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Simultaneous Determination of 147 Pesticide Residues in Traditional Chinese Medicines by GC−MS/MS

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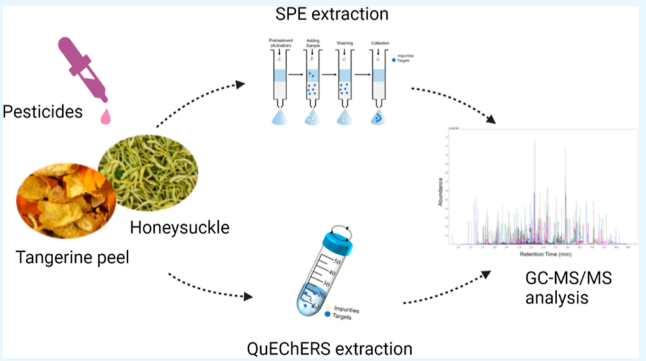
ABSTRACT: Determination of pesticide residues remains a challenge in traditional Chinese medicines in which complex compounds may interfere with analysis signals. This study reports the development of a simple, effective, and high-throughput method combining gas chromatography−tandem mass spectrometry (GC−MS/MS) with either QuEChERS or solid phase extraction (SPE) to determine 147 pesticide residues in traditional Chinese medicines simultaneously. In SPE, the mixture of *n*-hexane and ethyl acetate (1:1, v/v) was selected to extract 147 pesticides in honeysuckle, and the extracted pesticides were determined by GC−MS/MS. The limits of detection for all pesticides were within 0.01−0.05 mg/kg. The recoveries were within 70−120% and the relative standard deviations were below 20% for over 90% pesticides. The coefficients of determination were up to 0.999 for the linearity between MS signals and different concentrations of pesticides (20−200 ng/mL). The analytical performance was confirmed in determining pesticide residues in dried tangerine peel. SPE achieved comparable recoveries for all pesticides compared to the QuEChERS method.



1. INTRODUCTION

Detection of pesticide residues in traditional herbal medicines is a major concern because of the adverse effects of these chemical hazards on human health. Traditional medicines play an important role in preventing and treating diverse diseases. According to the report by World Health Organization, 80% population worldwide use traditional medicines, especially herbal medicines.[1] Traditional Chinese medicines such as honeysuckle flowers have been applied to treat exopathogenic wind-heat, carbuncles, sores, furuncles, epidemic febrile diseases, and some infection diseases in China for over 1500 years.[2] In addition, traditional Chinese medicines have been widely used to produce functional foods and various food ingredients.[2−4] Therefore, there is a high demand in traditional herbal medicines. To meet the public demand for traditional herbs, hundreds of pesticides have been applied to herbal plants during production to prevent infections and diseases caused by the insects. However, pesticide residues left in traditional herbal medicines may cause adverse effects on humans including cancer, neurotoxicity, respiratory morbidity, dermatitis, and reproductive abnormalities.[5] Development of effective methods to determine pesticide residues in traditional Chinese medicines is highly necessary.

Gas chromatography−tandem mass spectrometry (GC−MS/MS) is an analytical technique featuring high accuracy, precision, and sensitivity to determine multiple pesticides in the agri-food and pharmaceutical industries.[6−9] Gas chromatography has been used to separate pesticides that can be vaporized without decomposition. Mass spectroscopy is an analytical technique used to detect the mass-to-charge ratio of pesticide ions and provide "fingerprint" information of the target molecules. GC coupled with MS/MS is the recommended method for detecting pesticides in several countries due to its advantages of simultaneous detection of various analytes. Sample pretreatment is a critical step to determine pesticides in complex sample matrices before GC−MS/MS detection because pretreatment methods can remove the nontarget compounds that may affect the signals of the analytes. QuEChERS is a rapid, easy-to-use, cost-effective, robust, and safe sample pretreatment method for determining pesticides in foods and herbs. Acetonitrile was used as the solvent to extract pesticides from sample matrices by QuEChERS, and the extracts were purified by adsorbents (e.g., primary secondary amine, octadecyl-modified silica, and graphitized carbon black), followed by detection using GC−MS/MS. For

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example, 243 pesticide residues extracted from cardamom by modified QuEChERS were determined by GC−MS/MS. The recoveries for all pesticides were 70−120%, and relative standard deviations (RSDs) were <20%.[10] In another study, Zhang and co-authors evaluated the cleanup efficiency of QuEChERS for determining multiple pesticide residues in cinnamon bark, and 26% pesticides did not achieve high recoveries and low RSDs due to the complexity of herbal sample matrices.[11] Similar results were reported in another study where QuEChERS was used to extract pesticides from chamomile, thyme, and marjoram.[12] Traditional Chinese medicines have complicated components that can interfere with the extraction and detection of pesticides.[13] Thus, a modified QuEChERS or alternative sample pretreatment method(s) should be developed to integrate with GC−MS/MS to improve the analytical performance of determining multiple pesticide residues in traditional Chinese medicines.

Honeysuckle is a popular herbal plant for both medical and food uses. Detection of pesticide residues in honeysuckle by GC−MS/MS is still limited. A previous study only detected seven fungicides in honeysuckle using supercritical fluid extraction and GC-electron capture detection with extraction recoveries of 82.9−97.8% and detection limits of 0.05−20 μg/kg.[14] In practical applications, hundreds of pesticides might have been used in the production of herbs. Simultaneous detection of a large number of pesticides in honeysuckle is therefore highly needed. The objective of this study was to separately develop an optimized QuEChERS and a modified solid phase extraction (SPE) in combination with GC−MS/MS for simultaneous determination of 147 pesticide residues in traditional Chinese medicines. As an alternative to QuEChERS, SPE was applied for sample cleanup as a prerequisite for determining pesticides in traditional Chinese medicines. A total of 147 pesticides in honeysuckle treated by modified SPE were determined by GC−MS/MS with high sensitivity, accuracy, and precision. To further validate the detection efficiency of this assay, comparison of extraction efficiency of SPE and QuEChERS was investigated via extraction and determination of pesticide residues in honeysuckle and dried tangerine peel.

2. MATERIALS AND METHODS

2.1. Chemicals, Reagents, and Materials. Sodium chloride, anhydrous magnesium sulfate, and sodium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Acetonitrile, ethyl acetate, *n*-hexane, and methylbenzene were of HPLC grade and purchased from Sigma-Aldrich (St. Louis, USA). Primary and secondary amines, octadecyl-modified silica, and graphitized carbon black were purchased from DIKMA Technologies (Beijing, China). GCB/NH_2 column (0.25 g, 6 mL) was purchased from Shimadzu (Kyoto, Japan).

2.2. Standard Solutions. The stock solutions of pesticides were prepared at 1 mg/mL in ethyl acetate and stored in dark at −18 °C. The use of ethyl acetate is due to its low toxicity compared to that of acetone. The working solutions were prepared by mixing and diluting the pesticide stock solutions.

2.3. Sample Preparation. *2.3.1. Solid Phase Extraction.* A total of 2 g of dried honeysuckle or tangerine peel were weighed into a centrifuge tube. The sample was spiked with standard mixture of pesticides to achieve concentrations of 0.1, 0.2, and 1 mg/kg. An appropriate volume of water was then added to completely rehydrate the sample by vortexing. Then, 15 mL of ethyl acetate/*n*-hexane (1:1, v/v) and 5 g of sodium chloride were added for pesticide extraction, followed by vortexing and sonication for 30 min and centrifugation at 4200 rpm for 5 min (SIGMA3-18KS, Sigma-Aldrich, Germany). The supernatant was transferred into another tube and 15 mL of ethyl acetate/*n*-hexane (1:1, v/v) was added to the residue. The sample was re-extracted following the same procedure without adding sodium chloride. The two portions of extract were combined, dried by nitrogen purging, and re-dissolved in 2 mL of acetonitrile/methylbenzene (3:1, v/v). The solution was loaded into GCB/NH_2 column for purification. Another 12 mL of the same solvent was used to rinse the column. The two eluates were combined, dried by nitrogen purging, and re-dissolved in 1 mL of *n*-hexane solution for further analysis.

2.3.2. QuECheRS Procedure. Dried honeysuckle or tangerine peel were weighed at 2 g each in a 50 mL centrifuge tube. Then, 10 mL of deionized water was added and shaken by vortex. The sample was allowed to stand for 30 min. Afterward, 15 mL of acetonitrile/acetic acid (99:1, v/v), 6 g of anhydrous magnesium sulfate, 1.5 g of sodium acetate, and two ceramic homogenizers were added, followed by shaking for 1 min and centrifugation at 4200 rpm for 5 min. The extract was then transferred to a 50 mL centrifuge tube containing 1200 mg of magnesium sulfate, 400 mg PSA, 400 mg C_{18}, and 200 mg GCB. The mixture was vortexed for 1 min and centrifuged at 4200 rpm for 5 min. Then, the supernatant was transferred to a new tube and dried by blowing nitrogen. The dried residue was dissolved in 1 mL of ethyl acetate for GC−MS/MS analysis.

2.4. GC−MS/MS Analysis. GC−MS/MS analysis was performed by using a Shimadzu GCMS-TQ8040 triple-quadrupole mass spectrometer equipped with an electron ionization interface (Kyoto, Japan). Analytes were separated using a capillary column Restek Rxi-5sil-MS column (30 m × 0.25 mm × 0.25 μm) from Shimadzu. Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. Column temperature was programed as follows: the initial temperature was 60 °C (hold for 1 min), ramped to 180 °C at a rate of 25 °C/min, increased to 310 °C at a rate of 10 °C/min and then maintained for 10 min. The injector temperature was set at 250 °C in the splitless mode. The mass spectrometer was operated in the multiple reaction monitoring (MRM) mode. The ion source and transfer line temperatures were 230 and 300 °C, respectively. The basic information of pesticides and the parameters of MS are summarized in Table S1.

3. RESULTS AND DISCUSSION

3.1. Solvent Selection for SPE. Acetonitrile, *n*-hexane, acetone, and ethyl acetate are common extracting solvents for the treatment of multiclass pesticides. The extraction efficiency of acetonitrile, 1% (v/v) acetic acid in acetonitrile, ethyl acetate, ethyl acetate/*n*-hexane (1:1, v/v), *n*-hexane, and acetone/*n*-hexane (1:5, v/v) were evaluated by extracting six pesticides in honeysuckle (Figure 1). Ethyl acetate and *n*-hexane resulted in the lowest recoveries for etrimfos (<60%). The highest recoveries for etrimfos, δ-HCH, dithiopyr, chlorpyrifos, and fluorine naphthalene were achieved using ethyl acetate/*n*-hexane (1:1, v/v). For extracting EPN, ethyl acetate/*n*-hexane (1:1, v/v) and acetonitrile resulted in comparable recoveries. Previous studies reported that acetonitrile could damage GC column due to its high polarity and large solvent expansion volume. Thus, the extracted samples need to be dried for acetonitrile removal before GC−MS

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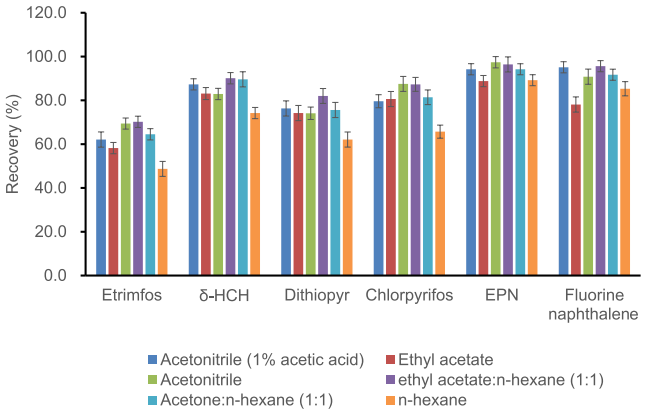

Figure 1. Recoveries of six pesticides from honeysuckle using various extracting solvents by SPE.

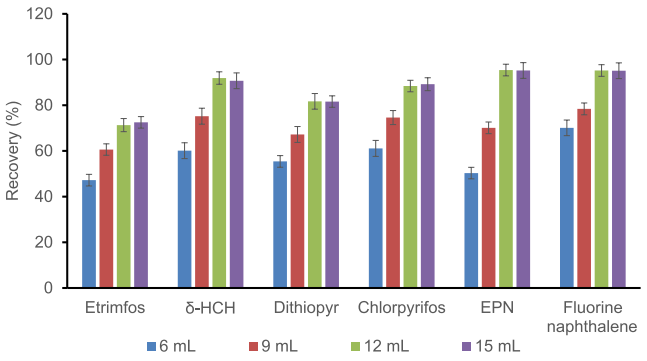

Figure 2. Extraction efficiency of six pesticides from honeysuckle using different amounts of acetonitrile/methylbenzene (3:1, v/v) by SPE.

analysis.[15,16] Considering the time-consuming drying procedure, ethyl acetate/*n*-hexane (1:1, v/v) was selected in the current study as the extracting solvent for SPE.

3.2. Optimization of Sample Cleanup by SPE Column.

GCB/NH_2 column was used for SPE and the optimum volume of eluent was investigated. GCB/NH_2 column is a mixed-mode purification column retaining various impurities (e.g., pigments and alkaloids). This column is suitable for the cleanup of traditional Chinese herbal medicines with complex matrices. The recoveries of extracting six pesticides from honeysuckle by different amounts of acetonitrile/methylbenzene (3:1, v/v) were evaluated (Figure 2). The recoveries increased with the volume from 6 to 12 mL with no further improvement at 15 mL. Thus, 12 mL of acetonitrile/methylbenzene (3:1, v/v) was selected.

3.3. Optimization of Sample Cleanup by QuEChERS.

In the QuEChERS method, PSA (for fatty acids and polar pigments), C_{18} (for lipids and non-polar impurities), and GCB (for pigments) were used to purify extracts from honeysuckle. The recoveries of the cleaned extracts of six pesticides (0.1 mg/kg) in honeysuckle were determined separately with each sorbent (200, 400, or 600 mg) and the results are shown in Table S2. Individual tests indicated that 400 mg of PSA, 400 mg of C_{18}, and 200 mg of GCB resulted in the highest recoveries at 85.1−93.2, 82.6−91.9, and 84.6−90.2%, respectively. Therefore, the combination of PSA (400 mg), C_{18} (400 mg), and GCB (200 mg) was selected as the QuEChERs sorbent for sample cleanup.

3.4. Optimization of GC−MS/MS.

GC−MS/MS is capable of simultaneously analyzing multiple pesticides on a MRM mode. For each pesticide, GC was applied to separate targeted pesticide from others and MS ionized the pesticide into fragment ions. After primary ionization, one molecular ion was selected as the parent ion. Then, the selected parent ion was ionized at the corresponding optimum collision energy in the electron bombardment scanning mode. After secondary ionization, one fragment ion was selected as the product ion. Total ion chromatograms of 147 pesticide standard mixtures are shown in Figure 3. The optimum conditions of MS/MS

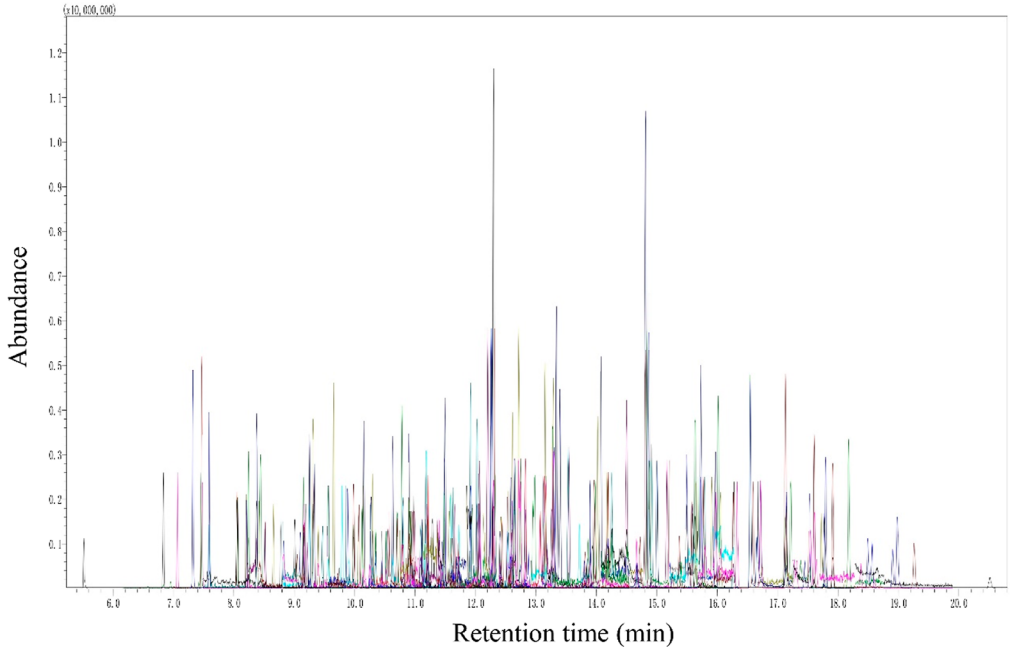

Figure 3. Total ion chromatograms of 147 pesticide standard mixture.

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Table 1. Basic Validation Data for 147 Pesticides Extracted by SPE Coupled with GC−MS/MS

pesticides	equation	r^2	LOD (mg/kg)	LOQ (mg/kg)
chlorpropham	$f(x) = 6007.481144x - 22634.439024$	0.9999	0.01	0.033
cadusafos	$f(x) = 18189.152064x - 71957.414634$	0.9998	0.01	0.033
α-HCH	$f(x) = 7951.932653x - 32868.862245$	0.9993	0.01	0.033
thiometon	$f(x) = 4223.248980x - 21777.668367$	0.9995	0.03	0.100
β-BHC	$f(x) = 6475.019887x - 32409.268293$	0.9997	0.02	0.067
γ-BHC	$f(x) = 6460.195779x - 30082.560976$	0.9996	0.01	0.033
cyanophos	$f(x) = 17258.839587x - 104614.31707$	0.9998	0.01	0.033
pyroquilon	$f(x) = 20204.736735x - 87256.688776$	0.9997	0.04	0.133
diazinon	$f(x) = 4807.094184x - 24806.195122$	0.9997	0.01	0.033
chlorothalonil	$f(x) = 2807.605102x - 31200.408163$	0.9980	0.01	0.033
etrimfos	$f(x) = 1404.421013x - 7149.585366$	0.9991	0.04	0.133
δ-HCH	$f(x) = 5263.483959x - 35708.731707$	0.9996	0.02	0.067
MCPA-thioethyl	$f(x) = 4467.959287x - 22751.365854$	0.9994	0.03	0.100
iprobenfos	$f(x) = 22864.116135x - 97209.878049$	0.9999	0.02	0.067
fipronil-desulfinyl	$f(x) = 8689.682653x - 34310.362245$	0.9992	0.04	0.133
acetochlor	$f(x) = 6973.159662x - 34016.804878$	0.9997	0.03	0.100
vinclozolin	$f(x) = 3823.787617x - 15591.512195$	0.9997	0.03	0.100
parathion-methyl	$f(x) = 5286.831895x - 39216.317073$	0.9993	0.01	0.033
tolclofos-methyl	$f(x) = 18789.444747x - 108059.85366$	0.9994	0.01	0.033
alachlor	$f(x) = 12506.550281x - 56790.829268$	0.9997	0.01	0.033
heptachlor	$f(x) = 11629.075510x - 65014.040816$	0.9993	0.03	0.100
prometryn	$f(x) = 5634.151970x - 19753.804878$	0.9997	0.02	0.067
dithiopyr	$f(x) = 11341.012570x - 40316.707317$	1.0000	0.01	0.033
pirimiphos-methyl	$f(x) = 3014.631238x - 16785.048780$	0.9995	0.01	0.033
fenitrothion	$f(x) = 7084.409662x - 63847.804878$	0.9990	0.04	0.133
bromacil	$f(x) = 5617.407129x - 8907.341463$	0.9999	0.01	0.033
pentachlorothioanisole	$f(x) = 6129.445918x - 22246.923469$	0.9994	0.01	0.033
malathion	$f(x) = 14112.622514x - 89237.341463$	0.9998	0.04	0.133
metolachlor	$f(x) = 30465.065009x - 144524.56098$	0.9999	0.02	0.067
chlorpyrifos	$f(x) = 7584.554128x - 39080.829268$	0.9994	0.03	0.100
aldrin	$f(x) = 3164.933114x - 11922.243902$	0.9998	0.02	0.067
chlorthal-dimethyl	$f(x) = 9889.813884x - 34278.243902$	0.9998	0.02	0.067
fenpropimorph	$f(x) = 7955.360319x + 12080.926829$	0.9998	0.01	0.033
parathion	$f(x) = 4135.782552x - 28893.585366$	0.9993	0.02	0.067
triadimefon	$f(x) = 8855.840713x - 45940.634146$	0.9994	0.03	0.100
tetraconazole	$f(x) = 2822.516417x - 12599.707317$	0.9996	0.02	0.067
isocarbophos	$f(x) = 1395.683396x - 13053.073171$	0.9996	0.01	0.033
dicofol	$f(x) = 6546.147936x - 32451.585366$	0.9998	0.02	0.067
butralin	$f(x) = 1738.110788x - 10383.121951$	0.9999	0.04	0.133
fthalide phthalide	$f(x) = 16325.503061x - 39381.994898$	0.9998	0.03	0.100
pirimiphos-ethyl	$f(x) = 8193.874490x - 40950.709184$	0.9994	0.02	0.067
bromofos	$f(x) = 9330.083865x - 43761.121951$	0.9997	0.03	0.100
diphenamid	$f(x) = 25444.408255x - 123079.65854$	0.9996	0.01	0.033
fipronil-sulfide	$f(x) = 12768.249625x - 71438.560976$	0.9995	0.02	0.067
pendimethalin	$f(x) = 5044.551501x - 32758.756098$	0.9998	0.02	0.067
fipronil	$f(x) = 6111.756660x - 36304.292683$	0.9997	0.03	0.100
penconazole	$f(x) = 9463.720075x - 41430.487805$	0.9997	0.01	0.033
heptachlor-*exo*-epoxide	$f(x) = 2844.061726x - 13338.219512$	0.9996	0.02	0.067
chlozolinate	$f(x) = 2703.653940x - 3266.609756$	0.9999	0.01	0.033
isofenphos	$f(x) = 22291.733583x - 121871.29268$	0.9997	0.01	0.033
allethrin (1)	$f(x) = 3549.890713x + 6750.073171$	0.9998	0.05	0.167
heptachlor-*endo*-epoxide	$f(x) = 110.834522x - 703.390244$	0.9992	0.02	0.067
allethrin (2)	$f(x) = 3548.836538x - 7793.000000$	0.9997	0.05	0.167
phenthoate	$f(x) = 9191.324390x - 76101.536585$	0.9995	0.03	0.100
quinalphos	$f(x) = 10108.761257x - 58112.170732$	0.9993	0.02	0.067
mephosfolan	$f(x) = 14600.655441x - 90646.365854$	0.9996	0.01	0.033
procymidone	$f(x) = 7320.140619x - 22242.024390$	0.9999	0.03	0.100
triadimenol (1)	$f(x) = 42891.826923x - 42105.000000$	0.9999	0.01	0.033
triflumizole	$f(x) = 3437.885741x - 11276.317073$	0.9998	0.05	0.167
triadimenol (2)	$f(x) = 1966.470098x - 470.512195$	0.9999	0.02	0.067
bromophos-ethyl	$f(x) = 12296.809475x - 59546.585366$	0.9997	0.05	0.167

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Table 1. continued

pesticides	equation	r^2	LOD (mg/kg)	LOQ (mg/kg)
methidathion	$f(x) = 37742.469887x - 268946.26829$	0.9996	0.03	0.100
trans-chlordane	$f(x) = 1306.900281x - 5630.829268$	0.9999	0.02	0.067
propaphos	$f(x) = 3762.834522x + 10022.609756$	0.9997	0.01	0.033
chinomethionate	$f(x) = 18295.448124x - 101093.80488$	0.9996	0.03	0.100
o,p′-DDE	$f(x) = 33085.359006x - 136740.53659$	0.9997	0.01	0.033
paclobutrazol	$f(x) = 16435.941932x - 72886.560976$	0.9998	0.05	0.167
butachlor	$f(x) = 6326.143152x - 26192.487805$	0.9997	0.02	0.067
cis-chlordane	$f(x) = 1265.956848x - 4198.512195$	0.9995	0.05	0.167
alpha-endosulfan	$f(x) = 391.197092x - 3687.097561$	0.9999	0.03	0.100
ditalimfos	$f(x) = 4945.131989x - 28127.926829$	0.9996	0.02	0.067
fipronil-sulfone	$f(x) = 8174.382739x - 39347.804878$	0.9997	0.01	0.033
napropamide	$f(x) = 20176.841276x - 109203.29268$	0.9998	0.03	0.100
flutolanil	$f(x) = 82398.813483x - 165578.14832$	0.9998	0.03	0.100
prothiophos	$f(x) = 8200.450657x - 41859.268293$	0.9998	0.03	0.100
isoprothiolane	$f(x) = 3805.117167x - 17985.585366$	0.9997	0.01	0.033
p,p′-DDE	$f(x) = 22716.165197x - 97317.780488$	0.9998	0.01	0.033
oxadiazon	$f(x) = 12268.989212x - 60214.878049$	0.9998	0.01	0.033
thifluzamide	$f(x) = 9296.122514x - 35732.341463$	0.9999	0.03	0.100
dieldrin	$f(x) = 1409.910319x - 4209.073171$	0.9999	0.02	0.067
myclobutanil	$f(x) = 22728.070732x - 86021.756098$	1.0000	0.01	0.033
o,p′-DDD	$f(x) = 42643.848405x - 94318.634146$	0.9999	0.01	0.033
flusilazole	$f(x) = 6487.158818x - 23653.317073$	0.9999	0.04	0.133
oxyfluorfen	$f(x) = 1768.194184x - 12503.195122$	0.9995	0.01	0.033
bupirimate	$f(x) = 7330.573827x - 37093.878049$	0.9995	0.01	0.033
kresoxim-methyl	$f(x) = 6955.364916x - 33926.951220$	0.9998	0.04	0.133
chlorfenapyr	$f(x) = 1612.442402x - 1528.609756$	0.9996	0.03	0.100
cyproconazole (1)	$f(x) = 22559.043688x + 1523.609756$	0.9999	0.02	0.067
cyproconazole (2)	$f(x) = 16808.158320x - 75578.902439$	0.9992	0.01	0.033
endrin	$f(x) = 2391.139024x - 11288.658537$	0.9997	0.01	0.033
chloropropylate	$f(x) = 36437.956848x - 179949.51220$	0.9997	0.04	0.133
fensulfothion	$f(x) = 2853.925141x - 31041.414634$	0.9996	0.01	0.033
β-endosulfan	$f(x) = 412.277955x - 1046.707317$	0.9998	0.01	0.033
diniconazole	$f(x) = 12180.926173x - 37045.121951$	1.0000	0.04	0.133
oxadixyl	$f(x) = 24171.512101x - 106820.65854$	0.9997	0.03	0.100
p,p′-DDD	$f(x) = 49264.499812x - 119128.78049$	0.9999	0.02	0.067
ethion	$f(x) = 15628.770356x - 106312.31707$	0.9996	0.01	0.033
o,p′-DDT	$f(x) = 32526.227298x - 333620.43902$	0.9995	0.04	0.133
mepronil	$f(x) = 15513.827861x - 55731.097561$	0.9999	0.01	0.033
triazophos	$f(x) = 7599.079831x - 39463.902439$	0.9999	0.01	0.033
carbofenothion	$f(x) = 4133.168199x - 20397.292683$	0.9997	0.04	0.133
cyanofenphos	$f(x) = 4388.168293x - 16201.902439$	0.9999	0.01	0.033
edifenphos	$f(x) = 4504.077486x - 30412.658537$	0.9995	0.02	0.067
propiconazol (1)	$f(x) = 8950.783353x - 17900.167411$	0.9994	0.02	0.067
endosulfan sulfate	$f(x) = 530.017636x - 3484.634146$	0.9995	0.03	0.100
propiconazol (2)	$f(x) = 7042.373374x - 14266.842704$	0.9998	0.01	0.033
pyraflufen-ethyl	$f(x) = 5868.075797x - 22610.682927$	0.9999	0.02	0.067
p,p′-DDT	$f(x) = 34045.879644x - 467884.68293$	0.9982	0.01	0.033
hexazinone	$f(x) = 39289.713884x - 216906.24390$	0.9998	0.01	0.033
thenylchlor	$f(x) = 7521.343902x - 32047.365854$	0.9998	0.05	0.167
fluroxypyr-meptyl	$f(x) = 3126.294934x - 13382.073171$	0.9997	0.02	0.067
tebuconazole	$f(x) = 10712.027298x - 41011.439024$	0.9997	0.05	0.167
epoxiconazole	$f(x) = 24891.502627x - 109920.07317$	0.9998	0.03	0.100
pyridaphenthion	$f(x) = 8652.029550x - 45806.073171$	0.9995	0.02	0.067
iprodione	$f(x) = 708.813508x - 5995.804878$	0.9999	0.01	0.033
tetramethrin (1)	$f(x) = 33838.091307x - 14649.024390$	0.9994	0.03	0.100
bromuconazole (1)	$f(x) = 13505.721701x - 32219.634146$	0.9995	0.01	0.033
phosmet	$f(x) = 17238.113696x - 85741.024390$	0.9998	0.01	0.033
bifenthrin	$f(x) = 85143.242697x - 44639.469663$	0.9995	0.01	0.033
EPN	$f(x) = 19443.086210x - 162951.36585$	0.9995	0.03	0.100
bromopropylate	$f(x) = 18806.899906x - 99668.390244$	0.9997	0.02	0.067
tetramethrin	$f(x) = 35692.455689x - 146759.68293$	0.9996	0.01	0.033

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Table 1. continued

pesticides	equation	r^2	LOD (mg/kg)	LOQ (mg/kg)
fenpropathrin	$f(x) = 4344.763508x - 15130.804878$	0.9996	0.01	0.033
fluorine naphthalene	$f(x) = 2277.163321x - 10405.585366$	1.0000	0.04	0.133
bromuconazole (2)	$f(x) = 12593.896811x - 18963.707317$	0.9998	0.01	0.033
phenothrin (1)	$f(x) = 1585.951720x - 3533.634146$	0.9999	0.01	0.033
tetradifon	$f(x) = 2862.935835x - 8443.926829$	0.9996	0.04	0.133
phenothrin (2)	$f(x) = 15164.290056x - 10775.341463$	0.9999	0.02	0.067
phosalone	$f(x) = 18317.290994x - 108008.46342$	0.9996	0.03	0.100
azinphos-methyl	$f(x) = 9894.324015x - 71629.097561$	0.9998	0.05	0.167
pyriproxyfen	$f(x) = 21254.395403x - 119781.12195$	0.9997	0.02	0.067
cyhalothrin (1)	$f(x) = 5849.765478x - 8530.804878$	0.9997	0.05	0.167
cyhalofop-butyl	$f(x) = 10652.675704x - 49699.073171$	0.9997	0.03	0.100
mefenacet	$f(x) = 39067.391182x - 209694.68293$	0.9997	0.02	0.067
acrinathrin (1)	$f(x) = 1988.097561x + 1586.292683$	0.9995	0.01	0.033
cyhalothrin (2)	$f(x) = 5644.911632x - 13196.804878$	0.9997	0.01	0.033
mirex	$f(x) = 29551.878049x - 162650.31707$	0.9995	0.04	0.133
acrinathrin (2)	$f(x) = 4768.339686x - 26772.560976$	0.9998	0.01	0.033
pyrazophos	$f(x) = 19435.041557x - 108856.12195$	0.9996	0.01	0.033
fenarimol	$f(x) = 8701.607974x - 29410.829268$	0.9997	0.04	0.133
pyraclofos	$f(x) = 2530.350750x - 7893.878049$	0.9998	0.02	0.067
fenoxaprop-ethyl	$f(x) = 11319.247749x - 42435.365854$	0.9999	0.03	0.100
bitertanol (1)	$f(x) = 41430.139892x - 111896.43902$	0.9998	0.01	0.033
permethrin (1)	$f(x) = 9678.451987x - 11270.853659$	0.9997	0.04	0.133
bitertanol (2)	$f(x) = 41114.957317x - 37125.512195$	0.9997	0.01	0.033
permethrin (2)	$f(x) = 12997.917240x - 5843.926829$	0.9999	0.04	0.133
fenbuconazole	$f(x) = 40076.029737x - 100280.29268$	0.9997	0.01	0.033
cyfluthrin (1)	$f(x) = 5248.044715x - 4691.195122$	0.9999	0.01	0.033
cyfluthrin (2)	$f(x) = 6347.869472x - 9718.048780$	0.9999	0.04	0.133
cyfluthrin (3)	$f(x) = 7802.724203x - 3077.097561$	0.9997	0.03	0.100
cyfluthrin (4)	$f(x) = 6481.098030x - 6735.439024$	0.9998	0.02	0.067
cypermethrin (1)	$f(x) = 14725.573066x - 12245.609756$	1.0000	0.01	0.033
halfenprox	$f(x) = 7756.647561x - 39932.146341$	0.9997	0.01	0.033
cypermethrin (2)	$f(x) = 19988.820826x - 39275.609756$	0.9996	0.04	0.133
cypermethrin (3)	$f(x) = 15514.952059x - 25147.320718$	0.9997	0.01	0.033
flucythrinate (1)	$f(x) = 37879.244841x - 98260.731707$	0.9998	0.01	0.033
cypermethrin (4)	$f(x) = 22005.287054x - 2613.585366$	0.9999	0.04	0.133
flucythrinate (2)	$f(x) = 33114.255535x - 105044.48781$	0.9995	0.03	0.100
silafluofen	$f(x) = 24016.949531x - 110654.95122$	0.9997	0.02	0.067
pyrimidifen	$f(x) = 24527.157974x - 69925.829268$	1.0000	0.01	0.033
fenvalerate (1)	$f(x) = 2923.864786x - 12770.804878$	0.9996	0.04	0.133
tau-fluvalinate (1)	$f(x) = 16996.483677x - 51983.951220$	0.9997	0.04	0.133
tau-fluvalinate (2)	$f(x) = 14870.671295x - 32658.707317$	0.9998	0.01	0.033
fenvalerate (2)	$f(x) = 3138.717380x - 4943.317073$	0.9999	0.01	0.033
difenoconazole (1)	$f(x) = 27178.515143x - 30270.951220$	0.9999	0.04	0.133
difenoconazole (2)	$f(x) = 27526.910954x - 71022.780488$	0.9999	0.02	0.067
deltamethrin (1)	$f(x) = 5245.898061x + 155.390244$	0.9998	0.03	0.100
deltamethrin (2)	$f(x) = 7743.003090x - 45579.073171$	0.9997	0.01	0.033
imibenconazole	$f(x) = 2661.346341x - 10336.219512$	0.9998	0.04	0.133

(e.g., retention time, MRM transitions, and collision energy) are summarized in Table S1.

3.5. Method Validation. The modified method for simultaneous determination of 147 pesticides spiked in honeysuckle was validated in terms of linearity, sensitivity, accuracy, and precision. The sensitivity was presented as limit of detection (LOD) and limit of quantification (LOQ). The accuracy and precision were indicated by recovery and RSD, respectively.

3.5.1. Linearity and Sensitivity. Linear regression was performed based on the concentration of the standards (20, 50, 100, 150, 200 ng/mL) against the corresponding peak area (Table 1). The satisfactory linearity between the peak area and sample concentration was observed for all pesticides as all the correlation coefficients (r^2) were >0.999, indicating that the developed method could be used for quantitative analysis of pesticide residues. LOD is defined as the minimum concentration that can be detected and LOQ is the minimum concentration that can be quantified. LOD is 3 SD_{blank}/b and LOQ is 10 SD_{blank}/b, where SD_{blank} is the standard deviation of the blank sample and b is the corresponding slope of the linear calibration curve.[17] LODs of all pesticides ranged from 0.01 to 0.05 mg/kg and LOQs were 0.033−0.167 mg/kg (Table 1). The obtained LODs and LOQs in the current study were

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Table 2. Recoveries and RSDs of 147 Pesticides Spiked in Honeysuckle at 0.1, 0.2, and 1 mg/kg by GC−MS/MS Analysis (SPE, $n = 6$)

pesticides	0.1 mg/kg		0.2 mg/kg		1 mg/kg	
	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)
chlorpropham	67.8	13.07	72.8	17.01	70.78	14.21
cadusafos	88.7	12.44	84.43	18.11	72.29	15.39
α-HCH	75.0	15.78	83.7	12.62	73.41	19.97
thiometon	79.1	23.26	74.09	17.88	79.73	10.71
β-BHC	62.7	9.08	75.56	11.67	77.96	6.15
γ-BHC	77.5	15.41	80.81	6.84	74.67	7.06
cyanophos	71.5	11.90	64.72	7.94	80.51	16.33
pyroquilon	72.9	5.26	64.41	6.73	87.46	8.90
diazinon	77.6	8.76	72.60	6.35	79.49	12.21
chlorothalonil	67.9	8.38	70.3	5.86	76.35	5.34
etrimfos	75.8	15.16	71.8	19.01	79.97	13.84
δ-HCH	83.7	8.56	69.46	14.11	74.78	11.72
MCPA-thioethyl	75.5	11.71	79.55	7.91	89.54	13.55
iprobenfos	65.5	4.89	81.37	7.77	77.24	9.10
fipronil-desulfinyl	65.4	9.35	86.13	11.67	80.42	0.68
acetochlor	68.0	10.28	76.70	6.84	71.91	11.51
vinclozolin	77.4	10.28	99.67	9.16	69.75	7.94
parathion-methyl	72.8	13.10	71.46	2.93	71.54	17.25
tolclofos-methyl	76.6	10.06	71.22	8.62	89.14	12.59
alachlor	70.3	11.88	68.35	2.17	77.66	9.50
heptachlor	75.4	10.63	89.10	9.32	75.56	14.87
prometryn	83.6	12.82	73.20	10.08	87.99	5.25
dithiopyr	77.8	1.53	98.67	15.71	75.75	10.11
pirimiphos-methyl	81.0	10.54	82.39	12.11	84.88	7.44
fenitrothion	88.0	11.34	81.81	6.06	77.56	14.17
bromacil	83.5	7.83	96.42	14.91	88.43	7.80
pentachlorothioanisole	76.9	8.29	77.36	16.48	77.61	10.91
malathion	71.1	8.04	79.11	22.87	79.72	10.05
metolachlor	79.7	9.25	77.82	22.46	79.57	8.79
chlorpyrifos	110.3	12.24	75.26	11.12	72.53	5.40
aldrin	76.3	14.06	89.33	9.71	75.80	10.43
chlorthal-dimethyl	70.9	7.91	79.20	1.93	70.07	7.88
fenpropimorph	71.9	7.77	85.12	4.52	86.51	4.19
parathion	71.5	10.41	79.41	15.33	74.62	10.01
triadimefon	101.4	7.24	105.60	13.47	85.98	1.95
tetraconazole	86.4	6.17	66.58	8.73	80.12	2.88
isocarbophos	79.7	4.76	68.07	10.45	69.97	6.72
dicofol	78.8	11.08	74.63	12.41	87.81	2.73
butralin	77.7	11.11	87.28	10.45	70.78	8.98
fthalide phthalide	69.4	8.36	74.53	9.62	79.85	5.86
pirimiphos-ethyl	92.9	6.78	70.75	1.60	76.32	4.71
bromofos	80.6	7.56	75.18	8.86	82.59	11.49
diphenamid	100.5	10.86	85.57	3.86	84.33	1.63
fipronil-sulfide	70.3	11.87	75.30	7.26	80.56	4.94
pendimethalin	71.8	7.82	87.35	10.05	72.07	6.72
fipronil	69.5	9.18	65.36	9.69	79.30	3.62
penconazole	87.1	9.35	71.97	1.91	83.62	0.96
heptachlor-*exo*-epoxide	72.4	17.01	81.18	8.85	78.88	8.61
chlozolinate	81.8	18.11	71.58	5.80	78.88	2.93
isofenphos	76.8	12.62	95.85	7.02	71.07	2.41
heptachlor-*endo*-epoxide	82.0	17.88	72.98	13.12	78.36	9.21
phenthoate	78.6	11.67	71.34	15.36	81.91	6.87
quinalphos	76.4	6.84	78.00	11.32	77.62	6.31
mephosfolan	94.8	7.94	88.60	13.29	83.88	4.05
procymidone	86.7	6.73	80.45	15.53	84.29	2.05
triflumizole	78.6	6.35	77.37	2.63	78.37	2.21
bromophos-ethyl	77.5	5.86	84.40	3.16	79.37	4.21
methidathion	75.28	4.20	96.82	5.03	105.73	13.09

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Table 2. continued

pesticides	0.1 mg/kg		0.2 mg/kg		1 mg/kg	
	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)
trans-chlordane	81.40	13.05	88.46	6.10	66.80	8.02
propaphos	81.79	7.12	87.55	8.45	77.38	8.65
chinomethionate	78.9	8.33	87.1	3.85	78.67	8.66
o,p′-DDE	82.84	9.64	72.4	9.60	75.51	4.38
paclobutrazol	88.95	5.87	81.13	2.65	82.47	2.18
butachlor	86.58	13.20	76.41	7.64	90.12	5.45
cis-chlordane	81.65	14.49	71.04	21.90	73.19	6.86
alpha-endosulfan	82.99	6.01	86.56	20.79	77.25	9.40
ditalimfos	77.61	13.94	70.19	13.81	84.98	6.69
fipronil-sulfone	74.96	5.88	78.67	2.45	83.50	3.72
napropamide	83.26	4.02	81.35	15.05	86.39	3.71
flutolanil	77.25	7.77	97.83	2.82	83.23	2.02
prothiophos	83.20	6.51	81.33	11.13	81.03	3.56
isoprothiolane	77.90	11.11	71.93	18.55	80.79	2.10
p,p′-DDE	84.27	5.19	87.49	12.63	83.43	2.35
oxadiazon	86.03	10.70	72.53	12.18	83.47	1.25
thifluzamide	85.97	8.08	81.34	16.22	83.74	2.11
dieldrin	83.61	4.09	87.17	8.05	73.35	7.84
myclobutanil	89.01	7.18	80.31	16.07	77.40	5.44
o,p′-DDD	83.46	13.14	99.55	9.87	76.23	1.39
flusilazole	87.56	8.19	65.45	11.36	81.05	3.56
oxyfluorfen	83.30	7.85	88.17	11.14	87.38	3.65
bupirimate	86.35	7.88	69.78	12.73	80.10	1.65
kresoxim-methyl	87.86	12.29	68.40	10.61	84.72	1.82
chlorfenapyr	81.21	12.66	69.80	18.88	121.78	6.22
endrin	86.86	10.35	79.33	15.76	80.01	5.16
chloropropylate	74.68	7.78	75.18	14.91	82.09	1.02
fensulfothion	88.38	13.44	80.38	1.38	84.43	3.48
β-endosulfan	73.49	5.99	70.07	6.33	81.23	6.71
diniconazole	76.80	6.93	74.90	5.15	80.15	0.85
oxadixyl	80.19	8.10	94.65	16.75	75.92	9.94
p,p′-DDD	85.48	1.29	78.71	9.84	84.24	2.63
ethion	73.51	5.45	90.86	9.11	71.06	5.71
o,p′-DDT	83.02	9.23	84.45	8.57	100.20	8.45
mepronil	77.79	8.84	78.09	8.51	83.08	1.19
triazophos	88.23	6.63	74.85	2.10	94.77	4.10
carbofenothion	83.24	12.94	53.44	4.01	73.76	2.54
cyanofenphos	85.36	3.99	65.88	12.60	85.08	2.20
edifenphos	87.33	1.33	80.42	11.25	105.89	14.31
endosulfan sulfate	83.37	4.36	85.76	14.59	82.09	11.70
pyraflufen-ethyl	85.14	10.62	84.86	7.06	82.32	1.94
p,p′-DDT	88.66	3.26	123.39	5.50	110.41	9.75
hexazinone	89.29	5.09	86.32	3.18	73.63	8.61
thenylchlor	88.50	6.41	89.82	20.34	111.89	12.48
fluroxypyr-meptyl	84.18	10.92	89.33	8.59	84.65	2.21
tebuconazole	87.98	7.00	78.57	9.65	77.04	3.64
epoxiconazole	97.81	7.96	88.59	12.30	79.47	3.62
pyridaphenthion	87.76	13.46	72.82	6.92	89.53	4.43
iprodione	87.61	2.53	72.71	3.37	93.22	14.59
phosmet	89.08	8.36	94.79	3.50	122.23	19.17
bifenthrin	86.64	12.23	83.23	17.75	80.82	3.27
EPN	95.08	7.75	74.03	6.27	84.69	3.25
bromopropylate	84.53	12.72	88.63	9.74	71.57	1.25
fenpropathrin	84.70	9.51	80.92	17.98	77.55	3.62
fluorine naphthalene	84.89	9.32	75.09	13.37	84.42	0.97
tetradifon	86.12	10.33	72.44	14.82	79.23	3.19
phosalone	96.69	4.08	82.95	14.13	96.79	7.07
azinphos-methyl	79.61	13.97	96.56	7.77	112.06	18.10
pyriproxyfen	85.71	2.68	99.99	7.70	83.66	4.78

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Table 2. continued

pesticides	0.1 mg/kg		0.2 mg/kg		1 mg/kg	
	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)
cyhalofop-butyl	84.76	8.45	84.76	2.23	83.61	2.22
mefenacet	89.07	14.17	76.28	7.33	99.60	8.85
mirex	82.20	14.02	92.05	5.18	82.84	1.43
pyrazophos	86.37	4.41	89.32	11.40	88.29	3.85
fenarimol	88.39	8.08	74.47	5.26	82.04	3.98
pyraclofos	85.08	15.96	68.73	13.46	114.72	12.91
fenoxaprop-ethyl	80.42	13.33	72.63	14.95	81.26	11.54
fenbuconazole	91.30	15.98	87.57	15.71	72.79	7.54
halfenprox	72.54	2.61	93.91	13.77	83.58	0.95
silafluofen	91.60	6.45	82.40	3.38	83.95	1.55
pyrimidifen	69.9	5.90	77.03	10.70	83.23	8.55
imibenconazole	70.2	12.36	88.93	7.66	91.81	13.17
allethrin	77.68	7.05	112.16	9.20	97.67	12.76
triadimenol	73.65	6.78	100.44	7.06	73.98	1.73
cyproconazole	72.00	12.59	75.46	11.49	79.40	3.58
propiconazole	78.12	11.25	74.29	14.97	77.93	2.55
tetramethrin	76.86	6.18	89.13	11.99	83.31	1.32
bromuconazole	78.56	10.02	75.91	6.13	85.11	1.75
phenothrin	80.53	10.13	85.73	8.43	95.42	5.26
cyhalothrin	80.51	7.24	77.71	8.50	76.52	0.92
acrinathrin	96.02	7.72	82.02	9.76	85.85	1.18
bitertanol	86.59	10.57	72.88	15.24	78.02	4.46
permethrin	92.99	15.83	79.66	7.49	84.37	2.74
cyfluthrin	85.80	1.53	79.75	11.29	84.12	1.05
cypermethrin	70.12	8.24	81.90	6.86	62.06	1.68
flucythrinate	72.57	7.85	92.53	9.32	83.69	0.84
fenvalerate	71.78	5.68	93.92	6.22	83.45	1.65
tau-fluvalinate	89.48	12.82	70.39	15.50	77.38	2.88
difenoconazole	85.28	10.11	80.89	13.46	78.75	2.07
deltamethrin	92.42	14.32	81.78	8.39	83.70	2.59

Table 3. Recoveries of Comparision between SPE and QuEChERs for Extracting Six Pesticides in Honeysuckle and Dried Tangerine Peel

pesticides	honeysuckle				tangerine peel			
	SPE		QuEChERs		SPE		QuEChERs	
	recovery/%	RSD/%	recovery/%	RSD/%	recovery/%	RSD/%	recovery/%	RSD/%
δ-HCH	86.9	5.83	92.1	5.05	84.1	6.75	82.3	7.95
chlorpyrifos	88.4	7.18	88.1	3.09	86.3	8.21	87.1	8.41
bifenthrin	90.1	5.12	87.3	6.43	89.1	6.12	88.2	5.75
pendimethalin	85.4	6.73	86.9	8.03	87.2	6.03	85.3	6.53
fipronil	88.2	6.94	90.2	9.08	86.1	6.35	87.1	5.98
fenpropimorph	83.2	7.8	87.4	4.99	85.9	7.31	86.7	7.32

higher than that reported in previous studies that detected seven pesticides in honeysuckle by GC−MS/MS with LODs of 0.00005−0.008 mg/kg and LOQs of 0.00015−0.025 mg/kg but meet the requirement of sensitivity for various commodities.[18,19]

3.5.2. Accuracy and Precision. To evaluate the accuracy and precision of the modified method, honeysuckle was spiked with a standard pesticide mixture at 0.1, 0.2, and 1 mg/kg (n = 6). Table 2 shows the recoveries and RSDs for all pesticides with different spiking levels. Recoveries of most pesticides spiked at all levels ranged from 70% to 120%, meeting the requirements of the European Commission for pesticides.[20] The recoveries of 9 out of 147 pesticides were below 70% but above 60% at 0.1 mg/kg level. The recoveries of 15 out of 147 pesticides at 0.2 mg/kg level fell outside the range of 70−120%. At the level of 1 mg/kg, the recoveries of 4 out of 147 pesticides were 62.06−69.97%, and only chlorfenapyr and phosmet were associated with higher recoveries at 121.78 and 122.23%, respectively. RSD was also calculated to evaluate the precision of the method. RSDs for almost all pesticides at different spiked levels were less than 20%. Although the RSDs of five pesticides at 0.2 mg/kg and one pesticide at 0.1 mg/kg were up to 20.34−23.26%, all RSDs at 1 mg/kg were below 20%. The excellent analytical performance of the modified method in accuracy and precision was verified by determining 147 pesticides in honeysuckle simultaneously.

3.6. Comparison of Two Sample Pretreatment Methods for Real Samples. Traditional Chinese herbal medicine extract contains a complicated matrix including proteins, polysaccharides, fats, pigments, flavonoids, and

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alkaloids, making it challenging to determine pesticide residues. The extraction procedure is the key step in different detection methods for quantitatively detecting pesticides in complex matrices. In the current study, honeysuckle and tangerine peel were used as the model matrix to evaluate the extraction efficiency of two sample pretreatment methods, namely SPE and QuEChERS. Tangerine peel (i.e., polysaccharide, limonin, flavonoids, alkaloids, essential oils, and trace elements)[21] has more pigments and a more complex matrix than honeysuckle (i.e., essential oils, organic acids, flavones, iridoids, and saponins).[22] Recoveries of two pretreatment methods for detecting six pesticides (0.1 mg/kg) spiked in both herbal medicines are compared and summarized in Table 3. The QuEChERS method achieved comparable or higher recoveries (86.9−92.1%) for most pesticides in honeysuckle than that by the SPE approach (83.2−90.1%). The SPE approach resulted in slightly lower recoveries for three pesticides and higher recoveries for other pesticides spiked in the dried tangerine peel. Taken together, both sample pretreatment methods could effectively extract all pesticides from both tangerine peel and honeysuckle, while QuEChERS (∼1 h) took less time compared to SPE (∼2 h).

4. CONCLUSIONS

GC−MS/MS is an analytical approach for determination of multiple pesticides in food and pharmaceutical industries. However, it faces the challenge of detecting multiple pesticides in traditional Chinese medicines with complex compounds that could interfere with the signals of target compounds. This study reported the development of an optimized QuEChERS and a modified SPE approach, coupled with GC−MS/MS for simultaneous determination of 147 pesticide residues in traditional Chinese medicines. The developed method for pesticide detection was verified with satisfying sensitivity, accuracy, and precision. The extraction efficiency using QuECheRS and SPE was compared by extracting pesticides in honeysuckle and dried tangerine peel. Both QuECheRS and SPE showed a satisfactory extraction efficiency (>83.2%) for six pesticides spiked in real samples. The entire test included GS−MS/MS detection of 0.5 h and QuEChERS extraction of ∼1 h or SPE extraction of ∼2 h. Therefore, the QuEChERS method has superior properties with respect to time-saving as compared to the SPE approach.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c03178.

Basic information of pesticides and the parameters of MS for analysis of pesticides and recoveries of six pesticides from honeysuckles using various adsorbents by QuEChERS (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) World Health Organization. African Traditional Medicine Day. 2013, https://www.afro.who.int/media-centre/events/african-traditional-medicine-day-2013 (accessed Jan 10, 2023).
(2) Abba, M.; Abdullahi, M.; Md Nor, M. H.; Chong, C. S.; Ibrahim, Z. Isolation and Characterisation of Locally Isolated *Gluconacetobacter Xylinus* BCZM Sp. With Nanocellulose Producing Potentials. *IET Nanobiotechnol.* **2018**, *12*, 52−56.
(3) Chau, C. F.; Wu, S. H. The Development of Regulations of Chinese Herbal Medicines for Both Medicinal and Food Uses. *Trends Food Sci. Technol.* **2006**, *17*, 313−323.
(4) Wang, K. H.; Lin, R. D.; Hsu, F.-L.; Huang, Y.-H.; Chang, H.-C.; Huang, C.-Y.; Lee, M.-H. Cosmetic Applications of Selected Traditional Chinese Herbal Medicines. *J. Ethnopharmacol.* **2006**, *106*, 353−359.
(5) Whitacre, D. M.; Gunther, F. A.; Whitacre, D. M.; Albert, L. A.; Hutzinger, O.; Knaak, J. B.; Mayer, F. L.; Morgan, D. P.; Park, D. L.; Tjeerdema, R. S.; De Voogt, P.; Yang, R. S. H.; Gerba, C. P.; Giesy, J.; Stevens, J. T.; Ware, G. Reviews of Environmental Contamination and Toxicology. *Reviews of Environmental Contamination and Toxicology*; Springer New York: New York, NY, 2010; Vol. *202*.
(6) Chamkasem, N.; Ollis, L. W.; Harmon, T.; Lee, S.; Mercer, G. Analysis of 136 Pesticides in Avocado Using a Modified QuEChERS Method with LC-MS/MS and GC-MS/MS. *J. Agric. Food Chem.* **2013**, *61*, 2315−2329.
(7) Song, N. E.; Lee, J. Y.; Mansur, A. R.; Jang, H. W.; Lim, M. C.; Lee, Y.; Yoo, M.; Nam, T. G. Determination of 60 pesticides in hen eggs using the QuEChERS procedure followed by LC-MS/MS and GC-MS/MS. *Food Chem.* **2019**, *298*, 125050.
(8) Varela-Martínez, D. A.; González-Curbelo, M. Á.; González-Sálamo, J.; Hernández-Borges, J. Analysis of multiclass pesticides in dried fruits using QuEChERS-gas chromatography tandem mass spectrometry. *Food Chem.* **2019**, *297*, 124961.
(9) Xu, R.; Wu, J.; Liu, Y.; Zhao, R.; Chen, B.; Yang, M.; Chen, J. Analysis of Pesticide Residues Using the Quick Easy Cheap Effective Rugged and Safe (QuEChERS) Pesticide Multiresidue Method in Traditional Chinese Medicine by Gas Chromatography with Electron Capture Detection. *Chemosphere* **2011**, *84*, 908−912.
(10) Ahammed Shabeer, T. P.; Girame, R.; Utture, S.; Oulkar, D.; Banerjee, K.; Ajay, D.; Arimboor, R.; Menon, K. R. K. Optimization of Multi-Residue Method for Targeted Screening and Quantitation of 243 Pesticide Residues in Cardamom (Elettaria Cardamomum) by Gas Chromatography Tandem Mass Spectrometry (GC-MS/MS) Analysis. *Chemosphere* **2018**, *193*, 447−453.
(11) Zhang, Z.; Dong, M.; Hao, X.; Han, L.; Song, S.; Yao, W. Evaluation of Cleanup Procedures in Pesticide Multi-Residue Analysis with QuEChERS in Cinnamon Bark. *Food Chem.* **2019**, *276*, 140−146.
(12) Taha, S. M.; Gadalla, S. A. Development of an Efficient Method for Multi Residue Analysis of 160 Pesticides in Herbal Plant by Ethyl Acetate Hexane Mixture with Direct Injection to GC-MS/MS. *Talanta* **2017**, *174*, 767−779.
(13) Parrilla Vázquez, P.; Ferrer, C.; Martínez Bueno, M. J.; Fernández-Alba, A. R. Pesticide Residues in Spices and Herbs: Sample Preparation Methods and Determination by Chromatographic Techniques. *TrAC, Trends Anal. Chem.* **2019**, *115*, 13−22.
(14) Xue, J.; Li, H.; Liu, F.; Jiang, W.; Hou, F. Vortex-Assisted Matrix Solid−Liquid Dispersive Microextraction for the Analysis of Triazole Fungicides in Cotton Seed and Honeysuckle by Gas Chromatography. *Food Chem.* **2016**, *196*, 867−876.
(15) Li, L.; Li, W.; Ge, J.; Wu, Y.; Jiang, S.; Liu, F. Use of Graphitic Carbon Black and Primary Secondary Amine for Determination of 17 Organophosphorus Pesticide Residues in Spinach. *J. Sep. Sci.* **2008**, *31*, 3588−3594.
(16) Li, S.; Yu, P.; Zhou, C.; Tong, L.; Li, D.; Yu, Z.; Zhao, Y. Analysis of pesticide residues in commercially available chenpi using a modified QuEChERS method and GC-MS/MS determination. *J. Pharm. Anal.* **2020**, *10*, 60−69.
(17) Guo, Q.; Deng, M.; Yu, B.; Tan, L. Analysis of the Residues of 20 Organochlorine Pesticides in Herba Epimedii, a Chinese Herbal Medicine, by Solid-Phase Extraction with Gas Chromatography/Negative Chemical Ionization−Mass Spectrometry. *J. AOAC Int.* **2010**, *93*, 295−305.
(18) European Commission. Analytical Quality Control and Method Validation for Pesticide Residues Analysis in Food and Feed (SANTE/12682/2019). 2019, pp 1−48, https://www.eurl-pesticides.eu/userfiles/file/EurlALL/AqcGuidance_SANTE_2019_12682.pdf (accessed Jan 10, 2023).
(19) European Directorate for the Quality of Medicines & HealthCare. *European Pharmacopoeia (Ph. Eur.)*, 11th ed., 2021.
(20) Chinese Pharmacopoeia Commission. *Chinese Pharmacopoeia*, 10th ed.; China Medical Science Press, 2015.
(21) Zhang, H.; Cui, J.; Tian, G.; DiMarco-Crook, C.; Gao, W.; Zhao, C.; Li, G.; Lian, Y.; Xiao, H.; Zheng, J. Efficiency of Four Different Dietary Preparation Methods in Extracting Functional Compounds from Dried Tangerine Peel. *Food Chem.* **2019**, *289*, 340−350.
(22) Shang, X.; Pan, H.; Li, M.; Miao, X.; Ding, H. Lonicera Japonica Thunb.: Ethnopharmacology, Phytochemistry and Pharmacology of an Important Traditional Chinese Medicine. *J. Ethnopharmacol.* **2011**, *138*, 1−21.

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