods usually involve organic extraction of semivolatile pesticides from the plant matrix, a cleanup procedure to remove coextractives and interferences, and subsequent analysis such as capillary gas chromatography (GC) (*14*−*18*). However, pesticide procedures can be costly due to the large amounts of solvents and expensive consumables used, so there is a need for the methods to be fast, robust, and cost-efficient. Anastassiades et al. (*18*) proposed a method that utilizes smaller sample sizes, less solvent and glassware, and fewer procedures, and solid-phase dispersive sorbents as an economical alternative to solid-phase extraction cartridges. The use of GC with selective element detectors, such as the flame photometric detector in phosphorus mode (GC-FPD), is reliable because of its specificity for organic phosphorus present in OPs regardless of the complexity of most plant matrixes. GC with mass spectrometry/electron ionization/selective ion monitoring (GC-MS/SIM) is also a powerful analytical tool because it can provide confirmation by selective monitoring of target and qualifier ions and their relative abundances and ratios specific to the analyte of interest. Together, the advantages of both specificity and selectivity in GC-FPD and GC-MS/SIM can be complementary to each other in analyzing OPs in complex plant matrixes. The following work reveals a multiresidue procedure based on procedures developed by Anastassiades et al. (*18*) and Fillion et al. (*16*, *17*) to screen OPs in dried ground ginseng root by GC-FPD and GC-MS/SIM.

METHODS AND MATERIALS

Materials and Standards Preparation. The majority of organophosphorus pesticide standards were obtained from the U.S. Environmental Protection Agency (EPA) Pesticide Repository (Fort Meade, MD). Akton, pirimphos-ethyl, crotoxyphos, and propetamphos were purchased from Fluka Chemicals (Milwaukee, WI). Pesticide-grade acetonitrile and toluene, HPLC-grade water, and certified-grade anhydrous magnesium sulfate and sodium chloride were purchased from Fisher Scientific (Pittsburgh, PA). Internal standards, including acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and tributyl phosphate, were purchased from Aldrich Chemical Corp. (Milwaukee, WI) and Chem-Service (West Chester, PA). C18 sorbent was purchased from Varian Corp. (Harbor City, CA), and primary-secondary amine (PSA) sorbent and graphitized carbon were purchased from United Chemical Technologies (Bristol, PA). Dried and finely ground ginseng root (*P. ginseng* and *P. quinquefolius*) samples were purchased in bulk packages from commercially available sources. Each of the sources where the samples were purchased either guaranteed that the dried ground ginseng root was authentic or that the source participated in organizations that guaranteed product authenticity.

Stock solutions of individual pesticide standards were prepared by dissolving 50−100 mg of pesticides in 25 mL of toluene. The working standards used for quantitation were prepared by mixing 1−2 mL of each standard using a 250 mL volumetric flask to prepare a 20 μg/mL working standard. Successive dilutions of the stock pesticide standards were used to prepare 10, 5.0, 2.5, 1.0, 0.5, 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 standards were prepared by dissolving acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and tributyl phosphate to make 20 μg/mL working solutions. The fortification solutions were prepared in acetone.

Sample Preparation. A schematic of the extraction and cleanup procedure is shown in **Figure 1**. Dried, powdered ginseng root (2 g) was transferred into a PTFE screw-capped centrifuge tube. HPLC-grade water (10 mL) was added to the centrifuge tube and vigorously vortexed, followed by 15 mL of acetonitrile. The centrifuge tube was homogenized for 1 min with an UltraTurrax T25 homogenizer and an S25N-10G dispersing tool (IKA Works, Inc., Wilmington, NC). Magnesium sulfate (7.5 g) and sodium chloride (2.5 g) were slowly added to the homogenized ginseng/acetonitrile/water mixture, and the mixture was homogenized for 1 min. The sample was centrifuged at 4000 rpm for 5 min using a refrigerated centrifuge (ThermoElectron Corp., Milford, MA). The acetonitrile extract (12−15 mL) was transferred to a second Teflon centrifuge tube containing 0.5 g of C18 sorbent and 1.2 g of anhydrous magnesium sulfate, followed by shaking for 1 min. The tube was centrifuged at 4000 rpm for 5 min. The extract (10−12 mL) was transferred to a third Teflon centrifuge tube containing 0.4 g of PSA sorbent, 0.2 g of graphitized carbon, and 1.2 g of anhydrous magnesium sulfate. The extract was vortexed for 5 s, and 3 mL of toluene was added. The tube was shaken vigorously for 1 min and centrifuged at 4000 rpm for 5 min. The extract (12 mL) was transferred to a glass centrifuge tube and was reduced to near dryness (50−100 μL) using a nitrogen evaporator (N-EVAP, Organomation Associates, Inc., Berlin, MA). Toluene (0.5 mL), approximately 10 mg of magnesium sulfate, and 50 μL of internal standard solution were added to the centrifuge tube. The tube was vortexed and centrifuged at 1500 rpm for 5 min. The extract was transferred to GC autosampler vials for GC-MS and GC-FPD analysis.

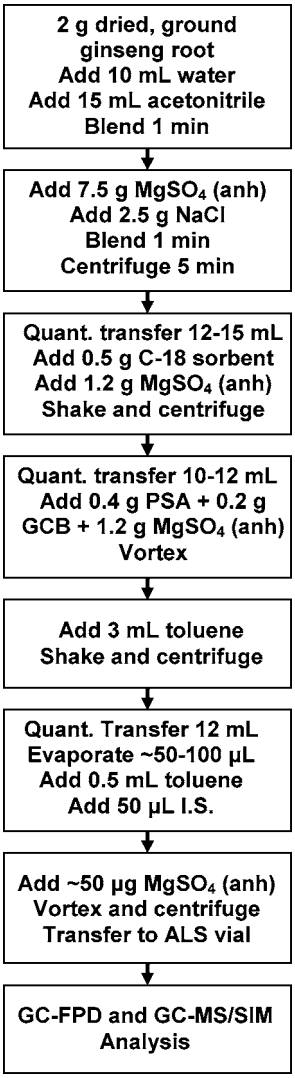

Figure 1. Flowchart of the method for the analysis of organophosphorus (OP) pesticides in dried ginseng powder.

GC-MS/SIM and GC-FPD Analysis. An Agilent 6890N gas chromatograph was equipped with an Agilent 5973N mass selective

detector (MSD, Agilent Technologies, Little Falls, DE) and fitted with a deactivated guard column (5 m × 0.25 mm i.d., Agilent Technologies) and HP-5MS column (30 m × 0.25 mm I.D. × 0.25 μm film thickness, Agilent Technologies). The carrier gas was ultrapure helium (Air Products, Hyattsville, MD) set at a constant flow of 1.5 mL/min using the retention time locking (RTL) program on the Agilent 6890 and chlorpyrifos-ethyl as the RTL standard. The temperature program rose from 110 °C (1 min hold) to 130 °C at a rate of 10 °C/min and increased to 230 °C at 4 °C/min, followed by a final ramp of 290 °C at 20 °C/min (7 min hold). The MSD was operated in electron impact (EI) mode at 70 eV. The inlet, 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 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 two or three qualifier ions as indicated in **Table 1**. Confirmation by mass spectrometry was established by the retention time of the target ion and the presence of two to three qualifier-to-target ion ratios as listed in **Table 2**. The target and qualifier ion abundances were determined by injection of individual pesticide standards utilizing full-scan conditions with the 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 ion by that of the target ion multiplied by 100%. Quantitation by GC-MS/SIM was based on the peak area ratio of the target ion of the analyte divided by the peak area of the target ion of the internal standard (the internal standard with the retention time closest to that of the pesticide) versus concentration of the calibration standards and using the GC-MSD ChemStation software.

The same GC-MSD instrument was also equipped with a flame photometric detector and fitted with a deactivated guard column (5 m × 0.53 mm i.d., Agilent Technologies) and a megabore DB-5 column (30 m × 0.53 mm × 1.5 μm film thickness, Agilent Technologies). The He carrier, air and hydrogen fuel, and He makeup gases were set at 10, 120, 80, and 20 mL/min, respectively. The injector and detector temperatures were set at 250 °C. The ginseng root extracts, standards, and blanks were injected (1 μL) into the GC in pulsed splitless mode (pulsed pressure = 20.0 psi, pulse time = 2.00 min) using an Agilent 7683 series autoinjector. Quantitation by GC-FPD was based on the peak area ratio of the peak area of the analyte divided by the peak area of the internal standard (tributylphosphate) versus concentration of the calibration standards and using the GC-MSD ChemStation software.

Fortification Studies. For fortification studies, a measured 2 g test portion of dried ground ginseng root was fortified with 1.0 mL of the appropriate solution (0.05, 0.2, or 2.0 μg/mL standards prepared in acetone) to a final concentration of 0.025, 0.1, or 1.0 μg/g, and the centrifuge tube was vigorously vortexed to distribute the pesticides. The same procedure described above was applied to the fortified samples. For quantitation by external calibration by GC-FPD or GC-MS/SIM, two different types of standards were prepared: solvent-only and matrix-matched standards. Solvent-only standards were prepared in toluene as described above, and matrix-matched standards were prepared by extracting pesticide-free ginseng samples (as described above) and fortifying the dried extracts with the solvent-only standards prepared in toluene. Both types of standards were prepared at concentration levels of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 2.5, and 5.0 μg/mL.

Standard Addition. Quantitation by standard addition requires prior knowledge of the presence of the incurred pesticide and its estimated concentration in the sample (*19*). An extract prepared by sample preparation procedures listed above was analyzed by GC-FPD and GC-MSD. For the incurred sample, diazinon was identified at a concentration of approximately 0.05 μg/g. Procedures for standard addition were similar to those for sample preparation except for the following modifications. After GCB/PSA cleanup, centrifugation, and volume reduction to near dryness (50−100 μL), 0.5 mL of pesticide standard prepared in toluene was added to individually prepared portions to form 0.05, 0.1, and 0.25 μg/g pesticide-added samples. To a fourth sample was added 0.5 mL of toluene to form the zero-added sample. The samples were treated with 10 mg of magnesium sulfate, and 50 μL of internal standard solution was added to each of the centrifuge tubes. The tubes were vortexed and centrifuged at 1500 rpm for 5 min. The extracts were transferred to GC autosampler vials for GC-MS and GC-FPD analysis.

Statistics and Calculations. Averages and standard deviations from fortification studies and linear regressions and correlation coefficients for standard addition studies were determined using Mircosoft Excel 2003. Pesticide concentrations from fortification studies for both the GC-MS/SIM and GC-FPD were calculated using the Agilent MSD ChemStation software version G1701DA using peak area response ratios of the pesticide analyte to internal standards versus pesticide concentrations. Calculations and plots of the response for standard addition calculations were achieved using Microsoft Excel 2003.

RESULTS AND DISCUSSION

Extraction Procedure. In this study, dispersive solid-phase extraction or "QuEChERS (quick, easy, cheap, effective, robust, and safe)" developed by Anastassiades et al. (*18*−*21*) was adopted for the determination of OPs in dried ground ginseng root. The procedure also stems from the work of Fillion et al. (*16*, *17*), who applied acetonitrile extraction of the sample, followed by cleanup procedures using C18, graphitized carbon and aminopropyl solid-phase extraction cartridges, and analysis by GC-MS. Anastassiades et al. (*18*) optimized and modified the procedure by using a lesser sample size and by dispersing the cleanup sorbent, primary-secondary amine (PSA), with the sample extract. The differences with the procedure shown in **Figure 1** with the other established methods are that (1) cleanup is achieved by solid-phase dispersion rather than solid-phase extraction and (2) additional cleanup is utilized by using C18 sorbent and adding graphitized carbon to the PSA sorbent. These modifications take advantage of preparing a clean extract, reducing preparation time, and reducing the cost of the procedure by using solid-phase sorbents rather than solid-phase extraction cartridges. The sample was homogenized and blended to ensure efficient extraction with acetonitrile and copious amounts of magnesium sulfate (anhydrous) and sodium chloride to form a one-phase organic extract. This extract was mixed with additional anhydrous magnesium sulfate and C18 sorbent to remove nonpolar coextractives, similar to the C18 solid-phase filtering described in Fillion's procedure. The extract was also treated with a combination of graphitized carbon, PSA sorbent, and anhydrous magnesium sulfate to remove additional interfering coextractives such as fatty acids, organic acids, sterols, and pigments. At this step, toluene was added to the acetonitrile to desorb planar pesticides such as coumaphos and leptophos from the graphitized carbon. This step is equivalent to the part of the procedure in Fillion's method in which the extract is applied to a tandem graphitized carbon/PSA cartridge and eluted with toluene/acetonitrile mixture. This final extract is reduced in volume before analysis by GC-MS/SIM. Despite the relative simplicity and minimal use of solvents and chemicals, one drawback of the procedure is that less sample (2 grams) is used than a typical fresh plant produces (10−15 g from Anastassiades work and 25−50 g from Fillion's procedure). The smaller sample size limits the ability to screen for pesticides at lower fortification levels. If one assumes that most fresh plant products are 80−90% water, the 2 g of the dried ground ginseng root is approximately equivalent to 10−20 g of fresh sample. Because the powdered ginseng root is dehydrated, water is added to rehydrate the sample before it is blended with acetonitrile and the salts.

Determination of OPs and Method Validation. One hundred and eight OPs were analyzed either by GC-FPD or by GC-MS/SIM as listed in **Table 1**. Tributyl phosphate was used

Table 1. Pesticide Name, Molecular Formula, and Weight; GC-FPD and GC-MS/SIM Retention Time, Target and Qualifier Ions, Percentage of Qualifier-to-Target Ratios, Limit of Detection, Concentration Range, and Regression Coefficient (r^2) of Organophosphorus Pesticides Used in the Study

			flame photometric detector				mass spectrometric detection				
pesticide	mol formula	mol wt	RT, FPD (min)	estimated LOD (ng/g)	range (ng/g)	r^2	RT, MS/SIM (min)	estimated LOD (ng/g)	range (ng/g)	r^2	**target** and qualifier ions (Q/T ratio %)
acenapthlene-d_{10}	$C_{12}D_{10}$	164.29	NA[a]	NA	NA	NA	11.55				**164**, 160 (95.4), 162 (42.0), 163 (18.7)
acephate	$C_4H_{10}NO_3PS$	183.17	13.56	25	50–5000	0.9996	10.93	500	1000–5000	0.9998	**136**, 94 (56.1), 142 (12.3), 183 (1.8)
akton	$C_{12}H_{14}Cl_3O_3PS$	375.64	31.36	25	50–5000	1.0000	27.53	10	25–5000	1.0000	**339**, 283 (130.5), 341 (70.7)
azinphos-ethyl	$C_{12}H_{16}N_3O_3PS_2$	345.38	38.75	25	50–5000	1.0000	36.64	10	25–5000	1.0000	**132**, 160 (80.9), 77 (72.9), 105 (22.3)
azinphos-methyl	$C_{10}H_{12}N_3O_3PS_2$	317.33	37.93	25	50–5000	1.0000	35.68	10	25–5000	0.9999	**160**, 77 (110.9), 132 (89.9), 104 (23.0)
azinphos-methyl oxon	$C_{10}H_{12}N_3O_4PS$	301.26	36.76	25	50–5000	0.9998	NA				
bromophos	$C_8H_8BrCl_2O_3PS$	366.00	29.11	50	100–5000	0.9999	25.24	2.5	10–5000	1.0000	**331**, 329 (73.6), 333 (28.9), 316* (5.0)
bromophos-ethyl	$C_{10}H_{12}BrCl_2O_3PS$	394.05	31.12	50	100–5000	0.9998	NA				
cadusafos	$C_{10}H_{23}O_2PS_2$	270.40	20.75	25	50–5000	0.9999	17.13	50	100–5000	0.9997	**159**, 158 (74.4), 213 (13.1), 270 (7.8)
carbophenothion	$C_{11}H_{16}ClO_2PS_3$	326.74	35.23	25	50–5000	0.9998	31.83	10	25–5000	0.9998	**342**, 157 (433.9), 199 (85.1)
carbophenothion oxon	$C_{11}H_{16}ClO_3PS_2$	310.67	33.76	25	50–5000	1.0000	30.19	50	100–5000	1.0000	**183**, 109 (119.1), 139 (44.8), 155 (33.9)
chlorfenvinphos, β-	$C_{12}H_{14}Cl_3O_4P$	359.57	30.25	25	50–5000	1.0000	26.62	10	50–5000	0.9999	**267**, 325 (34.3), 269 (63.7), 295 (16.2)
chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	350.59	28.32	25	50–5000	1.0000	24.55	10	25–5000	0.9999	**314**, 258 (69.2), 286 (39.7), 208 (52.0)
chlorpyrifos oxon	$C_9H_{11}Cl_3NO_4P$	334.52	28.10	25	50–5000	1.0000	24.46	10	50–5000	1.0000	**298**, 270 (115.2), 242 (125.9), 260 (31.2)
chlorpyrifos-methyl	$C_7H_7Cl_3NO_3PS$	322.54	25.97	25	50–5000	1.0000	22.17	5	25–5000	0.9999	**286**, 288 (68.6), 125 (71.8), 290 (14.6), 199 (6.5)
chlorthiophos	$C_{11}H_{15}Cl_2O_3PS_2$	361.25	34.68	25	50–5000	1.0000	31.13	10	25–5000	0.9999	**269**, 325 (67.8), 360 (8.5), 297 (22.0)
chrysene-d_{12}	$C_{18}D_{12}$	240.39	NA				34.17				**240**, 236 (23.2), 241 (18.9)
coumaphos	$C_{14}H_{16}ClO_5PS$	362.77	39.58	25	50–5000	1.0000	37.69	25	50–5000	1.0000	**362**, 226 (81.9), 210 (59.3), 334 (13.6), 364 (40.2)
coumaphos oxon	$C_{14}H_{16}ClO_6P$	346.70	38.88	25	50–5000	1.0000	37.01	50	100–5000	0.9997	**346**, 210 (47.2), 290 (35.4), 318 (21.9), 348 (31.5)
crotoxyphos	$C_{14}H_{19}O_6P$	314.30	30.25 30.68	25	50–5000	1.0000	NA				
cyanofos	$C_9H_{10}NO_3PS$	243.22	21.26	25	50–5000	1.0000	19.43	25	50–5000	1.0000	**243**, 109 (175.6), 125 (94.7), 180 (10.7)
DEF (tribufos)	$C_{12}H_{27}OPS_3$	314.52	32.62	50	100–5000	1.0000	28.94	50	100–5000	0.9990	**202**, 226 (41.7), 258 (28.8)
demeton-O	$C_8H_{19}O_3PS_2$	258.34	18.76	25	50–5000	0.9998	15.19	100	500–5000	0.9993	**88**, 171 (14.4), 115 (13.5), 143 (7.0)
demeton-O sulfoxide	$C_8H_{19}O_4PS_2$	274.34	26.35	25	50–5000	1.0000	NA				
demeton-S	$C_8H_{19}O_3PS_2$	258.34	21.76	25	50–5000	1.0000	18.21	50	100–5000	0.9999	**88**, 170 (11.3), 143 (8.2), 89 (14.1)
demeton-S-methyl	$C_6H_{15}O_3PS_2$	230.29	18.92	50	100–5000	1.0000	15.39	50	100–5000	1.0000	**88**, 109 (29.3), 142 (16.3), 230 (1.0)
demeton-S-sulfone	$C_8H_{19}O_5PS_2$	290.34	29.24	25	50–5000	1.0000	NA				
dialifor	$C_{14}H_{17}ClNO_4PS_2$	393.85	38.88	50	100–5000	0.9992	36.78	25	50–5000	0.9993	**208**, 210 (33.4), 357 (8.4), 186 (7.4)
diamidafos	$C_8H_{13}N_2O_2P$	200.18	21.30				NA				
diazinon	$C_{12}H_{21}N_2O_3PS$	304.35	23.77	25	50–5000	0.9997	20.16	10	50–5000	0.9995	**304**, 227 (73.6), 276 (52.4), 248 (54.8)
diazinon-OH	$C_{12}H_{21}N_2O_4PS$	320.35	19.21	50	100–5000	1.0000	NA				
diazinon oxon	$C_{12}H_{21}N_2O_5P$	288.28	23.09	25	50–5000	0.9999	19.72	5	5–5000	1.0000	**273**, 288 (22.7), 260 (17.5), 217 (18.2)
dicapthon	$C_8H_9ClNO_5PS$	297.65	28.55	50	100–5000	0.9999	24.76	10	50–5000	0.9996	**262**, 125 (40.6), 216 (9.7), 263 (9.4)
dichlorfenthion	$C_{10}H_{13}Cl_2O_3PS$	315.16	25.54	25	50–5000	1.0000	NA				
dichlorvos	$C_4H_7Cl_2O_4P$	185.52	8.21	25	50–5000	0.9999	5.66	10	50–5000	0.9989	**109**, 185 (24.0), 145 (7.6), 220 (3.6)
dicrotophos	$C_8H_{16}NO_5P$	237.19	20.34	50	100–5000	1.0000	17.09	250	500–5000	0.9996	**237**, 127 (2177.8), 67 (699.4), 109 (217.8), 193 (167.0)
dimethoate	$C_5H_{12}NO_3PS_2$	229.26	21.79				18.22	250	500–5000	1.0000	**87**, 93 (64.2), 125 (50.3), 229 (4.6)
dioxabenzofos	$C_8H_9O_3PS$	216.20	20.25	25	50–5000	1.0000	NA				
dioxathion	$C_{12}H_{26}O_6P_2S_4$	456.55	22.91 39.72	50	100–5000	1.0000	37.76	50	250–5000	1.0000	**270**, 97 (390.2), 153 (62.9), 197 (47.7)
disulfoton	$C_8H_{19}O_2PS_3$	274.41	23.94	25	50–5000	1.0000	20.15	50	100–5000	0.9999	**274**, 88 (2089.9), 142 (305.5), 186 (215.4)
ditalimfos	$C_{12}H_{14}NO_4PS$	299.28	31.76	25	50–5000	1.0000	28.00	10	25–5000	1.0000	**299**, 243 (108.9), 271 (35.4)
edifenphos	$C_{14}H_{15}O_2PS_2$	310.38	35.38	25	50–5000	0.9999	NA				
EPN	$C_{14}H_{14}NO_4PS$	323.31	37.03	25	50–5000	1.0000	34.48	25	100–5000	0.9999	**157**, 169 (47.9), 185 (24.6), 141 (29.3)
ethion	$C_9H_{22}O_4P_2S_4$	384.48	34.55	10	50–5000	0.9998	31.02	25	100–5000	0.9996	**231**, 153 (59.3), 199 (8.1), 384 (7.5)
ethion dioxon	$C_9H_{22}O_5P_2S_3$	368.42	31.61	25	50–5000	1.0000	28.28	100	250–5000	0.9997	**171**, 215 (34.5), 182 (15.4)
ethion monoxon	$C_9H_{22}O_6P_2S_2$	352.35	33.18	25	50–5000	0.9998	29.64	10	50–5000	0.9998	**171**, 215 (34.5), 322 (25.6), 368 (4.4)
ethoprop	$C_8H_{19}O_2PS_2$	242.34	19.31	25	50–5000	1.0000	15.78				**158**, 200 (23.1), 242 (12.3), 168 (10.6)
etrimfos	$C_{10}H_{17}N_2O_4PS$	292.30	24.48				NA				
famphur	$C_{10}H_{16}NO_5PS_2$	325.34	35.21	25	50–5000	1.0000	31.95	25	100–5000	1.0000	**218**, 217 (19.4), 282 (2.3), 202 (3.4)
fenamiphos	$C_{13}H_{22}NO_3PS$	303.36	32.01	25	50–5000	0.9929	28.96	10	50–5000	0.9995	**303**, 154 (81.9), 288 (25.5), 139 (18.9)
fenamiphos deisopropyl	$C_{10}H_{16}NO_3PS$	261.28	31.40	25	50–5000	0.9998	28.57	25	50–5000	1.0000	**261**, 154 (81.9), 139 (44.7)
fenamiphos sulfone	$C_{13}H_{22}NO_5PS$	335.36	36.81				34.58	25	50–5000	0.9995	**320**, 292 (61.1), 249 (7.7), 335 (4.9)
fenamiphos sulfoxide	$C_{13}H_{22}NO_4PS$	319.36	36.68	50	100–5000	1.0000	NA				
fenchlorphos	$C_8H_8Cl_3O_3PS$	321.55	36.65	25	50–5000	1.0000	22.83	5	25–5000	0.9999	**285**, 287 (68.4), 270 (6.3), 167 (9.7)
fenitrothion	$C_9H_{12}NO_5PS$	277.24	27.31	25	50–5000	0.9999	23.55	50	100–5000	0.9943	**277**, 260 (57.1), 214 (8.5), 228 (2.1)
fensulfothion	$C_{11}H_{17}O_4PS_2$	308.37	34.16	25	50–5000	0.9999	30.72	10	25–5000	1.0000	**293**, 308 (23.1), 265 (28.3), 292 (210.0)
fenthion	$C_{10}H_{15}O_3PS_2$	278.33	28.21	25	50–5000	1.0000	24.47	10	25–5000	1.0000	**278**, 279 (12.2), 263 (4.7), 169 (23.7)
fenthion oxon	$C_{10}H_{15}O_4PS$	262.27	26.72	25	50–5000	1.0000	23.13	25	100–5000	1.0000	**262**, 247 (16.7), 263 (11.8), 153 (12.5)
fenthion sulfone	$C_{10}H_{15}O_5PS_2$	310.33	33.01	25	50–5000	0.9999	NA				
fenthion sulfoxide	$C_{10}H_{15}O_4PS_2$	294.33	34.20	50	100–5000	1.0000	30.69				
fonophos	$C_{10}H_{15}OPS_2$	246.33	23.22	25	50–5000	0.9998	19.38	25	50–5000	0.9995	**246**, 109 (388.9), 137 (142.4), 174 (17.4)
fosthiazate	$C_9H_{18}NO_3PS_2$	283.35	33.15	50	100–5000	1.0000	NA				
heptenophos	$C_9H_{12}ClO_4P$	250.62	17.80	50	100–5000	0.9999	14.31	250	500–5000	0.9992	**250**, 124 (558.1), 200 (45.2), 215 (74.7)
iprobenfos	$C_{13}H_{21}O_3PS$	288.34	24.71	25	50–5000	0.9998	21.08	25	50–5000	0.9993	**204**, 123 (33.6), 246 (12.8), 288 (8.7)
iodofenphos	$C_8H_8Cl_2IO_3PS$	413.00	32.17	25	50–5000	1.0000	28.30	5	25–5000	0.9999	**377**, 379 (37.2), 250 (8.7), 362 (3.9)
isazophos	$C_9H_{17}ClN_3O_3PS$	313.74	24.37	25	50–5000	1.0000	20.75	25	50–5000	0.9998	**257**, 285 (53.3), 208 (68.4), 313 (19.9), 177 (82.5)
isofenphos	$C_{15}H_{24}NO_4PS$	345.40	30.27	25	50–5000	0.9998	26.55	25	50–5000	0.9995	**255**, 213 (280.5), 121 (259.3), 185 (128.9)

Table 1. (Continued)

			flame photometric detector				mass spectrometric detection				
pesticide	mol formula	mol wt	RT, FPD (min)	estimated LOD (ng/g)	range (ng/g)	r^2	RT, MS/SIM (min)	estimated LOD (ng/g)	range (ng/g)	r^2	**target** and qualifier ions (Q/T ratio %)
leptophos	$C_{13}H_{10}BrCl_2O_2PS$	412.07	37.99	25	50–5000	0.9999	35.62	10	50–5000	1.0000	**377**, 171 (158.3), 375 (73.6), 155 (40.6), 379 (28.5)
leptophos oxon	$C_{13}H_{10}BrCl_2O_3P$	396.00	36.93	25	50–5000	0.9998	34.37	10	25–5000	0.9999	**361**, 155 (152.6), 359 (75.6), 363 (27.2)
malaoxon	$C_{10}H_{19}O_7PS$	314.30	26.13	25	50–5000	1.0000	22.62	50	100–5000	1.0000	**268**, 195 (160.3), 142 (140.8), 173 (77.3)
malathion	$C_{10}H_{19}O_6PS_2$	330.36	27.86	25	50–5000	1.0000	24.23	25	50–5000	0.9999	**173**, 158 (50.6), 143 (27.8), 211 (7.0)
methamidophos	$C_2H_8NO_2PS$	141.13	7.28	50	100–5000	0.9997	5.21	100	250–5000	0.9917	**141**, 94 (285.6), 95 (165.9), 126 (14.2)
methidathion	$C_6H_{11}N_2O_4PS_3$	302.34	30.98	25	50–5000	1.0000	27.18	50	100–5000	0.9999	**145**, 85 (93.7), 125 (20.1), 302 (1.6)
mevinphos	$C_7H_{13}O_6P$	224.15	13.55	50	50–5000	0.9997	10.57	100	250–5000	0.9999	**127**, 192 (21.5), 109 (25.6), 164 (6.6)
monocrotophos	$C_7H_{14}NO_5P$	223.17	20.60	25	50–5000	0.9999	17.89	25	50–5000	0.9900	**192**, 223 (20.0), 193 (56.6), 127 (861.3), 67 (245.1)
naled	$C_4H_7Br_2Cl_2O_4P$	380.78	19.94	25	50–5000	0.9997	14.23	NA	NA	NA	**145**, 220 (13.3), 109 (516.4), 185 (94.9)
omethoate	$C_5H_{12}NO_4PS$	213.19	18.11	50	100–5000	0.9997	14.97	250	500–5000	0.9999	**156**, 110 (104.1), 109 (31.8), 126 (14.3)
paraoxon	$C_{10}H_{14}NO_6P$	275.20	26.60	25	50–5000	0.9997	23.03	50	100–5000	0.9998	**275**, 220 (95.3), 247 (64.7), 232 (81.6)
parathion	$C_{10}H_{14}NO_5PS$	291.26	28.34	25	50–5000	0.9998	24.61	10	50–5000	0.9999	**291**, 155 (56.2), 235 (20.9), 263 (12.1)
parathion-methyl	$C_8H_{10}NO_5PS$	263.21	21.76	25	50–5000	0.9998	22.20	25	100–5000	0.9998	**263**, 200 (10.0), 246 (6.9), 233 (9.0)
parathion-methyl oxon	$C_8H_{10}NO_6P$	247.14	23.91	25	50–5000	0.9999	20.40	100	250–5000	0.9999	**230**, 247 (74.0), 200 (50.9), 186 (31.3)
phenanthrene-d_{10}	$C_{14}D_{10}$	188.31	NA	NA	NA	NA	19.15	NA	NA	NA	**188**, 184 (13.4), 187 (9.6)
phorate	$C_7H_{17}O_2PS_3$	260.38	20.96	25	50–5000	1.0000	17.21	10	25–5000	0.9992	**260**, 231 (83.5), 121 (324.6), 97 (273.5)
phorate oxon	$C_7H_{17}O_3PS_2$	244.32	18.87	50	100–5000	1.0000	15.35				**171**, 244 (10.7), 138 (31.5), 156 (17.6)
phorate sulfone	$C_7H_{17}O_4PS_3$	292.38	28.05	25	50–5000	0.9998	24.36	250	500–5000	0.9996	**292**, 153 (4700.6), 125 (4404.1), 199 (3268.0)
phorate sulfoxide	$C_7H_{17}O_3PS_3$	276.38	27.67	25	50–5000	0.9998	NA				
phosalone	$C_{12}H_{15}ClNO_4PS_2$	367.81	37.92	25	50–5000	0.9997	35.64	25	50–5000	0.9996	**182**, 184 (34.2), 367 (16.0), 154 (19.0)
phosmet	$C_{11}H_{12}NO_4PS_2$	317.33	36.94	25	50–5000	0.9999	34.37	25	50–5000	0.9999	**160**, 161 (10.2), 133 (4.7), 317 (1.9)
pirimphos–methyl	$C_{11}H_{20}N_3O_3PS$	305.33	27.43	25	50–5000	1.0000	23.75	5	25–5000	0.9999	**290**, 276 (87.7), 305 (65.2), 233 (34.2)
profenofos	$C_{11}H_{15}BrClO_3PS$	373.63	32.46	50	100–5000	1.0000	28.71	25	50–5000	1.0000	**339**, 139 (213.4), 208 (221.5), 374 (36.3)
propetamphos	$C_{10}H_{20}NO_4PS$	281.31	23.20	25	50–5000	1.0000	19.70	100	250–5000	0.9998	**236**, 138 (525.3), 194 (240.3), 222 (88.1)
prothiophos	$C_{11}H_{15}Cl_2O_2PS_2$	345.25	32.35	25	50–5000	1.0000	28.45	10	50–5000	1.0000	**309**, 267 (104.1), 162 (110.7)
pyraclofos	$C_{14}H_{18}ClN_2O_3PS$	360.80	38.84	25	50–5000	0.9999	36.82	10	50–5000	1.0000	**360**, 194 (83.7), 362 (100.0), 139 (68.7)
pyrazophos	$C_{14}H_{20}N_3O_5PS$	373.37	38.67	25	50–5000	1.0000	36.68	25	50–5000	1.0000	**221**, 232 (31.5), 373 (12.5), 328 (5.0)
pyridaphenthion	$C_{14}H_{17}N_2O_4PS$	340.34	36.87	25	50–5000	1.0000	34.36	10	50–5000	1.0000	**340**, 199 (67.7), 188 (66.3), 77 (120.1)
quinalphos	$C_{12}H_{15}N_2O_3PS$	298.32	30.39	25	50–5000	1.0000	26.61	25	50–5000	0.9999	**298**, 146 (765.3), 157 (483.0), 270 (54.6)
sulfotep	$C_8H_{20}O_5P_2S_2$	322.32	20.77	25	50–5000	0.9998	17.19	5	25–5000	0.9998	**322**, 202 (61.6), 238 (33.1), 266 (25.6)
sulprofos	$C_{12}H_{19}O_2PS_3$	322.45	34.94	25	50–5000	0.9999	31.48	10	25–5000	1.0000	**322**, 280 (11.1), 230 (8.1), 198 (9.5)
tebupirimphos	$C_{13}H_{23}N_2O_3PS$	318.37	24.75	25	50–5000	1.0000	21.07	10	25–5000	1.0000	**318**, 261 (131.5), 234 (126.6), 276 (52.8)
temephos	$C_{16}H_{20}O_6P_2S_3$	466.48	48.87	50	100–5000	0.9999	43.75	100	250–5000	0.9978	**466**, 109 (24.7), 203 (15.5), 171 (8.3), 467 (19.4)
terbufos	$C_9H_{21}O_2PS_3$	288.44	23.10	25	50–5000	1.0000	19.35	50	100–5000	0.9999	**231**, 153 (28.7), 186 (14.7), 288 (5.3)
terbufos oxon	$C_9H_{21}O_3PS_2$	272.37	21.28	50	100–5000	1.0000	NA				
terbufos oxon sulfone	$C_9H_{21}O_5PS_2$	304.37	27.81				NA				
terbufos sulfone	$C_9H_{21}O_4PS_3$	320.42	29.89	25	50–5000	1.0000	NA				
tetrachlorvinphos	$C_{10}H_9Cl_4O_4P$	365.96	31.49	25	50–5000	0.9999	27.77	10	25–5000	0.9998	**329**, 331 (95.0), 333 (31.3), 240 (12.3)
thiometon	$C_6H_{15}O_2PS_3$	246.36	21.43	25	50–5000	1.0000	17.67	100	250–5000	1.0000	**88**, 125 (), 93 (), 246 ()
tolclofos-methyl	$C_9H_{11}Cl_2O_3PS$	301.13	26.18	25	50–5000	0.9999	22.36	5	10–5000	1.0000	**265**, 267 (36.1), 125 (24.4), 250 (10.3)
triazophos	$C_{12}H_{16}N_3O_3PS$	313.32	34.97	25	50–5000	0.9999	31.75	50	100–5000	0.9999	**285**, 257 (139.5), 208 (135.3), 313 (37.1)
tributyl phosphate (I.S.)	$C_{12}H_{27}O_4P$	266.32	19.61	NA	NA	NA	NA	NA	NA	NA	
trichlorfon	$C_4H_8Cl_3O_4P$	257.44	14.35	25	50–5000	0.9999	5.66	50	100–5000	0.9905	**185**, 109 (453.2), 145 (30.8), 220 (15.8)
triphenyl phosphate	$C_{18}H_{15}O_4P$	326.28	36.17	NA	100–5000	1.0000	33.27	5	10–5000	1.0000	**326**, 325 (83.8), 215 (31.1), 170 (30.6)
vamidothion	$C_8H_{18}NO_4PS_2$	287.36	31.36	50	100–5000	1.0000	NA				
zinophos (thionazin)	$C_8H_{13}N_2O_3PS$	248.26	18.57	25	50–5000	1.0000	15.04	100	250–5000	0.9999	**97**, 143 (56.6), 192 (19.2), 248 (13.5)

[a] Not analyzed.

as a quantitative internal standard for GC-FPD, whereas the deuterated polycyclic hydrocarbons acenapthlene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} were used for GC-MS/SIM. Retention times, estimated limits of detection (LODs), quantitation, and regression coefficients of 103 OPs were determined by GC-FPD in phosphorus mode. For most of the OPs, the limit of detection (defined by a minimum of 3 times the background contributed from the detector) was 0.025 μg/g. Quantitation for most of the OPs was determined in the 0.050−5.0 μg/g range (prepared in the ginseng matrix) and resulted with regression coefficients $r^2 > 0.999$. The consistency of these values is attributed to the fact that the OPs are indiscriminately combusted into highly energetic molecular products containing the phosphorus atom that emits chemiluminescent light (*21*). **Figure 2** shows chromatograms generated from GC-FPD using an HP-5 megabore column (30 m × 0.53 mm i.d. × 1.5 μm film thickness) of an American ginseng root extract fortified at 1.0 μg/g. The peak shapes of polar OPs such as acephate, dichlorvos, methamidophos, and mevinphos and of nonpolar OPs such as coumaphos, leptophos, and temephos are symmetric and consistent. The chromatogram of the ginseng blank shows few unidentified peaks, and most of the peaks from the fortified OP mixes (*1*−*4*) are distinguishable and can be used for quantitation. However, one drawback of the GC-FPD as well as other element-selective detector is the potential coelution of other OPs. For example, both dimethoate and parathion-methyl elute at the same retention time using a megabore column, which will make the identification of a sample containing both pesticides difficult.

Therefore, GC-MS/SIM was also used to detect OPs from the same ginseng root extract, with values shown in **Table 1** and the reconstructed chromatogram in SIM mode shown in **Figure 3**, as a result of the screened ions listed in the GC-MS/SIM program shown in **Table 2**. An advantage of GC-MS/SIM over element selective detectors is that the identity of the analyte can be confirmed on the basis of characteristic mass ions and the ratios of qualifiers to target masses. A significant background from the ginseng root matrix is observed in the blank, target,

Table 2. GC-MS/SIM Program Used To Analyze Organophosphorus Pesticides in Ginseng

group	time (min)	ions (dwell time, ms)				scan rate (cycles/s)	pesticide
1	4.00	94 (35)	95 (35)	109 (35)	126 (35)	2.47	methamidophos, dichlorvos
		141 (35)	145 (35)	185 (35)	220 (35)		
2	9.00	94 (20)	109 (20)	127 (20)	136 (20)	2.17	mevinphos, acephate, trichlorfon, acenapthlene-d_{10}
		142 (20)	160 (20)	162 (20)	163 (20)		
		164 (20)	183 (20)	185 (20)	192 (20)		
		221 (20)					
3	13.00	88 (10)	97 (10)	109 (10)	110 (10)	1.59	heptenophos, omethoate, zinophos, demeton-O, phorate oxon, demeton-S-methyl, ethoprop, naled
		115 (10)	124 (10)	126 (10)	138 (10)		
		142 (10)	143 (10)	145 (10)	156 (10)		
		158 (10)	168 (10)	171 (10)	185 (10)		
		192 (10)	200 (10)	215 (10)	220 (10)		
		230 (10)	242 (10)	244 (10)	248 (10)		
		250 (10)					
4	16.50	67 (10)	87 (10)	88 (10)	89 (10)	1.42	dicrotophos, cadusafos, monocrotophos, sulfotep, phorate, thiometon, demeton-S, dimethoate
		93 (10)	97 (10)	109 (10)	121 (10)		
		125 (10)	127 (10)	143 (10)	158 (10)		
		159 (10)	170 (10)	192 (10)	193 (10)		
		202 (10)	213 (10)	223 (10)	229 (10)		
		231 (10)	237 (10)	238 (10)	246 (10)		
		260 (10)	266 (10)	270 (10)	322 (10)		
5	18.50	109 (10)	125 (10)	137 (10)	138 (10)	1.89	phenanthrene-d_{10}, cyanophos, terbufos, fonophos, propetamphos, diazinon oxon
		153 (10)	174 (10)	180 (10)	184 (10)		
		186 (10)	188 (10)	189 (10)	194 (10)		
		217 (10)	222 (10)	231 (10)	236 (10)		
		243 (10)	246 (10)	260 (10)	273 (10)		
		288 (10)					
6	19.85	88 (10)	91 (10)	123 (10)	142 (10)	1.37	diazinon, disulfoton, parathion-methyl oxon, isazophos, iprobenfos, tebupirimphos, dichlorfenthion
		177 (10)	186 (10)	199 (10)	200 (10)		
		204 (10)	208 (10)	223 (10)	227 (10)		
		230 (10)	234 (10)	246 (10)	247 (10)		
		248 (10)	251 (10)	257 (10)	261 (10)		
		274 (10)	276 (10)	279 (10)	281 (10)		
		285 (10)	288 (10)	304 (10)	313 (10)		
		318 (10)					
7	21.40	125 (10)	142 (10)	153 (10)	167 (10)	1.32	chlorpyrifos-methyl, parathion-methyl, malaoxon, tolclofos-methyl, fenchlorphos, parathion oxon, fenthion oxon, fenitrothion
		173 (10)	195 (10)	199 (10)	200 (10)		
		214 (10)	220 (10)	228 (10)	232 (10)		
		233 (10)	246 (10)	247 (10)	250 (10)		
		260 (10)	262 (10)	263 (10)	265 (10)		
		267 (10)	268 (10)	270 (10)	275 (10)		
		277 (10)	285 (10)	286 (10)	287 (10)		
		288 (10)	290 (10)				
8	23.55	125 (10)	143 (10)	153 (10)	1155 (10)	1.32	pirimphos-methyl, phorate sulfoxide, malathion, phorate sulfone, chlorpyrifos oxon, fenthion, chlorpyrifos, parathion, dicapthon
		158 (10)	169 (10)	173 (10)	199 (10)		
		208 (10)	211 (10)	216 (10)	233 (10)		
		235 (10)	242 (10)	258 (10)	260 (10)		
		262 (10)	263 (10)	265 (10)	270 (10)		
		276 (10)	278 (10)	279 (10)	286 (10)		
		290 (10)	291 (10)	292 (10)	298 (10)		
		305 (10)	314 (10)				
9	25.00	316 (50)	329 (50)	331 (50)	333 (50)	3.77	bromophos
10	26.30	85 (15)	105 (15)	121 (15)	125 (15)	1.65	β-chlorfenvinphos, isofenfos, quinalphos, crotoxyphos, methidathion
		127 (15)	145 (15)	146 (15)	157 (15)		
		166 (15)	185 (15)	193 (15)	213 (15)		
		255 (15)	267 (15)	269 (15)	270 (15)		
		295 (15)	298 (15)	302 (15)	325 (15)		
11	27.35	139 (10)	154 (10)	162 (10)	171 (10)	1.32	akton, fenamiphos deisopropyl, tetrachlorvinphos, ethion dioxon, ditalimfos, iodofenphos, fenamiphos, prothiophos, DEF (tribufos)
		182 (10)	202 (10)	208 (10)	215 (10)		
		226 (10)	240 (10)	243 (10)	250 (10)		
		258 (10)	261 (10)	267 (10)	271 (10)		
		283 (10)	288 (10)	299 (10)	303 (10)		
		309 (10)	329 (10)	331 (10)	333 (10)		
		339 (10)	341 (10)	362 (10)	374 (10)		
		377 (10)	379 (10)				
12	29.20	109 (20)	136 (20)	139 (20)	155 (20)	2.35	ethion monoxon, fenthion sulfone, carbophenothion oxon
		171 (20)	183 (20)	215 (20)	233 (20)		
		247 (20)	310 (20)	322 (20)	368 (20)		

Table 2. (Continued)

group	time (min)	ions (dwell time, ms)				scan rate (cycles/s)	pesticide
13	30.35	153 (10) 199 (10) 218 (10) 265 (10) 280 (10) 293 (10) 313 (10) 360 (10)	157 (10) 202 (10) 230 (10) 269 (10) 282 (10) 294 (10) 322 (10) 384 (10)	169 (10) 208 (10) 231 (10) 278 (10) 285 (10) 297 (10) 325 (10)	198 (10) 217 (10) 257 (10) 279 (10) 292 (10) 308 (10) 342 (10)	1.32	fenthion sulfoxide, fensulfothion, ethion, chlorthiophos, sulprofos, triazophos, carbophenothion, famphur
14	32.75	170 (50)	215 (50)	325 (50)	326 (50)	3.77	triphenylphosphate (surrogate)
15	33.50	77 (10) 141 (10) 161 (10) 196 (10) 241 (10) 304 (10) 321 (10) 361 (10)	109 (10) 155 (10) 169 (10) 199 (10) 249 (10) 317 (10) 335 (10) 363 (10)	132 (10) 157 (10) 185 (10) 236 (10) 276 (10) 319 (10) 340 (10)	133 (10) 160 (10) 188 (10) 240 (10) 292 (10) 320 (10) 359 (10)	1.32	chrysene-d_{12}, fenamiphos sulfoxide, azinphos-methyl oxon, phosmet, leptophos oxon, fenamiphos sulfone, pyridaphenthion, EPN
16	35.10	77 (20) 155 (20) 184 (20) 379 (20)	104 (20) 160 (20) 367 (20)	132 (20) 171 (20) 375 (20)	154 (20) 182 (20) 377 (20)	2.17	azinphos-methyl, phosalone, leptophos
17	36.10	77 (10) 139 (10) 208 (10) 290 (10) 348 (10) 373 (10)	93 (10) 160 (10) 210 (10) 318 (10) 357 (10)	105 (10) 186 (10) 221 (10) 328 (10) 360 (10)	132 (10) 194 (10) 232 (10) 346 (10) 362 (10)	1.89	azinphos-ethyl, pyrazophos, dialifor, pyraclofos, coumaphos oxon
18	37.25	97 (35) 226 (35) 364 (35)	153 (35) 270 (35)	197 (35) 334 (35)	210 (35) 362 (35)	2.20	coumaphos, dioxathion
19	42.00	109 (50) 467 (50)	171 (50)	203 (50)	466 (50)	3.03	temephos

and qualifier ions characteristic of most OP compounds that can be extracted for identification and quantitation. Although mass/charge ions given in **Tables 1** and **2** are used for the characterization and identification of the OPs, not all of the ions were used due to low abundances and interferences from the ginseng root matrix. Generally, qualifier-to-target ratio percentages of <10% were not used for confirmation and were replaced with retention time matching from GC-FPD results prepared from standards. Therefore, confirmation for the OP identity was determined by either GC-MS retention time and three to four qualifier-to-target ratio percentages alone or both GC-MS and GC-FPD retention times and two to three qualifier-to-target ratio percentages. In addition to retention times, LODs, and linearity, the MS parameters such as target and qualifier ions and qualifier-to-target ratios were determined for 85 OPs. The LODs, range, and r^2 values were not as consistent as the values (i.e., 0.025−0.05 μg/g for LODs) obtained by GC-FPD, probably as a result of MS determination being more dependent on the physical and chemical nature of the OP molecule rather than the formation of an excited phosphorus species that is detected by the FPD. Polar and more volatile compounds such as acephate, demeton, and their related metabolites, dicrotophos, dimethoate, heptenophos, methamidophos, monocrotophos, and zinophos, and oxygenated metabolites of parent OPs such as fenthion sulfone and sulfoxide, malaoxon, omethoate, and terbufos oxon and sulfone were not sensitive (>0.250 μg/g) and could not be detected by GC-MS. However, most nonpolar OP pesticides could be easily detected by GC-MS/SIM at levels lower than 0.05 μg/g and r^2 > 0.99 up to 5.0 μg/g such as bromophos, chlorpyrifos, diazinon, pirimphos-methyl, and tolclofos-methyl, due to the presence of unequivocal signals from the target and qualifier ions and high qualifier-to-target ratios (>50%) of these compounds.

Fortification Studies. The recoveries from fortification studies of 103 OPs were evaluated by GC-FPD based on external calibration using toluene and ginseng root-matched standards and GC-MS/SIM using ginseng root-matched standards only, are shown in **Table 3**. The dried, powdered American ginseng was fortified with OPs to levels of 0.025, 0.1, and 1.0 μg/g. These fortified samples were prepared for analysis as previously described under Materials and Methods and analyzed. The recovery ranges for OPs detected and analyzed by GC-FPD using calibration standards prepared in toluene at the 0.025, 0.1, and 1.0 μg/g levels were from 20 (akton) to 454% (vamidothion), from 43% (ditalimfos) to 161% (fenamiphos sulfoxide), and from 32 (naled) to 125% (fenamiphos sulfoxide). The recovery range for OPs that could be detected and analyzed by GC-FPD using ginseng-matched standards at the 0.025, 0.1, and 1.0 μg/g levels were from 22 (fenamiphos) to 130% (methamidophos), from 12 (naled) to 110% (dicapthon), and from 37 (naled) to 117% (dicapthon), respectively. When toluene and ginseng root-matched standards were used, 63 and 89 pesticides had recoveries in the range of 70−120% at all three fortification levels of 0.025, 0.1, and 1.0 μg/g, respectively. Naled was poorly analyzed by GC-FPD primarily because it eluted from the tailing edge from the internal standard, tributyl phosphate. For GC-MS, many OP compounds could not be detected at the 0.025 μg/g level because of interferences from the matrix and could not confirm the identity of the analytes. However, confirmation could be determined at the higher 0.1 and 1.0 μg/g levels. The

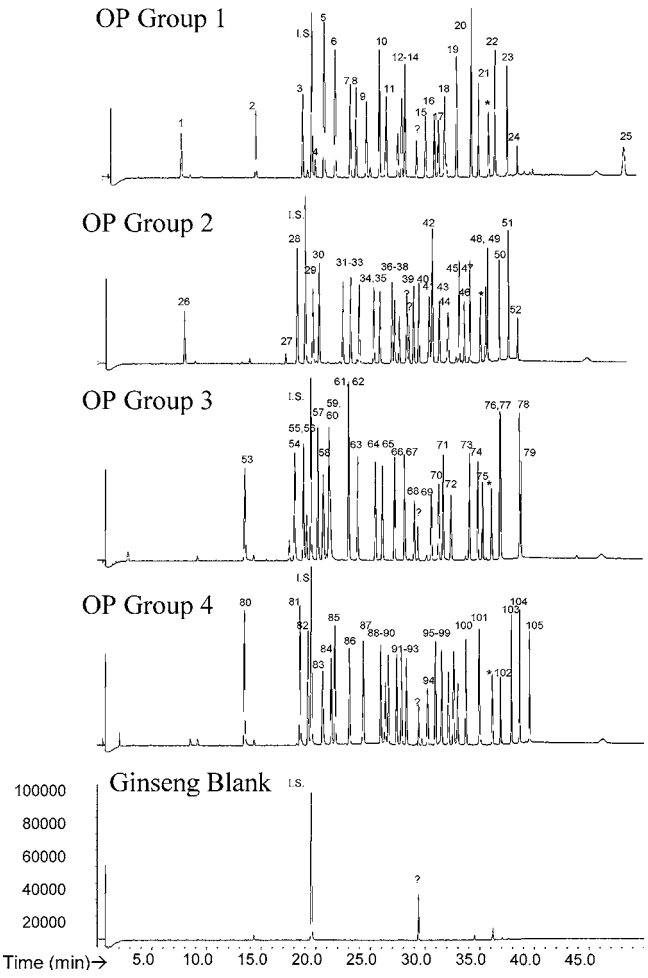

Figure 2. GC-FPD of an American ginseng (*P. quinquefolius*) root extract fortified at 1.0 μg/mL OP pesticides. There are four groups of OP pesticides to show separation of each compound. I.S. and "–" indicate the presence of the internal standard, tributylphosphate and triphenylphosphate, respectively. "?" indicates unidentified peaks. 1, methamidophos; 2, trichlorfon; 3, demeton-O; 4, naled; 5, sulfotep; 6, dimethoate; 7, fonophos; 8, diazinon; 9, iprobenfos; 10, parathion-methyl; 11, paraoxon; 12, phorate sulfoxide; 13, phorate sulfone; 14, parathion; 15, isofenfos; 16, bromophos-ethyl; 17, tetrachlorvinphos; 18, fenamiphos; 19, ethion monoxon; 20, ethion; 21, carbophenothion; 22, azinphos-methyl oxon; 23, phosalone; 24, dialifor; 25, temephos; 26, dichlrovos; 27, heptenophos; 28, phorate oxon; 29, dicrotophos; 30, phorate; 31, propetamphos; 32, disulfoton; 33, tebupirimphos; 34, malaoxon; 35, fenthion oxon; 36, terbufos sulfone oxon; 37, chlorpyrifos oxon; 38, dicapthon; 39, terbufos sulfone; 40, quinalphos; 41, vamidothion; 42, ethion dioxon; 43, prothiophos; 44, fosthiazate; 45, fenthion sulfoxide; 46, chlorthiophos; 47, famophos; 48, fenamiphos sulfoxide; 49, pyridaphenthion; 50, leptophos; 51, pyraclofos; 52, dioxathion; 53, mevinphos; 54, omethoate; 55, demeton-S-methyl; 56, diazinon-OH; 57, dioxabenzofos; 58, cadusafos; 59, cyanofos; 60, diamidophos; 61, diazinon oxon; 62, terbufos oxon; 63, parathion-methyl oxon; 64, dichlorfenthion; 65, tolclofos-methyl; 66, fenitrothion; 67, fenthion; 68, bromophos-methyl; 69, crotoxyphos; 70, akton; 71, ditalimfos; 72, profenofos; 73, fensulfothion; 74, sulprofos; 75, edifenphos; 76, phosmet; 77, EPN; 78, azinphos-ethyl; 79, coumaphos oxon; 80, acephate; 81, zinophos; 82, ethoprop; 83, monocrotophos; 84, thiometon; 85, demeton-S; 86, terbufos; 87, isazophos; 88, chlorpyrifos-methyl; 89, demeton-S-sulfone; 90, fenchlorphos; 91, pirimphos-methyl; 92, malathion; 93, chlorpyrifos; 94, chlorfenvinphos; 95, methidathion; 96, fenamiphos-deisopropyl; 97, iodofenphos; 98, DEF (tribufos); 99, fenthion sulfoxide; 100, carbophenothion oxon; 101, triazophos; 102, leptophos oxon; 103, azinphos-methyl; 104, pyrazophos; 105, coumaphos.

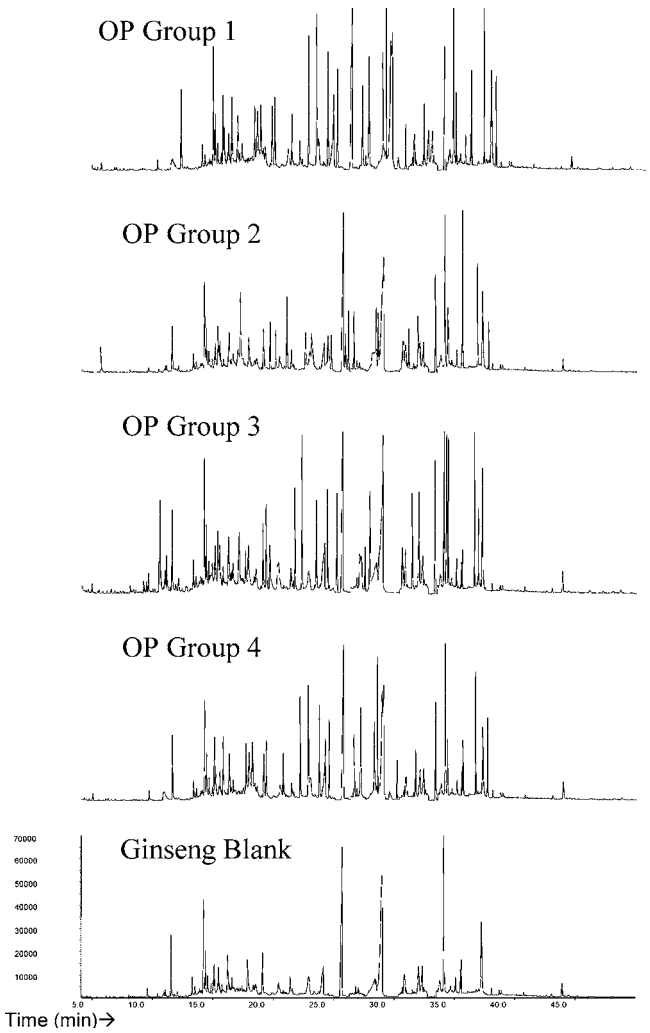

Figure 3. Reconstructed GC-MS/SIM chromatograms from a ginseng extract fortified at 5 μg/mL. See Methods and Materials and **Tables 1** and **2** for details on GC-MS/SIM conditions.

recovery ranges for OPs that could be detected and analyzed by GC-MS/SIM at the 0.025, 0.1, and 1.0 μg/g levels were from 66 (isazophos, phosalone) to 116% (parathion-methyl), from 49 (ditalimfos) to 236% (trichlorfon), and from 58 (ditalimfos) to 137% (trichlorfon), respectively. Seventy-five pesticides had recoveries in the range of 70−120% at fortification levels of 0.1 and 1.0 μg/g, whereas 51 OPs could be determined at the 0.025 μg/g level. With the use of both GC-FPD and GC-MS/SIM instruments, the recoveries of many of the OPs were >90% with a relative standard deviation of ≤10%.

Matrix Effects. We investigated which OP pesticides could be quantitated by GC-FPD using solvent-only calibration standards by comparing recovery results based on solvent (toluene)-only and matrix (ginseng root)-matched standards. The results shown in **Table 3** compare the recovery results calculated by the two different types of calibration standards at 0.025, 0.10, and 1.0 μg/g using GC-FPD. The results at the two higher levels, 0.10 and 1.0 μg/g, show minor differences between solvent-only and matrix-matched standards but were consistent primarily because the recoveries were acceptable in the 70−120% range, with exceptions for acephate, azinphos-methyl oxon, dicrotophos, fosthiazate, monocrotophos, terbufos oxon sulfone, and vamidothion. At the 0.025 μg/g level, there are distinctions between results using the two types of calibration standards, suggesting that matrix enhancement is concentration- and

Table 3. Recoveries (Percent) of Organophosphorus Pesticides Extracted from Dried Ginseng Powder Fortified at 0.025, 0.1, and 1.0 μg/g Levels[a]

	GC-FPD (toluene, external calibration)			GC-FPD (matrix, external calibration)			GC-MS/SIM (matrix, external calibration)		
pesticide	0.025 μg/g	0.10 μg/g	1.0 μg/g	0.025 μg/g	0.10 μg/g	1.0 μg/g	0.025 μg/g	0.10 μg/g	1.0 μg/g
acephate	271 ± 3	131 ± 8	88 ± 2	113 ± 1	93 ± 5	80 ± 1	nd	nd	82 ± 9
akton	20 ± 4	77 ± 2	97 ± 3	110 ± 1	93 ± 3	95 ± 2	97 ± 2	101 ± 3	97 ± 1
azinphos-methyl oxon	198 ± 1	137 ± 6	110 ± 6	93 ± 2	92 ± 3	98 ± 1	nd	nd	nd
azinphos-ethyl	30 ± 3	85 ± 5	98 ± 3	82 ± 1	86 ± 3	95 ± 1	92 ± 2	100 ± 1	105 ± 5
azinphos-methyl	103 ± 4	114 ± 3	111 ± 1	86 ± 5	95 ± 2	96 ± 1	102 ± 4	98 ± 5	94 ± 1
bromophos-ethyl	68 ± 1	90 ± 4	90 ± 4	80 ± 1	80 ± 3	91 ± 3	na	na	na
bromophos-methyl	74 ± 5	89 ± 2	93 ± 3	na	93 ± 3	91 ± 2	92 ± 1	90 ± 4	98 ± 2
cadusafos	89 ± 2	93 ± 2	94 ± 1	96 ± 2	97 ± 1	92 ± 1	nd	112 ± 4	106 ± 2
carbophenothion	88 ± 6	92 ± 2	91 ± 4	87 ± 1	89 ± 7	97 ± 2	93 ± 7	96 ± 2	97 ± 3
carbophenothion oxon	81 ± 3	99 ± 3	98 ± 1	93 ± 2	99 ± 4	97 ± 2	76 ± 6	101 ± 6	97 ± 2
chlorfenvinphos	57 ± 6	94 ± 3	97 ± 1	96 ± 5	99 ± 6	98 ± 1	87 ± 1	104 ± 5	97 ± 1
chlorpyrifos	75 ± 7	93 ± 3	90 ± 1	95 ± 5	98 ± 5	93 ± 1	76 ± 6	99 ± 4	92 ± 1
chlorpyrifos oxon	nd	69 ± 3	87 ± 3	97 ± 4	91 ± 3	94 ± 1	93 ± 9	95 ± 2	94 ± 2
chlorpyrifos-methyl	80 ± 2	97 ± 4	96 ± 1	92 ± 1	98 ± 6	94 ± 1	81 ± 2	101 ± 6	92 ± 1
chlorthiophos	65 ± 37	79 ± 3	88 ± 3	79 ± 2	89 ± 1	88 ± 1	90 ± 8	92 ± 2	85 ± 1
coumaphos	49 ± 5	84 ± 4	84 ± 1	68 ± 1	76 ± 1	80 ± 1	88 ± 2	82 ± 5	79 ± 2
coumaphos oxon	79 ± 3	91 ± 7	91 ± 3	80 ± 7	91 ± 1	89 ± 1	108 ± 5	91 ± 4	94 ± 2
crotoxyphos	80 ± 2	97 ± 5	100 ± 3	105 ± 4	97 ± 4	98 ± 2	na	na	na
cyanofos	93 ± 6	90 ± 6	100 ± 6	81 ± 2	94 ± 1	93 ± 1	nd	98 ± 3	104 ± 2
DEF (tribufos)	81 ± 6	95 ± 3	93 ± 1	91 ± 2	97 ± 3	92 ± 1	nd	99 ± 8	92 ± 6
demeton-O	91 ± 3	77 ± 4	85 ± 10	87 ± 5	78 ± 3	91 ± 8	nd	71 ± 3	94 ± 10
demeton-S	101 ± 3	87 ± 17	91 ± 1	89 ± 5	97 ± 6	91 ± 1	nd	98 ± 6	91 ± 1
demeton-S-methyl	197 ± 4	84 ± 10	76 ± 5	95 ± 1	89 ± 8	78 ± 9	nd	86 ± 3	95 ± 4
demeton-S-sulfone	148 ± 1	110 ± 7	103 ± 4	94 ± 3	94 ± 1	98 ± 1	na	na	na
dialifor	90 ± 8	96 ± 3	91 ± 5	50 ± 4	69 ± 10	99 ± 1	79 ± 3	91 ± 1	102 ± 5
diazinon	103 ± 1	97 ± 4	94 ± 4	96 ± 2	97 ± 3	98 ± 3	94 ± 2	91 ± 1	99 ± 2
diazinon-OH	80 ± 3	96 ± 4	98 ± 2	103 ± 2	98 ± 2	97 ± 1	na	na	na
diazinon oxon	83 ± 11	96 ± 3	96 ± 2	96 ± 1	102 ± 2	94 ± 1	nd	nd	nd
dicapthon	na	79 ± 2	96 ± 3	101 ± 3	110 ± 3	117 ± 3	104 ± 4	98 ± 2	93 ± 2
dichlorfenthon	71 ± 2	91 ± 5	95 ± 2	99 ± 1	94 ± 4	93 ± 1	na	na	na
dichlorvos	67 ± 2	84 ± 2	88 ± 3	99 ± 4	84 ± 2	89 ± 1	108 ± 2	76 ± 6	96 ± 3
dicrotophos	312 ± 3	127 ± 1	104 ± 3	101 ± 2	95 ± 1	93 ± 1	nd	92 ± 7	88 ± 3
dioxabenzofos	82 ± 3	94 ± 3	94 ± 1	100 ± 1	98 ± 2	92 ± 1	na	na	na
dioxathion	63 ± 10	80 ± 3	97 ± 1	89 ± 3	90 ± 5	94 ± 1	nd	96 ± 3	95 ± 1
disulfoton	71 ± 1	85 ± 1	91 ± 2	92 ± 3	90 ± 1	90 ± 1	nd	92 ± 1	92 ± 1
ditalimfos	35 ± 8	43 ± 4	54 ± 6	78 ± 10	54 ± 1	52 ± 5	67 ± 4	49 ± 1	58 ± 4
edifenphos	68 ± 10	97 ± 3	99 ± 4	104 ± 2	100 ± 3	96 ± 2	na	na	na
EPN	48 ± 2	87 ± 2	101 ± 8	74 ± 1	94 ± 1	97 ± 2	106 ± 6	98 ± 6	103 ± 4
ethion	87 ± 1	95 ± 5	96 ± 5	93 ± 2	90 ± 2	99 ± 3	88 ± 9	90 ± 1	100 ± 4
ethion dioxon	101 ± 1	90 ± 1	94 ± 3	100 ± 1	96 ± 3	96 ± 1	nd	67 ± 24	92 ± 3
ethion monoxon	97 ± 1	98 ± 4	99 ± 6	93 ± 2	92 ± 2	99 ± 3	nd	100 ± 6	101 ± 3
ethoprop	93 ± 2	99 ± 4	98 ± 1	96 ± 1	107 ± 3	86 ± 1	nd	nd	nd
famphur	120 ± 6	116 ± 2	115 ± 4	87 ± 1	97 ± 2	97 ± 1	76 ± 1	95 ± 3	95 ± 1
fenamiphos	100 ± 4	94 ± 2	94 ± 4	22 ± 8	96 ± 2	96 ± 4	81 ± 3	86 ± 1	97 ± 5
fenamiphos deisopropyl	80 ± 3	105 ± 4	92 ± 4	80 ± 3	97 ± 3	90 ± 1	92 ± 16	102 ± 3	94 ± 2
fenamiphos sulfone	na	na	na	na	na	na	92 ± 6	96 ± 2	99 ± 4
fenamiphos sulfoxide	435 ± 9	161 ± 3	125 ± 5	100 ± 5	96 ± 2	92 ± 2	na	na	na
fenchlorphos	72 ± 2	75 ± 5	89 ± 1	86 ± 2	99 ± 5	92 ± 1	74 ± 3	98 ± 6	91 ± 1
fenitrothion	78 ± 2	96 ± 4	99 ± 3	105 ± 3	97 ± 2	96 ± 2	nd	90 ± 3	106 ± 8
fensulfothion	58 ± 7	98 ± 5	102 ± 4	98 ± 4	96 ± 4	101 ± 1	98 ± 2	97 ± 7	105 ± 3
fenthion	73 ± 4	88 ± 3	95 ± 4	93 ± 3	94 ± 1	93 ± 2	95 ± 5	92 ± 3	102 ± 3
fenthion oxon	62 ± 2	97 ± 2	94 ± 3	80 ± 3	93 ± 1	96 ± 2	95 ± 1	95 ± 2	94 ± 2
fenthion sulfone	116 ± 2	108 ± 4	104 ± 2	118 ± 5	97 ± 3	98 ± 2	na	na	na
fenthion sulfoxide	109 ± 1	106 ± 3	104 ± 4	86 ± 2	92 ± 3	94 ± 1	na	na	na
fonophos	98 ± 2	97 ± 3	96 ± 6	95 ± 4	99 ± 3	98 ± 4	97 ± 2	93 ± 2	98 ± 2
fosthiazate	346 ± 7	156 ± 10	105 ± 3	111 ± 3	94 ± 4	93 ± 1	na	na	na
heptenophos	nd	97 ± 4	95 ± 3	56 ± 7	91 ± 6	94 ± 2	nd	80 ± 15	93 ± 4
iodofenphos	82 ± 9	96 ± 3	92 ± 1	95 ± 3	95 ± 2	89 ± 1	74 ± 1	96 ± 7	89 ± 2
iprofenfos	111 ± 4	105 ± 5	105 ± 6	93 ± 2	97 ± 1	98 ± 3	89 ± 8	95 ± 5	101 ± 3
isazophos	85 ± 4	96 ± 4	96 ± 1	92 ± 2	99 ± 6	98 ± 1	66 ± 7	99 ± 3	96 ± 1
isofenfos	81 ± 2	98 ± 6	98 ± 5	96 ± 9	94 ± 2	100 ± 4	93 ± 5	85 ± 6	99 ± 4
leptophos	43 ± 2	71 ± 1	79 ± 2	50 ± 3	78 ± 5	79 ± 1	69 ± 2	75 ± 1	76 ± 2
leptophos oxon	46 ± 5	84 ± 2	87 ± 2	85 ± 1	82 ± 1	81 ± 1	82 ± 5	84 ± 6	81 ± 2
malaoxon	96 ± 7	102 ± 4	102 ± 4	87 ± 7	93 ± 2	97 ± 2	82 ± 13	91 ± 3	96 ± 1
malathion	97 ± 3	100 ± 4	101 ± 1	87 ± 6	101 ± 6	99 ± 1	nd	98 ± 3	97 ± 3
methamidophos	257 ± 2	115 ± 3	72 ± 4	130 ± 4	72 ± 3	66 ± 3	nd	76 ± 2	60 ± 8
methidathion	96 ± 2	103 ± 4	101 ± 1	99 ± 6	104 ± 5	98 ± 1	nd	104 ± 5	97 ± 2
mevinphos	100 ± 6	94 ± 5	94 ± 2	117 ± 3	98 ± 4	92 ± 1	nd	90 ± 1	103 ± 3
monocrotophos	278 ± 4	144 ± 5	100 ± 3	108 ± 5	102 ± 5	92 ± 3	nd	nd	91 ± 7
naled (dibrom)	nd	nd	32 ± 5	nd	12 ± 7	37 ± 5	na	na	na
omethoate	95 ± 4	89 ± 4	87 ± 4	119 ± 4	92 ± 5	86 ± 2	nd	88 ± 3	86 ± 13

Table 3. (Continued)

pesticide	GC-FPD (toluene, external calibration)			GC-FPD (matrix, external calibration)			GC-MS/SIM (matrix, external calibration)		
	0.025 μg/g	0.10 μg/g	1.0 μg/g	0.025 μg/g	0.10 μg/g	1.0 μg/g	0.025 μg/g	0.10 μg/g	1.0 μg/g
paraoxon	130 ± 1	115 ± 1	104 ± 7	95 ± 8	91 ± 4	97 ± 2	nd	101 ± 4	98 ± 3
parathion	58 ± 2	84 ± 6	92 ± 5	94 ± 1	98 ± 2	99 ± 3	111 ± 1	100 ± 2	98 ± 4
parathion-methyl oxon	88 ± 2	95 ± 3	99 ± 3	105 ± 1	102 ± 1	97 ± 2	na	na	na
parathion-methyl	na	na	na	na	na	na	116 ± 1	103 ± 6	99 ± 3
phorate	95 ± 3	77 ± 2	96 ± 2	86 ± 3	93 ± 1	95 ± 1	84 ± 8	97 ± 2	92 ± 2
phorate oxon	104 ± 1	96 ± 2	98 ± 3	96 ± 2	94 ± 1	96 ± 1	na	na	na
phorate sulfone	90 ± 2	98 ± 4	103 ± 6	112 ± 22	97 ± 2	100 ± 4	na	na	na
phorate sulfoxide	108 ± 6	100 ± 3	102 ± 5	101 ± 3	90 ± 4	99 ± 3	nd	nd	nd
phosalone	88 ± 1	100 ± 4	98 ± 5	69 ± 4	84 ± 3	95 ± 4	66 ± 3	89 ± 2	97 ± 4
phosmet	61 ± 6	91 ± 4	98 ± 5	102 ± 3	95 ± 2	95 ± 1	97 ± 5	99 ± 4	102 ± 2
pirimphos-methyl	77 ± 3	100 ± 4	98 ± 1	89 ± 3	99 ± 5	96 ± 1	78 ± 4	103 ± 5	94 ± 1
profenofos	89 ± 2	96 ± 6	95 ± 4	88 ± 4	96 ± 1	95 ± 2	88 ± 3	97 ± 3	102 ± 2
propetamphos	78 ± 2	97 ± 1	101 ± 3	90 ± 3	95 ± 1	98 ± 1	82 ± 4	92 ± 2	96 ± 2
prothiophos	74 ± 5	83 ± 2	90 ± 2	85 ± 2	91 ± 1	90 ± 1	68 ± 8	88 ± 1	90 ± 3
pyraclofos	75 ± 2	90 ± 1	96 ± 1	65 ± 1	91 ± 2	90 ± 1	77 ± 3	91 ± 1	91 ± 3
pyrazophos	41 ± 7	80 ± 3	83 ± 1	73 ± 3	79 ± 2	81 ± 2	80 ± 6	80 ± 4	81 ± 2
pyridaphenthion	79 ± 2	78 ± 1	83 ± 3	93 ± 4	97 ± 2	97 ± 1	93 ± 2	96 ± 1	97 ± 3
quinalphos	51 ± 1	85 ± 1	95 ± 3	94 ± 4	92 ± 1	94 ± 1	95 ± 3	96 ± 2	93 ± 2
sulfotep	106 ± 2	101 ± 3	97 ± 4	91 ± 7	98 ± 3	98 ± 4	94 ± 4	95 ± 1	100 ± 4
sulprofos	85 ± 3	87 ± 4	94 ± 4	98 ± 4	92 ± 2	92 ± 3	89 ± 2	89 ± 3	100 ± 2
tebupirimphos	83 ± 6	96 ± 1	96 ± 3	87 ± 2	94 ± 3	96 ± 1	95 ± 3	93 ± 3	97 ± 2
temephos	na	na	na	101 ± 6	79 ± 1	100 ± 5	nd	103 ± 11	97 ± 5
terbufos	94 ± 4	98 ± 3	93 ± 1	91 ± 1	101 ± 6	95 ± 1	nd	103 ± 3	93 ± 2
terbufos oxon	158 ± 6	123 ± 4	114 ± 4	88 ± 8	95 ± 4	99 ± 2	na	na	na
terbufos sulfone	65 ± 5	95 ± 1	103 ± 3	98 ± 4	96 ± 2	99 ± 1	na	na	na
tetrachlorvinphos	93 ± 6	97 ± 6	99 ± 6	95 ± 7	100 ± 4	97 ± 1	92 ± 3	95 ± 1	99 ± 3
thiometon	89 ± 5	83 ± 17	91 ± 2	87 ± 5	95 ± 6	89 ± 3	nd	95 ± 4	90 ± 2
tolclofos-methyl	85 ± 5	92 ± 4	95 ± 3	106 ± 2	94 ± 1	93 ± 2	96 ± 2	95 ± 4	102 ± 1
triazophos	75 ± 6	96 ± 3	92 ± 3	97 ± 3	99 ± 5	93 ± 1	73 ± 4	105 ± 6	99 ± 2
trichlorfon	280 ± 4	123 ± 4	94 ± 5	69 ± 5	65 ± 3	89 ± 4	nd	236 ± 13	137 ± 20
vamidothion	454 ± 47	158 ± 7	118 ± 4	99 ± 1	95 ± 4	92 ± 2	na	na	na
zinophos	95 ± 1	97 ± 5	97 ± 1	92 ± 2	98 ± 5	97 ± 1	103 ± 16	104 ± 9	96 ± 4

[a] Recoveries were determined by external calibration using matrix (ginseng)-matched standards for GC-FPD and GC-MS/SIM by the amount of pesticide determined from the fortification divided by the calculated amount of pesticide multiplied by 100%. Comparison between recoveries determined by external calibration using ginseng-matched and solvent (toluene)-only standards was determined by GC-FPD only. na, not analyzed; nd, not detected.

analyte-dependent. Early eluting and polar compounds such as acephate, demeton-S-methyl, dicrotophos, fosthiazate, methamidophos, monocrotophos, and vamidothion and OP metabolities such as oxons, sulfones, and sulfoxides of azinphos-methyl, fenamiphos, and the late-eluting OP, temephos, had recoveries of >120% at the 0.025 μg/g level. The results presented in this study are consistent with studies by Maštovská et al. (*22*), Erney et al. (*23*), and Schenck and Lehotay (*24*), who attributed matrix-induced enhancement to components in the matrix blocking active sites in the injection liner that protect the analyte from thermal degradation. The OPs showing matrix enhancement tend to be polar or thermally labile, and these compounds prepared in toluene solvent are more susceptible to thermal degradation than the standards prepared in the ginseng matrix. At higher pesticide concentrations, enhancement is minimized due to the presence of a larger number of analytes adsorbing onto the active sites to compensate for any initial losses due to thermal degradation (*25*). The OP recoveries which showed agreement between the recoveries using solvent-only and matrix-matched standards in a megabore column (30 m × 0.53 mm i.d.) are also the result of a faster flow rate (10 mL/min) used than typical for capillary columns, which reduces the residence times these pesticides spend in the injection liner, minimizing enhancement effects. The results in **Table 3** allow us to apply external calibration using standards prepared in solvent and to avoid the use of standard addition for a majority of the nonpolar OPs. Eventually, the continual use of a mature column (from repeated and numerous injections of the sample extracts into the column) will cause the chromatographic peaks of standards prepared in the toluene solvent to tail and broaden, an indication that column maintenance or replacement is required.

Analysis of Incurred Diazinon in Dried Ground Ginseng Root. The procedure was applied to dried, ground American and Asian ginseng root samples, and the application of the procedure and analysis by GC-FPD and GC-MS/SIM are revealed in **Figures 4** and **5**, respectively. The ginseng root extract was prepared according to the procedures outlined in **Figure 1**. GC-FPD analysis of one of the samples, an American ginseng root extract, reveals suspected peaks shown in **Figure 4A**. Originally, triphenylphosphate was attempted to be used a surrogate, but the peak at 36.17 min, retention time matching by GC-FPD and GC-MS/SIM, and confirmation by GC-MS/SIM indicate its presence and so it was no longer considered. Retention time matching of the peak at 23.75 min suggests the presence of the OP insecticide diazinon. The suspected diazinon peak was quantitatively measured by external calibration using solvent-only and matrix-matched standards and standard addition. Standard addition was used for quantitation as shown in **Figure 4B**, and increasing the amount of diazinon (50, 100, and 250 ng/mL) in the ginseng root sample resulted in extrapolating the diazinon (as shown in the inset of **Figure 4B**) to determine the final concentration at 24.8 ± 2.9 μg/kg (n = 5, **Table 4**). This is in statistical agreement with 25.5 ± 1.8 μg/kg (n = 5) determined by external standard calibration using matrix-matched standards. GC-MS/SIM confirmed the presence of diazinon and was also used to evaluate the ginseng root sample using m/z 304 as the target and quantitation ion and m/z 227, 248, and 276 as the qualifier ions. The GC-MS/SIM

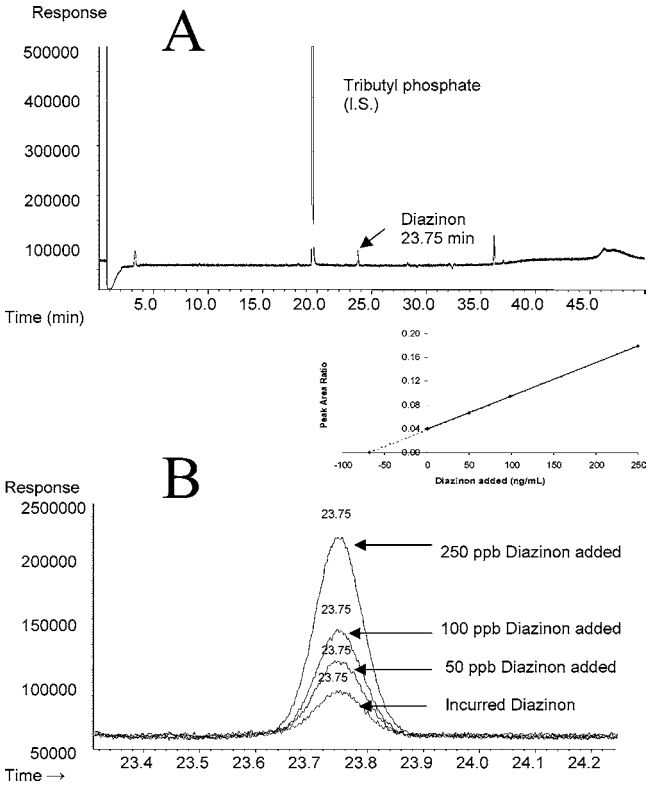

Figure 4. Presence of incurred diazinon in a ginseng sample determined by GC-FPD (phosphorus mode). (**A**) GC-FPD indicates the presence of diazinon due to the presence of a peak eluting at 23.75 min. The presence of other peaks (other than the I.S.) could not be identified. (**B**) Method of standard addition used to quantitate the amount of diazinon presence by adding 50, 100, and 250 ng/mL of calibration standard. (Inset) Standard addition for the determination of diazinon, $r^2 = 0.99994$.

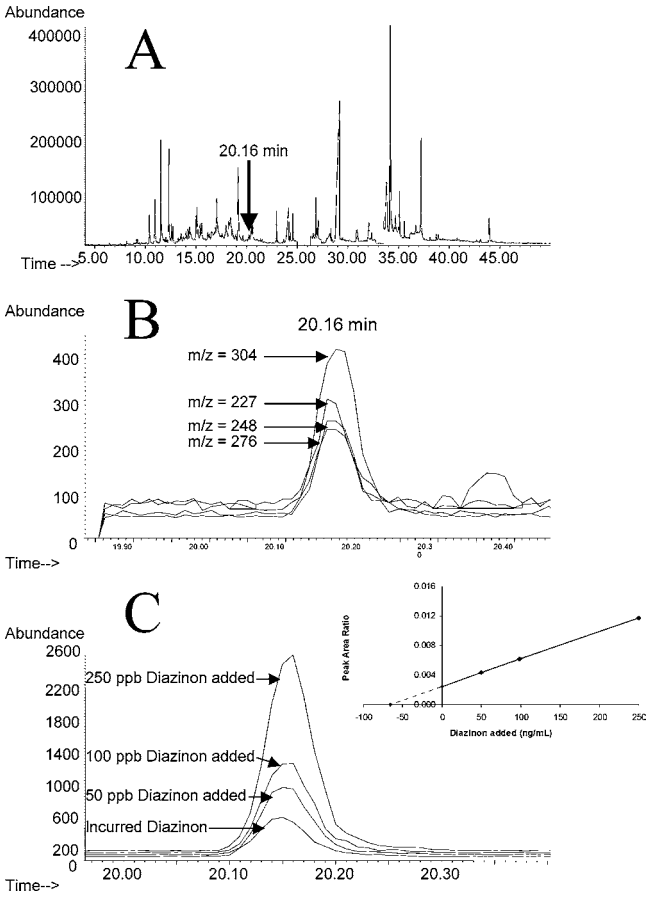

Figure 5. Presence of incurred diazinon from the same ginseng sample in **Figure 4** determined by GC-MS/SIM. (**A**) reconstructed GC-MS/SIM chromatogram of the ginseng extract; (**B**) identification of diazinon determined by target and qualifying ions (*m*/*z* 304, 227, 248, and 276), qualifier-to-target ratios, and retention times; (**C**) method of standard addition used to quantitate the amount of diazinon presence by adding 50, 100, and 250 ng/mL of calibration standard and using *m*/*z* 304 as the quantitation ion. (Inset) Standard addition for the determination of diazinon, $r^2 = 0.99991$.

chromatogram in **Figure 5A** of the cumulative ions listed in **Table 2** reveals little information, but extracting the ions as shown in **Figure 5B** and comparing the target-to-qualifier ratios provide unequivocal confirmation on the identity of diazinon present in the ginseng root sample. GC-MS/SIM was also used to quantitate diazinon, using similar procedures of external calibration and standard addition for the GC-FPD. Using *m*/*z* 304 as the quantitation ion, standard addition (**Figure 5C**) was successfully used to determine the concentration of diazinon at 24.7 ± 1.7 μg/kg ($n = 5$), which is in statistical agreement with 25.6 ± 1.9 μg/kg, obtained by external calibration using matrix-matched standards (**Table 4**).

Agreement between both detection methods in quantitation of incurred diazinon in the dried, ground American ginseng root is summarized in **Table 4**. Standard addition was shown to be very effective as both plots (insets in **Figures 4B** and **5C**) showed excellent linearities ($r^2 > 0.9999$) for FPD and MSD. However, the disadvantage of standard addition is that it requires prior knowledge and estimation of the incurred residue and requires additional labor and time to prepare samples with the standard additions. Although external calibration with matrix-matched standards shows agreement with both detectors and as well as with results determined by standard addition and is used for residue monitoring by the European Union (*22*), it is not an acceptable procedure in the United States because the matrix of the incurred sample may not necessarily be the same as the matrix the standards are prepared in. However, analysis by GC-FPD using standards prepared in solvent (toluene) and external calibration reveals a concentration of 25.6 ± 1.5 μg/kg (**Table 4**), which is in statistical agreement with the results obtained from GC-FPD and GC-MS/SIM analysis using external calibration using ginseng root-matched standards and standard addition.

Conclusion. With the development of this method, 108 OPs were analyzed in dried ground ginseng root. The sample preparation procedure is straightforward, relatively inexpensive,

Table 4. Comparison of Results Calculated by External Calibration Using Standards Prepared in Solvent (Toluene) and Matrix (Ginseng) and by Standard Addition of the Incurred Diazinon from a Ginseng Sample Using GC-FPD and GC-MS/SIM (*m*/*z* 304 as the Quantitative Ion)

	GC-FPD, 30 m × 0.53 mm i.d. × 1.5 μm HP-5 column			GC-MSD, 30 m × 0.25 mm i.d. × 0.25 μm HP-5MS		
	external calibration			external calibration		
	solvent (toluene)	matrix (ginseng)	standard addition	solvent (toluene)	matrix (ginseng)	standard addition
diazinon (μg/kg)	25.6 ± 1.5	25.5 ± 1.8	24.8 ± 2.9	40.7 ± 1.7	25.6 ± 1.9	24.7 ± 1.7

and fast. The combination of GC-FPD and GC-MS/SIM provides selectivity, confirmation, and quantitation. We were able to provide procedures to quantitate the OPs using external calibration using solvent-only standards and standard addition. Additional work to improve cleanup in dried plant products will be further investigated to improve on detection levels. This method is being applied to other botanical dietary supplements and modifications of the method, and the use of gas chromatography coupled with element-selective detectors such as the electrolytic conductivity (GC-ELCD) and halogen-specific (GC-XSD) will also be used to screen organohalogen pesticides.

ACKNOWLEDGMENT

We thank the U.S. EPA Pesticide Repository, Fort Meade, MD, and, in particular, Terry Cole for providing the majority of the OP standards used in this study, and the FDA PRL-SW Laboratory for providing the incurred, dried ground ginseng root sample.

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Received for review September 27, 2006. Revised manuscript received December 4, 2006. Accepted December 5, 2006. We appreciate the financial support of an interagency agreement with the National Institutes of Health, Y1-OD-6412-01.

JF062774Q