



Multiresidue Analysis of 113 Pesticides in Different Maturity Levels of Mangoes Using an Optimized QuEChERS Method with GC-MS/MS and UHPLC-MS/MS

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Abstract

In this study, a simple and high-throughput multiresidue pesticide analysis method based on the quick, easy, cheap, effective, rugged, safe (QuEChERS) extraction combined with gas chromatography-triple quadrupole mass spectrometry (GC-MS/MS) and ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) is presented for the determination of 113 pesticides in green and ripe mangoes. Different buffer systems and purification sorbents were optimized to get better recovery. Extracts from mangoes after acid acetonitrile and ammonium acetate extraction were directly injected to UHPLC-MS/MS analysis, whereas other GC-amenable compounds were treated with cleanup approaches with a mixture of sorbents [400 mg primary-secondary amine (PSA) and 400 mg graphitized carbon black (GCB)] for GC-MS/MS analysis. Recoveries for the majority of pesticides at spike levels of 10, 50, and 100 µg/kg were ranged between 70 and 120% with RSD values below 20%. Limits of detection (LODs) were below 4 µg/kg, whereas limits of quantification (LOQs) were below 10 µg/kg. Response linearity was good in the range between 5 and 500 µg/kg. The matrix effect for 56 pesticides by GC-MS/MS analysis exhibited a non-significant matrix effect ($\leq 25\%$) in green and ripe mangoes. For 57 pesticides used for UHPLC-MS/MS analysis, the optimized method in green mango provided no significant matrix effect ($\leq 25\%$) for 63% of the compounds, whereas only for 16 and 21% compounds, the matrix effect was medium (25–40%) and strong ($> 40\%$); the optimized method in ripe mango provided no significant matrix effect ($\leq 25\%$) for 61% of the compounds, whereas only for 26 and 12% compounds, the matrix effect was medium (25–40%) and strong ($> 40\%$). Following the application of a “top-down” approach, the expanded measurement uncertainty was both 21% on average (coverage factor $k = 2$, confidence level 95%) in green and ripe mangoes. The application of GC-MS/MS and UHPLC-MS/MS coupled with the modified QuEChERS extraction procedures was proved to adequately quantitate these pesticides in different maturity levels of mangoes.

Keywords Multiresidue analysis · QuEChERS · GC-MS/MS · UHPLC-MS/MS · Mango

Introduction

Mango is considered one of the most important tropical fruits and is widely acceptable throughout the world because of its attractive flavor, aroma, and color. Furthermore, mango is a good dietetic source of carotenoids, mineral salts, carbohydrates,

ascorbic acid, and B vitamins (Srivastava et al. 2014). According to FAO's latest statistics, China ranked second in mango production in the world during 2013 (Food and Agriculture Organization of the United Nations, Food and Agricultural Commodities Production 2013). However, the tropical agricultural environment is of high temperature and high humidity, and there are many types of pests and pathogens in mangoes. To increase its productivity and prevent economic losses, pesticides are used for pest and fungal control during mango growing and post-harvest stages. For example, a serious disease in mango is anthracnosis. The common practice is immersion of the mangoes in water containing fungicides such as thiabendazole (Filho et al. 2010). Despite the usefulness of pesticides for the control of pest and disease, agro-products are liable to contain or accumulate from agricultural practices and storage periods

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(Nieto-Garcia et al. 2015; Jin et al. 2012; Amvrazi and Albanis 2006; Yang et al. 2011; Stajnbaher and Zupancic-Kralj, 2003). Food intake with pesticides could be concerned to risks to a consumer's health (Slowik-Borowiec et al. 2015; Hayward et al. 2013; Chu et al. 2005; Castillo et al. 2012; Rissato et al. 2004). Therefore, several countries have established maximum residue limits (MRLs) for pesticides in food including mangoes. In this context, the monitoring of pesticides in mangoes is of significant importance to guarantee food safety, also adhering to current good manufacturing practices.

For that reason, analytical approaches for the determination and quantification of residues in mango are indispensable. Pesticide residue analysis in mango matrices is still difficult to perform due to the texture of mango varying depending on the maturity level of the fruit. Green mango has an acid matrix which could easily degrade some pesticides. Ripe mango has a viscous matrix with high sugar and fatty acid content, which could adversely affect the extraction efficiency and instrument performances. Thus, the preparation method of removing interferents from the matrix is important for the determination of pesticides. In the recent years, the most popular cleanup approach for pesticide residue analysis is the quick, easy, cheap, effective, rugged, safe (QuEChERS) approach which was first introduced by Anastassiades et al. (2003). Compared with traditional methods, QuEChERS is considered quick, easy, cheap, effective, rugged, and safe. Because of its advantages, many studies applied this method for the multiresidue pesticide analysis in food (Prestes et al. 2009; Chamkasem et al. 2013; Zhao et al. 2014; Palenikova et al. 2015; He et al. 2015; Koesukiwat et al. 2011; Furlani et al. 2011; Kwon et al. 2012; Cherta et al. 2013; Rejczak and Tuzimski 2015a, b, 2016). QuEChERS shows some important strengths such as being simple and quick, as well as weaknesses such as imperfect cleanup. Moreover, with the number of pesticides increasing, it is needed to apply efficient instruments to screen the largest possible pesticides at the lowest possible concentration at a short time. Gas chromatography (GC) or liquid chromatography (LC) coupled with triple quadrupole mass spectrometry showed that tandem mass spectrometry is one of the most efficient techniques in terms of low limits of detection, strong capacity of resisting disturbance, and simultaneous detection of many types of pesticides. Therefore, it is a preferred approach at present for the analysis of hundreds of pesticides using QuEChERS in combination with GC-MS/MS or LC-MS/MS (Qu et al. 2010; Wong et al. 2010; Anagnostopoulos et al. 2012; Navickiene et al. 2010; Rizzetti et al. 2016; Rejczak and Tuzimski 2015a).

Up to date, several researchers elaborated the QuEChERS procedure combined with triple quadrupole mass spectrometry for the extraction of pesticides in mango matrices. The first report on its application to pesticide extraction from mango matrices was published in 2009 by Banerjee et al. (2009), which determined 87 pesticides in mango by LC-MS/MS. Next, Navickiene et al. (2010) applied the QuEChERS

method with GC-MS/MS for the extraction of seven pesticides in mango. Then, Deme and Upadhyayula, 2015 used the QuEChERS approach for the determination of 40 pesticides in mango juices. After that, Sivaperumal et al. (2017) used the QuEChERS method for the analysis of 68 pesticide residues in mango matrices.

The main objective of the present work was to study the feasibility QuEChERS method coupled with GC-MS/MS and ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) to simultaneously determine 113 pesticides in different maturity levels of mangoes. The research was implemented to assess the fitness of the proposed method. An additional objective was to optimize the extraction method to improve sample cleanup capacity, reduce matrix interferents, and preparation time.

Experimental

Materials, Solvents, and Standards

The phytosanitary compounds listed in Tables 1 and 2 were purchased from Dr. Ehrenstorfer (Augsburg, Germany), with purity higher than 99%.

HPLC-grade acetonitrile, methanol, and hexane were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The pesticides were chosen considering their application in mangoes in China. All of the standards were individually dissolved in methanol at a concentration of 1000 mg/L. Calibration standard (listed in Table 1) solutions were prepared in hexane and in blank mango extracts (matrix-matched calibration), whereas calibration standard (listed in Table 2) solutions were prepared in methanol and in blank mango extracts (matrix-matched calibration).

For sample preparation, commercial QuEChERS extraction salt packets containing 6 g MgSO₄, 1.5 g CH₃COONa or 4 g MgSO₄, 1 g NaCl or 4 g MgSO₄, 1 g NaCl, 1 g sodium citrate, and 0.5 g disodium hydrogencitrate sesquihydrate were used. For *d*-SPE cleanup, preweighed mixtures containing 400 mg of primary secondary amine (PSA), 400 mg graphitized carbon black (GCB), 1200 mg anhydrous MgSO₄ or 150 mg PSA, 15 mg GCB, and 900 mg anhydrous MgSO₄ were used. These materials were purchased from Agilent (Agilent Technologies, Lake Forest, CA). Analytical-grade ammonium acetate and commercial QuEChERS extraction sorbent packets containing 500 mg Zr-Sep⁺ or 400 mg PSA, 80 mg GCB, 1200 mg anhydrous MgSO₄, and 480 mg Zr-Sep⁺ were acquired from Sigma-Aldrich (Supelco, Bellefonte, PA, USA).

Multiwalled carbon nanotubes (MWCNTs) (20–30 nm) were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Chengdu, China). Reagent-grade anhydrous MgSO₄, sodium chloride, and glacial acetic

Table 1 Retention times and MS/MS parameters of the selected pesticides for GC-MS/MS acquisition program

Compound	t_R (min)	MRM1	MRM2		
			CE1	CE2	
Dichlorvos	5.14	185 > 109	15	185 > 93	12
Demeton	8.47	114 > 81	10	88 > 60	5
Ethoprophos	9.55	158 > 114	10	158 > 97	20
Cadusafos	9.55	158.9 > 130.9	8	158.9 > 97	18
Sulfotep	9.59	322 > 266	10	322 > 202	15
Phorate	9.65	260 > 75	15	231 > 175	15
Alpha-HCH	9.70	219 > 183	10	219 > 145	20
Dimethoate	10.18	143 > 111	10	125 > 79	10
Beta-HCH	10.58	219 > 183	10	219 > 145	20
Gamma-HCH	10.77	219 > 183	10	219 > 145	20
Terbufos	11.10	231 > 175	10	231 > 157	15
Fonofos	11.13	246 > 137	5	246 > 109	20
Diazinon	11.70	304 > 179	12	179 > 137	20
Delta-HCH	11.66	219 > 183	10	181 > 145	15
Isazofos	12.15	257 > 161	10	257 > 119	20
Parathion methyl	13.35	263 > 109	10	125 > 79	10
Fenitrothion	14.64	260 > 125	15	260 > 109	15
Aldrin	15.11	262.9 > 193	28	262.9 > 203	26
Malathion	15.34	173 > 127	5	173 > 99	15
Phorate sulfone	15.33	153 > 97	10	125 > 97	10
Fenthion	15.55	278 > 169	15	278 > 109	15
Parathion	15.67	291 > 109	13	109 > 81	11
Chlorpyrifos	15.66	314 > 286	10	314 > 258	15
Triadimefon	15.81	208 > 181	5	208 > 127	15
Isofentofos	15.96	230 > 212	10	230 > 155	15
Isofenphos methyl	16.96	241 > 199	5	241 > 121	20
Quinalphos	17.75	298 > 190	15	298 > 156	15
Phenthoate	17.84	273.9 > 125	20	273.9 > 246	6
Procymidone	18.00	283 > 255	10	283 > 96	10
Methidathion	18.29	145 > 85	10	145 > 58	15
O,P-DDE	18.71	246 > 176	30	246 > 211	22
Endosulfan	18.74	338.9 > 160	18	338.9 > 266.9	8
Chlordane	18.96	372.8 > 336.8	10	372.8 > 263.9	28
Fenamiphos	19.83	303.1 > 195.1	8	303.1 > 154.1	18
Dieldrin	20.06	276.9 > 241	8	276.9 > 170	38
Profenofos	20.07	339 > 269	15	339 > 251	30
P,P-DDE	20.15	246 > 176	30	246 > 211	22
O,P-DDD	20.52	235 > 165	24	235 > 199	14
P,P-DDD	22.30	235 > 165	24	235 > 199	14
O,P-DDT	22.38	235 > 165	24	235 > 199	16
Triazophos	23.41	257 > 162	10	257 > 119	25
P,P-DDT	23.92	235 > 165	24	235 > 199	16
Phosmet	25.60	160 > 133	15	160 > 77	25
Bifenthrin	26.23	181 > 166	15	181 > 165	25
Phosalone	26.91	182 > 138	5	182 > 111	15
Fenpropathrin	26.34	265 > 210	10	265 > 89	25
Phosalone	26.91	182 > 138	5	182 > 111	15
Cyhalothrin	27.57	208 > 181	10	197 > 141	13
Permethrin	28.77	183 > 168	15	183 > 153	15
Pyridaben	28.84	147 > 132	15	147 > 117	25
Cyfluthrin	29.67	206 > 177	25	206 > 151	25
Cypermethrin	30.07	181 > 152	25	163 > 127	10
Flucythrinate	30.38	199 > 157	5	199 > 107	25
Fluvalinate	31.55	208 > 181	15	181 > 152	25
Fenvalerate	31.23	167 > 125	10	125 > 89	17
Difenoconazole	31.71	323 > 265	15	323 > 202	30
Deltamethrin	31.92	253 > 174	13	253 > 93	13

acid were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China).

GC-MS/MS Analysis

The analysis was carried out on a 7000 triple-quadrupole MS coupled to a 7890A GC, a 7693 autosampler, and a computer with MassHunter software (version B.05.00412) for data acquisition and processing (Agilent Technologies, Palo Alto, CA, USA). Pesticides were separated with HP-5 MS capillary columns from Agilent (0.25 mm i.d. \times 30 m \times 0.25 μ m film thickness). The flow rate of the carrier gas (helium) was 1 mL/min. The initial oven temperature was 70 °C (hold for 2 min), and it ramped to 150 °C at a rate of 25 °C/min, then raised to 200 °C at 3 °C/min, and the temperature was increased until 280 °C at a rate of 8 °C/min, which was held for 2 min. The total run time was 33.8 min. The injector temperature was 250 °C. The injected volume was 1.0 μ L with splitless mode. The temperatures of ion source and transfer line were 230 and 280 °C. The parameters of the MRM transition mode for all the test pesticides are provided in Table 1. The time of solvent delay was 4.0 min in order to prevent filament burnout. The collision gases were nitrogen and helium with flow rates at 1.5 and 2.25 mL/min for MRM mode. The calibration curve was made by solvent solution fortifying known concentration standards. Concentrations were obtained by comparing the peak area of the targets in the sample to the response of solvent solution standards in the calibration curve. Pesticide identification was confirmed by making a comparison between the expected retention time and the ratio of the two transition (primary/secondary) values to solvent solution standards, following the criteria for identification established by the FDA and European Union (EC Council Directive 2002).

UHPLC-MS/MS Analysis

The UHPLC-MS/MS system (Waters, Milford, USA) was performed using Waters Acquity UPLC™ liquid chromatography, consisting of an autosampler, a binary pump, and a column temperature controller, coupled with a Xevo TQ™ MS/MS triple quadrupole detector. An Acquity UPLC™ BEH C18 column (100 \times 2.1 mm i.d., 1.7 μ m particle size) from Waters (Wexford, Ireland) was used for UPLC separation at 35 °C with a sample injection volume of 5 μ L. MassLynx 4.1 software (Waters, Milford, USA) was used for instrument control and data processing. A binary mobile phase was composed of (A) 1 mM ammonium acetate in water and (B) methanol. A mobile phase gradient started at 10% B at a flow rate of 0.25 mL/min and went to 70% B at 2 min (curve 6) and held for 2.5 min then 95% B at 7 min (curve 6) and held until 9 min, and was concluded by column equilibration at the initial condition for 9.1 min (curve 6) and held for 1.9 min for a total run time of 11 min. MS determination was performed in the electrospray ionization positive/negative mode (ESI⁺ or ESI⁻) with monitoring of the ion transitions (precursor/product) using MRM for each pesticide. The MS source conditions

Table 2 Retention times and MRM conditions of the selected pesticides for UHPLC-MS/MS analysis

Compound	Ionization mode	t_R (min)	CV (v)	MRM1	CE 1	MRM2	CE 2
Cyromazine	ESI ⁺	1.92	25	167 > 60.2	20	167 > 108.1	20
Aldicarb sulfoxide	ESI ⁺	1.96	25	229 > 165.8	11	229 > 108.8	17
Aldicarb sulfone	ESI ⁺	2.04	25	223 > 147.7	9	223 > 85.8	12
Methomyl	ESI ⁺	2.27	15	162.7 > 87.9	8	162.7 > 105.9	8
Propamocarb	ESI ⁺	2.35	25	189.1 > 102	20	189.1 > 144	20
Imidacloprid	ESI ⁺	2.59	34	256.1 > 175.1	20	256.1 > 209.1	15
Thiamethoxam	ESI ⁺	2.63	26	292.1 > 181.1	28	292.1 > 211.2	16
3-Hydroxycarbofuran	ESI ⁺	2.69	25	238.1 > 162.9	14	238.1 > 180.9	8
Acetamiprid	ESI ⁺	2.73	27	223 > 90	34	223 > 125.9	20
Carbendazim	ESI ⁺	2.92	33	192 > 132.1	28	192 > 160.1	18
Aldicarb	ESI ⁺	3.08	25	212.9 > 89	14	212.9 > 98	10
Thiabendazole	ESI ⁺	3.16	35	202.1 > 131.1	25	202.1 > 175.1	23
Carbofuran	ESI ⁺	3.27	25	222 > 164.9	10	222 > 122.9	18
Carbaryl	ESI ⁺	3.35	20	201.9 > 144.9	5	201.9 > 126.9	28
Phorate sulfoxide	ESI ⁺	3.47	20	277 > 97	36	277 > 199	10
Pirimicarb	ESI ⁺	3.51	26	239.1 > 71.9	23	239.1 > 181.9	19
Isoproc carb	ESI ⁺	3.59	35	194 > 94.9	20	194 > 136.9	10
Chlordimeform	ESI ⁺	3.63	20	197.2 > 117.1	20	197.2 > 125.1	35
Atrazine	ESI ⁺	3.63	30	216.1 > 96.1	26	216.1 > 104	24
Metalaxyl	ESI ⁺	3.63	20	280.1 > 192.1	15	280.1 > 220	15
Chlorantraniliprole	ESI ⁺	3.71	20	484 > 286	15	484 > 453	15
Azoxystrobin	ESI ⁺	3.78	20	404.1 > 343.8	23	404.1 > 372	13
Pyrimethanil	ESI ⁺	4.21	37	199.9 > 167.8	25	199.9 > 182.9	26
Dimethomorph	ESI ⁺	4.29	25	388.1 > 165	25	388.1 > 300.9	10
Myclobutanil	ESI ⁺	4.45	20	289.1 > 70	15	289.1 > 125	18
Fipronil-desulfinyl	ESI ⁻	4.81	20	387 > 282	35	387 > 351	30
Fenbuconazole	ESI ⁺	4.91	36	337.1 > 70	30	337.1 > 125	30
Rotenone	ESI ⁺	4.95	30	395.3 > 192.2	34	395.3 > 213.2	33
Fipronil	ESI ⁻	5.00	20	435 > 250	25	435 > 330	17
Tebuconazole	ESI ⁺	5.04	27	353 > 133	18	353 > 297	3
Diflubenzuron	ESI ⁻	5.09	26	309.1 > 155.9	11	309.1 > 288.9	12
Iprodione	ESI ⁺	5.09	15	330 > 245	20	330 > 288	15
Fipronil sulfide	ESI ⁻	5.20	20	419 > 262	26	419 > 383	15
Chlorbenzuron	ESI ⁻	5.39	26	307.4 > 126.3	21	307.4 > 154.1	10
Coumaphos	ESI ⁺	5.44	20	363.3 > 307.0	20	363.3 > 227	25
Propiconazole	ESI ⁺	5.44	25	308.2 > 70	20	308.2 > 205.1	15
Fipronil sulfone	ESI ⁻	5.45	20	451 > 282	25	451 > 415	20
Imazalil	ESI ⁺	5.49	20	297 > 159	15	297 > 255	15
Tebuconazole	ESI ⁺	5.59	25	342.1 > 159.1	20	342.1 > 205.1	15
Phoxim	ESI ⁺	5.69	15	299.1 > 76.8	25	299.1 > 128.9	12
Triflumuron	ESI ⁺	5.74	25	339 > 139.1	35	339 > 156.1	16
Hexaconazole	ESI ⁺	5.79	20	314 > 70	35	314 > 159	20
Prochloraz	ESI ⁺	5.84	25	376.1 > 265.9	20	376.1 > 307.9	15
Diniconazole	ESI ⁺	6.09	25	326.1 > 70	23	326.1 > 159	13
Chlorfenapyr	ESI ⁻	6.40	25	346.9 > 79.1	38	346.9 > 130.9	33
Buprofezin	ESI ⁺	6.91	25	306.4 > 116.1	20	306.4 > 201.1	20
Hexythiazox	ESI ⁺	7.26	24	353 > 168.1	26	353 > 228.1	14
Pendimethalin	ESI ⁺	7.31	20	282.3 > 91	25	282.3 > 212.3	15

Table 2 (continued)

Compound	Ionization mode	t_R (min)	CV (v)	MRM1	CE 1	MRM2	CE 2
Propargite	ESI ⁺	7.46	20	368.1 > 81	15	368.1 > 175.1	15
Flufenoxuron	ESI ⁺	7.55	25	489 > 141.1	20	489 > 158.1	17
Fenpyroximate	ESI ⁺	7.66	20	422.2 > 214.2	15	422.2 > 366.2	15
Chlorfluazuron	ESI ⁺	7.91	33	539.9 > 158	40	539.9 > 383	15
Abamectin	ESI ⁺	8.45	90	895.6 > 449.2	47	895.6 > 751.3	41
Carbosulfan	ESI ⁺	8.61	28	381 > 76	30	381 > 118	23
Spinosad	ESI ⁺	9.10	60	746.5 > 98.2	35	746.5 > 142.2	33
Ivermectin	ESI ⁺	9.35	20	892.5 > 307.3	20	892.5 > 569.4	15
Emamectin benzoate	ESI ⁺	9.91	33	886.4 > 126	39	886.4 > 158	34

were as follows: capillary voltage, 2.8 kV; source temperature, 110 °C; desolvation temperature, 350 °C; desolvation gas (N₂) flow, 900 L h⁻¹, and cone gas (N₂) flow, 50 L h⁻¹. Collision-induced dissociation was performed using argon as collision gas with a flow rate at 0.21 mL min⁻¹. The cone voltage, collision energy parameters, ionization mode, and MRM transition for each pesticide analyzed are shown in Table 2.

Sample and Sample Preparation

Mangoes were obtained from different local markets in Haikou, Hainan Province, China. The fruits were skinned, cored, and homogenized in a food processor, with pulsed action until contents were uniform and had the consistency of smooth paste. Then, the samples were transferred to polypropylene (PP) bottles, labeled, and if necessary, stored at -20 °C until used.

Several steps of the QuEChERS method were optimized in order to obtain the best extraction. Ten grams of pesticide-free mango sample was transferred to a 50-mL polypropylene centrifuge tube; the matrices were spiked with adequate concentrations of standards, according to the spiking level at 0.05 mg/kg. After 30 min, four different buffer systems were added respectively. Four different buffer systems are listed as follows: (A) citrate buffer system (EN method), 10.0 mL acetonitrile and the preweights of 4.0 g anhydrous MgSO₄, 1.0 g NaCl, 1.0 g sodium citrate, and 0.5 g disodium hydrogen citrate sesquihydrate; (B) none buffer system, 10.0 mL acetonitrile and the preweights of 4.0 g anhydrous MgSO₄ and 1.0 g sodium chloride; (C) sodium acetate buffer system (AOAC method), 10.0 mL of 1% (v/v) acetic acid in acetonitrile, and the preweights of 6.0 g anhydrous MgSO₄ and 1.5 g CH₃COONa; and (D) ammonium acetate buffer system, 10.0 mL of 1% (v/v) acetic acid in acetonitrile, and the preweights of 4.0 g anhydrous MgSO₄ and 1.7 g CH₃COONH₄.

Next, the tubes were immediately shaken for 1 min to avoid crystallization and were centrifuged at 4500 rpm for 5 min.

Then, 1 mL of the supernatant was filtered through a 0.22- μ m PTFE filter for UHPLC-MS/MS analysis. Six milliliters of the supernatant was pipetted into a 15-mL dispersive tube containing sorbents.

The optimization of QuEChERS sorbents was carried out by the ammonium acetate buffer system. Briefly, after 10.0 mL acidified acetonitrile and ammonium acetate extraction as mentioned above, five different types of dispersive tubes containing different sorbents were optimized: (i) AOAC method, 400 mg primary secondary amine (PSA), 400 mg GCB, and 1200 mg anhydrous MgSO₄; (ii) EN method, 150 mg PSA, 15 mg GCB, and 900 mg anhydrous MgSO₄; (iii) 60 mg multiwalled carbon nanotubes; (iv) 500 mg Zr-Sep⁺; and (v) 400 mg primary secondary amine (PSA), 80 mg GCB, 1200 mg anhydrous MgSO₄, and 480 mg Zr-Sep⁺.

Then the tubes were shaken by hand for 1 min and centrifuged at 4500 rpm for 5 min. For the analysis by GC-MS/MS, a 2-mL aliquot of the upper layer was evaporated using a vacuum rotary evaporator and reconstituted with 1 mL of *n*-hexane.

Method Validation

The developed method was validated following the European Union SANTE/11945/2015 guidelines, which include recovery, precision, linearity, limits of detection (LODs), and limits of quantification (LOQs). Accuracy and precision analysis was conducted in terms of intra-day, inter-day, and intra-laboratory reproducibility studies. Intra-day accuracy and precision were studied by spiked mango blank samples with a mixture of the investigated pesticides for three levels at 10, 50, and 100 μ g/kg. Each concentration level comprised five replicates. Spiked samples were left for 30 min prior to preliminary treatment. The experiments were repeated in three following days, producing results ($n = 15$) for inter-day accuracy and precision evaluation. Intra-laboratory reproducibility was studied by two different analysts using the same

instrumentation, but using a self-produced solution for spiking procedures and calibration data. In total, 25 replicates ($n = 25$) were analyzed for each spiking level, and overall accuracy (recovery %) and precision (RSD%) are presented in Tables 3 and 4.

The calibration curves were obtained by injecting five levels of reference standard solutions. The matrix-matched calibration curves were constructed by a fortified appropriate volume mixed standard to the blank sample extract. Linearity was acceptable when the regression coefficient (r^2) was > 0.99 with mass accuracy ≤ 5 ppm for all the analytes (SANTE 2015).

The matrix-matched standard was also used to evaluate the matrix effect (ME) for each analyte in green and ripe mango samples. ME values were calculated as the difference between the signal from the pesticide in the matrix and the signal in the injection solvent, divided by the signal in the injection solvent; the derived value was then expressed as a percentage: $\%ME = [(peak\ area\ of\ matrix\ standard - peak\ area\ of\ solvent\ standard) / peak\ area\ of\ solvent\ standard] \times 100$.

For the limit of detection (LOD) and the limit of quantification (LOQ) study, blank mango samples were fortified with lower concentration levels of pesticides (0.1, 0.2, 0.5, 1, 2, 5, 10 $\mu\text{g}/\text{kg}$). LOD was determined by the characteristic ion of the lowest spiked concentration pesticide which shows a chromatographic signal that is at least three times its respective peak to peak noise. LOQ was estimated based on the lowest fortified concentration, which provides suitable recovery and precision (SANTE 2015).

The measurement uncertainty was estimated according to the “top-down” approach using the data obtained in the validation study (Walorczyk 2014; Medina-Pastor et al. 2011). The major uncertainty sources were from precision and accuracy/bias; see Eq. (1). Combined uncertainty was calculated from the measurement uncertainty of the lowest spiking level and the high spiking level, by using Eq. (2). Finally, the relative expanded uncertainty was determined by using the coverage factor $k = 2$ at the confidence level of 95%.

$$u(\%) = \sqrt{RSD^2 + \left(\frac{100-R}{2\sqrt{3}}\right)^2} \quad (1)$$

$$u_c(\%) = \sqrt{u_{0.01(\%)}^2 + u_{0.1(\%)}^2} \quad (2)$$

where $u(\%)$ represents measurement uncertainty, RSD represents relative standard deviation (%), R represents recovery(%), $u_c(\%)$ represents combined measurement uncertainty, $u_{0.01(\%)}$ represents measurement uncertainty at 0.01 mg/kg, and $u_{0.1(\%)}$ represents measurement uncertainty at 0.1 mg/kg.

Results and Discussion

In the study, 113 pesticides were analyzed by using the QuEChERS procedure. The optimized parameters of GC-MS/MS and UHPLC-MS/MS for all the pesticides are shown in Tables 1 and 2, which presented retention time, precursor ions, product ions, and collision energy. Due to the complexity of the green and mature mango matrices and the large number of the pesticides with different physical and chemical properties, the extraction and cleanup procedure must be paid more attention in the study.

Sample Extraction Solvents and Buffer Systems

Solvent extraction is a critical step for the analytical method to reduce the interferences in matrices and get acceptable sensitivity. According to the literature (Nannan et al. 2016), acetonitrile has good recoveries in QuEChERS extraction and the extracts could easily be separated from the aqueous phase through a salting-out effect. Thus, acetonitrile was chosen for the sample extraction. However, acetonitrile was seldom used in GC analysis for its large solvent expansion volume, high toxicity, and low volatility (Li et al. 2008). Therefore, acetonitrile extracts were evaporated using a vacuum rotary evaporation apparatus and redissolved with *n*-hexane for GC-MS/MS analysis.

The buffer systems were composed of different extraction solvents and salts. The different pH values of buffer systems would result in different recoveries for some specific pesticides, which undergo ionization and/or degradation during extraction. Besides, through a hydration pattern and salting out, the salt could increase the solubility of the polar pesticides in the organic phase (Frenich et al. 2008). Therefore, different buffer systems were investigated to improve the sensitivity.

Figures 1 and 2 show the obtained results of the selected pesticides of green mango using different buffer systems. It was demonstrated that the extraction efficiency of pesticides can be enhanced by using acetate buffers (method C and method D). The response areas of carbosulfan is almost zero using method A and B buffer systems. On the other hand, when method C and method D were used for the extraction of the target compound, the signal of carbosulfan dramatically increased. With the acetate buffers, the extraction efficiency of fenthion, bifenthrin, and others were also improved. This was possible because the pH of the green mango matrix was close to 2.0. In the presence of sodium acetate (method C) and ammonium acetate (method D) buffer systems, the pH of the extract gets close to 5.2–5.5, then the responses of some unstable pesticides in acid/neutral condition were improved. Moreover, with the addition of 1% acetic acid-acetonitrile, better extraction of instable pesticides was observed. Although sodium acetate (method C) and ammonium acetate (method D) generally gave preferable results, the best buffer

Table 3 Validation results of the developed method analyzed by GC-MS/MS (*n* = 25)

Pesticides	Green mango												
	Ripe mango					Green mango							
	Recovery (%)		Uncertainty (%)	LOD (µg/kg)	LOQ (µg/kg)	%ME	Recovery (%)		Uncertainty (%)	LOD (µg/kg)	LOQ (µg/kg)	%ME	
10 µg/kg	50 µg/kg	100 µg/kg	(%)	(µg/kg)	(µg/kg)	10 µg/kg	50 µg/kg	100 µg/kg	(%)	(µg/kg)	(µg/kg)	(%)	
Dichlorvos	93 (5)	97 (2)	96 (3)	13	2	6	96 (6)	94 (7)	98 (5)	16	2	7	7
Demeton	88 (8)	95 (7)	92 (4)	20	3	9	99 (3)	103 (4)	101 (5)	12	3	7	9
Ethionphos	97 (7)	96 (6)	103 (5)	17	3	7	107 (7)	103 (5)	105 (7)	20	2	6	13
Cadusafos	93 (9)	95 (7)	105 (8)	25	0.5	2	108 (7)	105 (8)	96 (6)	19	0.6	2	16
Sulfotep	95 (8)	93 (7)	96 (7)	22	2	7	107 (6)	97 (7)	93 (8)	21	2	8	15
Phorate	97 (4)	93 (5)	95 (6)	15	1	5	94 (7)	95 (6)	105 (8)	22	1.5	6	13
Alpha-HCH	99 (2)	98 (3)	100 (2)	6	0.5	2	101 (1)	102 (1)	102 (2)	5	0.5	2	5
Dimethoate	86 (7)	83 (12)	88 (11)	28	2	5	85 (5)	83 (7)	87 (8)	22	1.5	5	8
Beta-HCH	98 (2)	96 (1)	99 (3)	7	0.4	2	98 (5)	98 (2)	101 (3)	12	0.5	2	4
Gamma-HCH	101 (3)	97 (4)	103 (2)	7	0.3	1	95 (2)	96 (2)	101 (3)	8	0.3	1	4
Terbufos	97 (7)	93 (6)	94 (4)	17	2	7	97 (3)	93 (4)	96 (5)	12	1.5	6	8
Fonofos	95 (6)	99 (8)	103 (5)	16	1.5	6	103 (2)	101 (4)	105 (3)	8	1	5	13
Diazinon	94 (8)	98 (8)	96 (7)	22	1.5	5	95 (4)	93 (6)	98 (11)	24	1	5	-4
Delta-HCH	99 (3)	99 (1)	101 (2)	7	0.3	1	101 (3)	97 (2)	96 (2)	8	0.3	1	4
Isazofos	99 (3)	97 (4)	98 (3)	9	1	4	102 (2)	98 (4)	96 (9)	19	0.7	3	15
Parathion methyl	95 (4)	92 (7)	93 (4)	12	0.5	3	101 (7)	103 (6)	95 (7)	20	0.5	3	16
Fenitrothion	97 (6)	93 (7)	92 (6)	18	0.5	3	103 (4)	101 (7)	99 (8)	18	0.5	3	12
Aldrin	96 (5)	93 (6)	93 (7)	18	0.6	5	102 (1.3)	95 (10)	92 (9)	32	1	5	7
Malathion	92 (7)	95 (5)	96 (8)	22	1	5	104 (7)	98 (6)	97 (8)	21	1.5	5	8
Phorate sulfone	95 (5)	92 (3)	95 (6)	16	0.3	1	98 (5)	95 (11)	105 (7)	17	0.25	1	8
Fenthion	93 (10)	88 (12)	85 (12)	33	1	4	92 (7)	86 (6)	95 (8)	22	2	4	7
Parathion	92 (7)	88 (10)	101 (9)	23	1.5	6	102 (5)	95 (6)	104 (7)	17	2	6	6
Chlorpyrifos	69 (5)	68 (8)	69 (5)	29	1	4	69 (3)	72 (4)	68 (7)	30	2	5	3
Triadimefon	84 (9)	87 (12)	86 (8)	27	1.5	5	105 (7)	103 (8)	103 (7)	20	1	4	-7
Isocarbofos	96 (7)	94 (11)	103 (8)	21	2	7	103 (7)	105 (8)	104 (6)	19	2	8	9
Isotenphos methyl	95 (7)	93 (5)	99 (7)	20	2	6	96 (6)	98 (12)	104 (8)	20	2	7	13
Quinalphos	84 (6)	87 (4)	86 (7)	22	2	7	88 (7)	85 (8)	83 (11)	29	1.5	6	12
Phenthoate	104 (5)	95 (4)	97 (6)	16	3	10	93 (8)	98 (7)	99 (6)	20	3	10	15
Procymidone	95 (6)	98 (5)	95 (4)	15	1.5	5	92 (5)	93 (7)	95 (6)	17	1	5	4
Methidathion	95 (7)	96 (5)	94 (8)	22	2	7	94 (7)	92 (5)	92 (8)	22	3	7	9
O,P-DDE	97 (3)	95 (2)	104 (2)	8	0.1	0.5	104 (4)	103 (5)	98 (4)	12	0.1	0.5	2
Endosulfan	99 (7)	96 (5)	108 (5)	18	1.5	5	104 (7)	108 (6)	103 (5)	17	1.5	5	8
Chlordane	95 (8)	92 (7)	104 (6)	20	1	5	89 (10)	86 (13)	95 (10)	29	1	5	9
Fenamiphos	96 (8)	97 (5)	95 (10)	26	1.5	5	93 (7)	102 (5)	106 (6)	19	1	5	13
Dieldrin	91 (7)	93 (8)	102 (6)	19	3	10	104 (2)	101 (5)	96 (6)	13	2	10	16
Profenofos	70 (6)	72 (5)	73 (4)	27	1	5	69 (5)	71 (4)	69 (8)	32	1	5	7
P,P-DDE	96 (4)	93 (5)	97 (3)	10	0.1	0.6	101 (6)	103 (5)	97 (3)	14	0.2	0.8	4
O,P-DDD	97 (4)	95 (3)	93 (3)	11	0.1	0.5	104 (4)	103 (6)	96 (5)	13	0.1	0.5	-6
P,P-DDD	98 (6)	95 (7)	104 (9)	21	0.1	0.5	102 (3)	101 (2)	95 (2)	8	0.1	0.5	4
O,P-DDT	96 (5)	92 (7)	103 (6)	16	0.1	0.5	97 (5)	97 (6)	96 (6)	16	0.1	0.5	5
Triazophos	68 (7)	69 (6)	71 (4)	30	2	6	70 (8)	71 (9)	72 (7)	32	3	7	25
P,P-DDT	95 (3)	95 (4)	102 (6)	14	0.1	0.5	95 (6)	106 (6)	102 (5)	16	0.1	0.5	-4

Table 3 (continued)

Pesticides	Green mango										Ripe mango									
	Recovery (%)					Uncertainty (%)	LOD (µg/kg)	LOQ (µg/kg)	%ME	Recovery (%)					Uncertainty (%)	LOD (µg/kg)	LOQ (µg/kg)	%ME		
	10 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	50 µg/kg					100 µg/kg	10 µg/kg	50 µg/kg	100 µg/kg							
Phosmet	85 (7)	81 (12)	83 (10)	28	1	3	25	86 (7)	83 (8)	84 (11)	29	1	5	24						
Bifenthrin	93 (7)	95 (8)	92 (10)	25	0.5	2	12	102 (6)	98 (9)	107 (7)	19	0.4	2	8						
Fenpropathrin	97 (5)	92 (6)	95 (7)	18	2	7	14	104 (11)	93 (12)	96 (7)	26	1.5	6	9						
Phosalone	72 (10)	75 (12)	69 (11)	38	2	7	24	74 (13)	76 (10)	72 (11)	41	1.5	6	22						
Cyhalothrin	98 (7)	95 (9)	103 (8)	21	2	6	11	101 (7)	103 (11)	92 (8)	22	3	10	8						
Permethrin	90 (8)	87 (12)	95 (10)	26	1.5	6	13	105 (3)	94 (6)	93 (7)	16	2	7	10						
Pyridaben	94 (6)	93 (11)	92 (8)	21	0.8	3	15	102 (7)	95 (6)	95 (6)	19	0.3	1.5	-10						
Cyfluthrin	96 (12)	88 (8)	87 (9)	31	2	6	12	106 (7)	94 (11)	103 (12)	28	2	7	13						
Cypermethrin	95 (13)	91 (8)	92 (7)	30	2	7	13	91 (6)	94 (7)	93 (10)	24	2	8	11						
Flucythrinate	92 (12)	89 (7)	93 (6)	28	2	8	8	92 (7)	87 (14)	95 (13)	30	2.5	9	6						
Fluvalinate	93 (11)	87 (9)	91 (8)	28	2	7	6	85 (7)	89(10)	92 (11)	28	1.5	6	4						
Fenvalerate	94 (7)	85 (8)	91 (6)	19	1.5	6	13	86 (7)	87 (10)	105 (6)	20	2	7	17						
Difenoconazole	86 (7)	89 (9)	85 (6)	22	2	8	14	89 (7)	91 (5)	94 (10)	25	2	7	11						
Deltamethrin	87 (8)	90 (7)	92 (9)	26	1	6	10	92 (15)	86 (9)	93 (11)	38	1	5	7						

system was with ammonium acetate. Thus, ammonium acetate was selected for QuEChERS salt package for green mango pretreatment.

Figures 3 and 4 show the mean responses of the chosen pesticides extracted from 10 g of ripe mango using different buffer systems. It demonstrated no significant signal enhancement for most of the pesticides, except for dichlorvos and carbosulfan. The higher signal of dichlorvos and carbosulfan was observed using sodium acetate (method C) and ammonium acetate (method D). For the responses of pesticides, method C was comparable to method D. Therefore, the ammonium acetate buffer system (method D) was added in the ripe mango pretreatment to improve the extraction efficiency in the study.

Evaluation of Purification Sorbents

The cleanup step was important for target analysis because the matrices of mangoes were complex. Besides, due to a few drawbacks in maintaining GC-MS/MS compared with UHPLC-MS/MS, the cleanup steps were carried out only for solution which was injected into GC-MS/MS in this study. Various sorbents including GCB, PSA, Zr-Sep⁺, and multiwalled carbon nanotubes were tested; these sorbents were considered useful for removing special coextractive substances. PSA was a sorbent exhibiting retaining organic acids, sugars, and pigments (Nieto-Garcia et al. 2015). GCB could be useful to remove sterols and pigments such as carotenoid, which is the main component in mango. Zr-Sep⁺ is a sorbent which enables Lewis acid/base interactions for efficient interference removal (Rejczak and Tuzimski, 2017a, b). Multiwalled carbon nanotubes exhibited hydrophobicity and high surface area, which could remove lots of interferents (Deme and Upadhyayula 2015). Therefore, in order to find an efficient cleanup method to increase the lifetime of GC components from the column and inlet liner, we evaluated the five approaches by employing the following: (i) AOAC method, 400 mg PSA + 400 mg GCB; (ii) EN method, 150 mg PSA + 15 mg GCB; (iii) 60 mg multiwalled carbon nanotubes; (iv) 500 mg Zr-Sep⁺; and (v) 400 mg PSA + 80 mg GCB + 480 mg Zr-Sep⁺. The experiments were carried out at the concentration level of 0.05 mg/kg by adding the blank mango samples with the tested pesticides. The samples were extracted with 1% acetic acid-acetonitrile and salting out by anhydrous MgSO₄ and CH₃COONH₄, and then underwent dispersive SPE cleanup by the five methods. A total of 56 compounds for GC-MS/MS were analyzed by different purification sorbents. It was a qualified result when the recoveries were between 70 and 120% and RSD < 20%, as stipulated in the EU method validation criteria of SANTE, 2015. The number of compounds with qualified result can be observed in Fig. 5.

Maximum recoveries of the pesticides were achieved when 400 mg PSA and 400 mg GCB were used as sorbents. But when using 400 mg PSA and 400 mg GCB as sorbent, the

Table 4 Validation results of the developed method analyzed by UHPLC-MS/MS ($n=25$)

Pesticides	Ripe mango															
	Recovery (%)					Uncertainty (%)					%ME					
	10	50	100	LOD ($\mu\text{g/kg}$)	LOQ ($\mu\text{g/kg}$)	10	50	100	LOD ($\mu\text{g/kg}$)	LOQ ($\mu\text{g/kg}$)	10	50	100	LOD ($\mu\text{g/kg}$)	LOQ ($\mu\text{g/kg}$)	%ME
Cyromazine	87 (10)	93 (12)	85 (13)	1	3	35	88 (11)	84 (9)	1.5	5	27	88 (11)	84 (9)	1.5	5	17
Aldicarb sulfoxide	96 (5)	92 (8)	95 (7)	1.5	5	18	100 (2)	97 (3)	1	4	8	100 (2)	97 (3)	1	4	-59
Aldicarb sulfone	98 (5)	94 (4)	95 (7)	1	4	17	102 (4)	98 (3)	1	3	7	102 (4)	98 (3)	1	3	-9
Methomyl	95 (3)	102 (5)	97 (4)	1	3	11	90 (5)	94 (6)	1.5	5	17	103 (5)	94 (6)	1.5	5	-26
Propamocarb	96 (9)	89 (10)	88 (6)	0.01	0.05	23	90 (6)	94 (7)	0.02	0.08	17	94 (7)	94 (5)	0.02	0.08	-27
Imidacloprid	95 (8)	98 (6)	92 (4)	0.2	0.6	19	102 (4)	99 (5)	0.1	0.6	18	102 (4)	99 (5)	0.1	0.6	-29
Thiamethoxam	96 (5)	93 (3)	101 (4)	2	6	13	101 (4)	102 (3)	2.5	7	11	102 (3)	98 (4)	2.5	7	-35
3-Hydroxycarbofuran	99 (7)	95 (6)	94 (3)	1	4	16	100 (5)	96 (4)	1.5	5	13	102 (6)	96 (4)	1.5	5	23
Acetamiprid	85 (9)	94 (6)	96 (5)	0.01	0.05	22	94 (6)	92 (10)	0.02	0.07	28	92 (10)	92 (7)	0.02	0.07	-4
Carbendazim	100 (5)	97 (6)	94 (7)	0.05	0.15	18	95 (9)	94 (8)	0.06	0.2	23	94 (8)	92 (7)	0.06	0.2	210
Aldicarb	97 (3)	94 (4)	95 (5)	1	4	12	93 (7)	95 (4)	1	3	19	95 (4)	96 (6)	1	3	-26
Thiabendazole	103 (7)	95 (5)	96 (6)	0.05	0.1	19	92 (10)	96 (8)	0.04	0.15	26	93 (7)	96 (8)	0.04	0.15	71
Carbofuran	97 (6)	94 (5)	98 (8)	0.06	0.2	20	96 (6)	94 (4)	0.07	0.3	16	94 (4)	98 (5)	0.07	0.3	17
Carbaryl	92 (5)	94 (6)	94 (4)	0.3	1	14	106 (8)	107 (7)	0.2	1	21	106 (8)	93 (6)	0.2	1	-7
Phorate sulfoxide	93 (9)	96 (5)	104 (5)	1	3	21	103 (11)	98 (6)	1	4	24	103 (11)	94 (5)	1	4	19
Pirimicarb	96 (11)	98 (7)	96 (5)	0.02	0.1	24	96 (9)	103 (6)	0.03	0.1	22	98 (5)	103 (6)	0.03	0.1	24
Isoprocarb	94 (10)	96 (7)	92 (6)	0.2	0.6	24	93 (10)	97 (5)	0.3	1	23	95 (7)	97 (5)	0.3	1	22
Chlorimeform	95 (7)	94 (5)	92 (3)	0.1	0.4	16	100 (10)	96 (5)	0.15	0.5	22	96 (5)	97 (4)	0.15	0.5	-26
Atrazine	94 (12)	101 (7)	96 (5)	0.04	0.1	26	95 (10)	102 (5)	0.03	0.1	22	102 (5)	98 (4)	0.03	0.1	36
Metalaxyl	95 (11)	98 (6)	96 (8)	0.05	0.2	27	91 (7)	95 (4)	0.06	0.2	18	95 (4)	97 (5)	0.06	0.2	-18
Chlorantraniliprole	105 (7)	104 (6)	99 (5)	0.2	0.7	17	102 (9)	106 (6)	0.2	0.6	21	106 (6)	97 (5)	0.2	0.6	-22
Azoxystrobin	120 (11)	126 (9)	124 (6)	2	6	30	123 (8)	124 (6)	1.5	5	28	126 (7)	124 (6)	1.5	5	33
Pyrimethanil	97 (7)	95 (5)	99 (6)	0.1	0.5	19	103 (6)	105 (7)	0.1	0.5	16	103 (6)	104 (5)	0.1	0.5	6
Dimethomorph	103 (6)	99 (2)	98 (2)	0.03	0.1	13	106 (10)	103 (7)	0.04	0.2	23	103 (7)	96 (5)	0.04	0.2	-4
Myclbutamil	96 (11)	98 (10)	92 (8)	0.1	0.3	28	96 (7)	96 (6)	0.15	0.5	19	98 (5)	96 (6)	0.15	0.5	8
Fipronil desulfinyl	103 (7)	96 (6)	95 (4)	0.2	0.6	16	100 (6)	95 (5)	2	7	16	100 (6)	95 (5)	2	7	13
Fenbuconazole	96 (6)	97 (3)	98 (4)	0.2	0.6	15	101 (5)	102 (4)	0.25	0.7	12	102 (4)	99 (3)	0.25	0.7	26
Rotenone	100 (10)	93 (7)	101 (6)	0.2	0.6	23	95 (12)	94 (8)	0.3	1	30	94 (8)	96 (9)	0.3	1	14
Fipronil	98 (7)	102 (5)	101 (3)	1.5	5	15	102 (8)	103 (5)	2	5	20	103 (5)	99 (6)	2	5	5
Tebuconazole	99 (8)	98 (4)	95 (5)	3	10	19	94 (10)	97 (5)	2.5	8	24	97 (5)	95 (6)	2.5	8	-22
Diflubenzuron	96 (12)	100 (4)	102 (5)	3	10	26	103 (7)	102 (4)	3	10	15	103 (7)	101 (3)	3	10	-16
Iprodione	123 (7)	122 (3)	125 (5)	0.2	0.8	24	124 (7)	123 (4)	0.3	1	24	123 (4)	126 (5)	0.3	1	-5
Fipronil sulfide	102 (9)	96 (6)	101 (4)	1	3	20	105 (7)	101 (5)	1	3.5	17	101 (5)	96 (4)	1	3.5	-8
Chlorbenzuron	100 (7)	98 (6)	96 (5)	0.2	0.7	17	90 (7)	98 (6)	1.5	7	18	98 (6)	103 (5)	1.5	7	-49
Coumaphos	101 (8)	99 (5)	96 (4)	0.02	0.07	18	101 (7)	96 (6)	0.03	0.1	16	101 (7)	95 (4)	0.03	0.1	21
Propiconazole	103 (8)	96 (10)	105 (5)	0.2	0.6	43	103 (4)	105 (7)	0.15	0.5	13	105 (7)	98 (5)	0.15	0.5	19
Fipronil sulfone	101 (3)	99 (4)	100 (2)	2	5	7	98 (5)	101 (3)	1.5	4	11	101 (3)	97 (2)	1.5	4	22
Imazalil	102 (7)	97 (8)	96 (5)	0.2	0.6	17	101 (4)	98 (2)	0.1	0.4	10	101 (4)	99 (3)	0.1	0.4	24
Tebuconazole	104 (5)	97 (3)	96 (8)	0.1	0.5	19	103 (7)	97 (6)	0.15	0.6	21	103 (7)	98 (8)	0.15	0.6	26
Phoxim	103 (8)	97 (5)	95 (6)	0.2	1.0	20	102 (6)	96 (4)	3.5	10	14	102 (6)	103 (3)	3.5	10	8
Triflumuron	99 (8)	95 (7)	96 (6)	0.5	1.5	20	104 (8)	98 (7)	0.4	2	19	104 (8)	99 (5)	0.4	2	-11
Hexaconazole	103 (9)	96 (7)	98 (6)	2	6	22	90 (11)	104 (6)	1.5	6	25	104 (6)	95 (5)	1.5	6	-28
Prochloraz	103 (7)	97 (5)	96 (4)	0.2	0.8	16	107 (12)	103 (6)	0.15	0.6	26	103 (6)	97 (5)	0.15	0.6	7

Table 4 (continued)

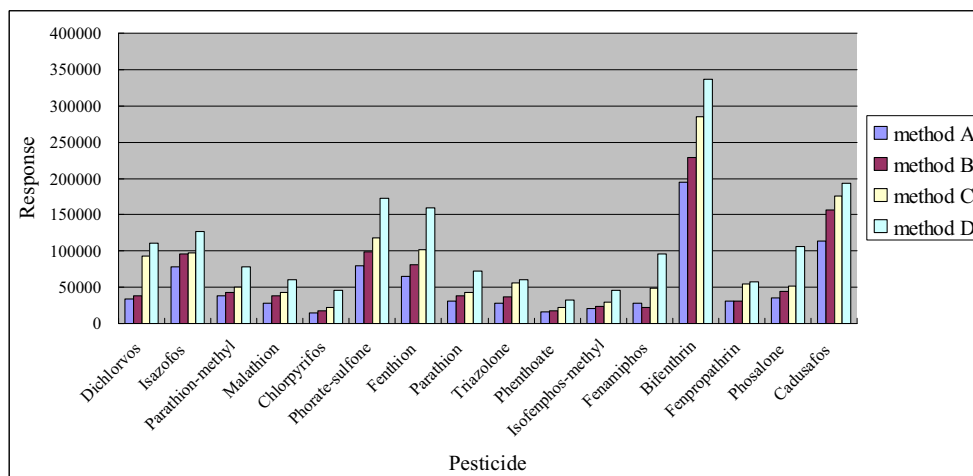
Pesticides	Ripe mango											
	Green mango					Ripe mango						
	Recovery (%)		Uncertainty (%)	LOD (µg/kg)	LOQ (µg/kg)	%ME	Recovery (%)		Uncertainty (%)	LOD (µg/kg)	LOQ (µg/kg)	%ME
10 (µg/kg)	50 (µg/kg)					10 (µg/kg)	50 (µg/kg)					
Diniconazole	104 (9)	96 (6)	20	0.1	0.4	5	104 (11)	97 (5)	25	0.15	0.4	13
Chlorfenapyr	106 (8)	94 (6)	19	0.1	0.5	-22	96 (9)	100 (5)	20	0.2	0.6	9
Buprofezin	96 (10)	97 (7)	22	0.1	0.5	-4	101 (8)	96 (5)	18	0.15	0.6	6
Hexythiazox	93 (7)	92 (5)	19	2	6	-23	95 (12)	97 (8)	26	1.5	5	-13
Pendimethalin	92 (13)	86 (11)	36	2	6	-28	100 (9)	97 (7)	22	1.5	5	-44
Propargite	91 (11)	88 (12)	31	3	10	-18	94 (13)	96 (10)	36	3	10	-17
Flufenoxuron	101 (9)	94 (7)	22	0.3	1	-47	102 (12)	98 (5)	27	0.25	1	-26
Fenpyroximate	92 (11)	88 (13)	29	0.1	0.5	-69	104 (10)	100 (8)	25	0.15	0.5	-49
Chlorfluazuron	96 (11)	96 (10)	27	1	5	-57	100 (10)	95 (12)	27	1.5	6	-27
Abamectin	104 (8)	103 (6)	19	0.15	0.5	-85	104 (13)	103 (6)	33	0.1	0.6	-35
Carbosulfan	65 (7)	57 (4)	37	0.02	0.06	-59	63 (8)	58 (3)	38	0.03	0.1	-34
Spinosad	93 (14)	88 (12)	32	0.05	0.2	-32	102 (9)	104 (7)	22	0.06	0.3	-16
Ivermectin	93 (10)	96 (11)	26	0.2	0.6	-48	94 (10)	93 (7)	23	0.15	0.5	-50
Emamectin benzoate	100 (11)	95 (9)	25	0.03	0.1	3	102 (12)	97 (9)	28	0.02	0.1	7

recoveries of profenofos, triazophos, chlorpyrifos, and phosalone were between 60 and 70%. Their low recoveries could be caused by absorption of planar molecule pesticides by GCB (Anastassiades et al. 2003; Slowik-Borowiec et al. 2015). Besides, in comparison with the EN method, efficiency of the purification using the AOAC method could be confirmed through visible decoloration of the extracts. Hence, we selected 400 mg PSA and 400 mg GCB as cleanup sorbent for further experiments.

Matrix Effect

The matrix effect should be calculated during method development, since specific co-extracted interfering components with analytes result in enhancement or suppression of the analytic signal, leading to overestimation or underestimation of the analyte concentrations (Rejczak and Tuzimski 2017b). There are several factors that affect the matrix effect, especially the nature of the matrix and the efficiency of sample preparation. In this study, the matrix effect (suppression or enhancement of exceeding 25%) is believed to significantly affect quantitative analytical results (Zhu et al. 2014). An assessment of matrix effects in raw and ripe mangoes matrices was carried out by comparing the detector response of the analyte in the specified matrices to the signal in pure solvent. The values of the matrix effect (%ME) are presented in Tables 3 and 4. For GC-MS/MS analysis, %ME values ranged from 2 to 25% in green mango and %ME values ranged from -10 to 25% in ripe mango. No pesticide exhibited a significant matrix effect in green and ripe mango for GC-MS/MS analysis. It is possible that the cleanup pretreatment for GC-MS/MS is relatively complete. For UHPLC-MS/MS analysis, the strongest suppression of 85% was shown for abamectin and the strongest signal enhancement of 186% was determined for carbendazim in green mango. In the case of ripe mango, the strongest signal suppression (59%) for aldicarb sulfoxide and enhancement (210%) for carbendazim are observed. For a better understanding of ME% by UHPLC-MS/MS analysis, the results were classified into three groups: no significant matrix effect (± 0 –25%), medium matrix effect (± 26 –40%), and high matrix effect (higher than ± 41 %) (Fig. 6a, b). No significant matrix effect was shown for 63 and 61% of the analytes for raw and ripe mangoes by UHPLC-MS/MS analysis. Medium matrix effect was shown for 16 and 26% of the analytes for raw and ripe mangoes by UHPLC-MS/MS analysis. A high matrix effect was shown for 21 and 12% of the analytes for raw and ripe mangoes by UHPLC-MS/MS analysis. In general, the matrix effect for UHPLC-MS/MS analysis is a little stronger than that for GC-MS/MS analysis. The most effective way to avoid matrix effects is to apply matrix-matched calibration standards. The results indicated that it is necessary to introduce matrix-matched calibration for UHPLC-MS/MS analysis to reduce the matrix effect, and

Fig. 1 Response of the selected pesticides extracted from 10 g of green mango using different buffer systems and analyzed by GC-MS/MS



directly employ solvent-matched calibration for GC-MS/MS analysis to save time, labor, and solvent.

Method Validation

The proposed QuEChERS method was evaluated for 113 pesticides in raw and ripe mango matrices. A validation study was carried out by accuracy (Recovery%) and precision (RSD%) including intra-day, inter-day (three following days), and intra-laboratory reproducibility. Overall accuracy and precision ($n = 25$) are presented in Tables 3 and 4.

Overall recoveries for most of pesticides were between 70 and 120% with RSD below 20% as shown in Tables 3 and 4. Some of the pesticides (chlorpyrifos, profenofos, triazophos, phosalone) had recoveries higher than 68%, but lower than 76% with RSD below 13%. The recoveries of carbosulfan were between 56 and 65% in ripe and raw mango matrices with RSD below 8%. Two of the

pesticides of iprodione and azoxystrobin had recoveries higher than 120%, but lower than 130%, with RSD below 11%.

Linearity was evaluated in all matrices, and the linear range was studied at five concentration levels, between 5 and 500 $\mu\text{g}/\text{kg}$. Good linearity guaranteed accurate quantification for all target pesticides, as the coefficients of determination (R^2) equal or higher than 0.99.

The LODs and LOQs were also investigated to evaluate the performance of the present method. LOD values were calculated at a signal to noise ratio greater than or equal to 3 ($S/N \geq 3$), and LOQ was estimated based on the minimum fortified concentration, which has been demonstrated to be accurately quantified by the method (SANTE 2015). In the raw mango matrix, LODs and LOQs ranged from 0.01 to 4 $\mu\text{g}/\text{kg}$ and from 0.05 to 10 $\mu\text{g}/\text{kg}$, respectively. In ripe mango, 113 pesticides had LODs that ranged from 0.02 to 3.5 $\mu\text{g}/\text{kg}$, and LOQs from 0.07 to 10 $\mu\text{g}/\text{kg}$, respectively. The values are presented in Tables 3 and 4.

Fig. 2 Response of the selected pesticides extracted from 10 g of green mango using different buffer systems and analyzed by UHPLC-MS/MS

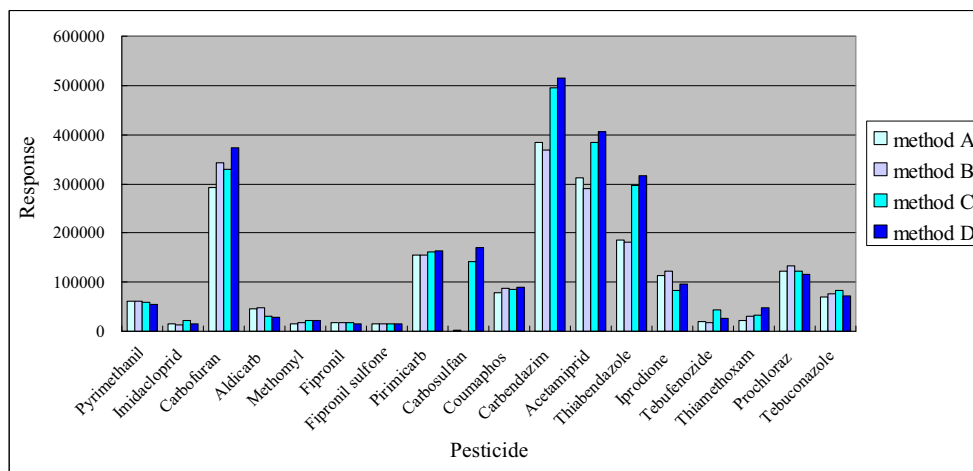
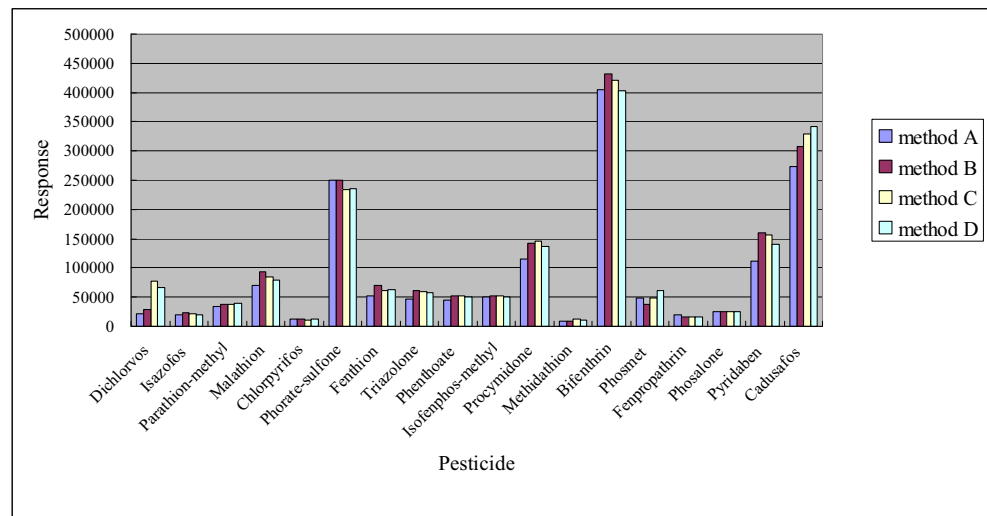


Fig. 3 Response of the selected pesticides extracted from 10 g of ripe mango using different buffer systems and analyzed by GC-MS/MS



There were many sources of uncertainties derived from steps of the presented method. The “top-down” approach could simplify the calculation procedure of uncertainties and evaluate the measurement uncertainties of all analytes using the data from the validation study including recovery and RSD; see Eqs. (1) and (2). The expanded measurement uncertainties were obtained by multiplying the combined standard uncertainty by 2 (coverage factor $k = 2$, i.e., 95% confidence level). The results are given in Tables 3 and 4. As seen, in the case of raw mango, the pesticides had uncertainties between 6% (alpha-HCH) and 38% (phosalone) with the overall average uncertainty of 21%. In the case of ripe mango, the pesticides had uncertainties between 5% (alpha-HCH) and 41% (phosalone) with the overall average uncertainty of 21%. In the green and ripe mango matrix, the majority of the compounds had uncertainties < 30%. The highest uncertainty

value was obtained for phosalone in consequence of poor recovery and high RSD of absorption of planar molecule pesticides by GCB. The expanded measurement uncertainty values below 50% for all the analytes proved that the method is suitable for the determination of the target pesticides in green and ripe mango samples.

Comparison of Proposed Method with Other Analytical Methods

It was the first time to propose the QuEChERS method for different maturity levels of mangoes. The method was comparable with other published multiresidue methods for the mango matrix in terms of the method validation parameters (Sivaperumal et al. 2017). Different cleanup sorbents were evaluated in terms of GCB, PSA, and relatively new sorbents

Fig. 4 Response of the selected pesticides extracted from 10 g of ripe mango using different buffer systems and analyzed by UHPLC-MS/MS

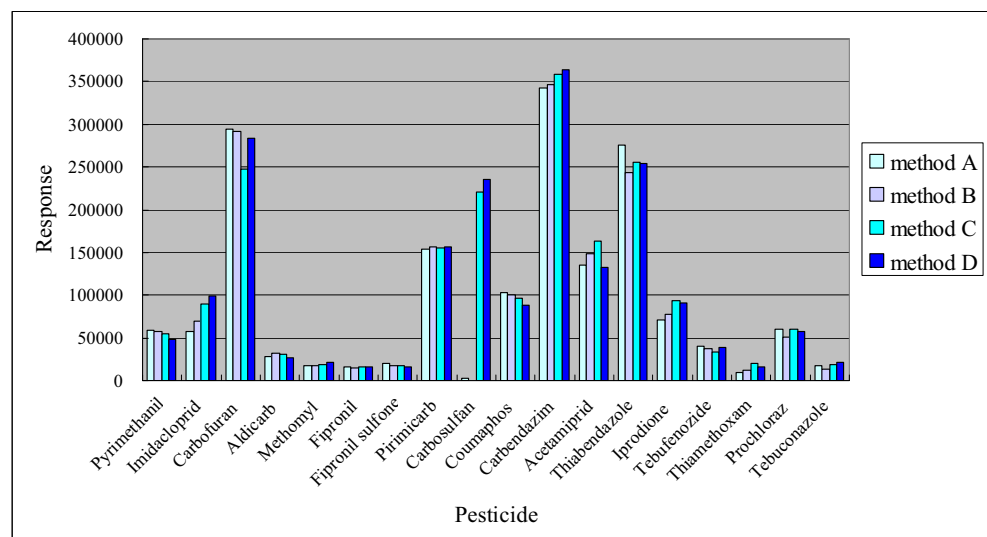
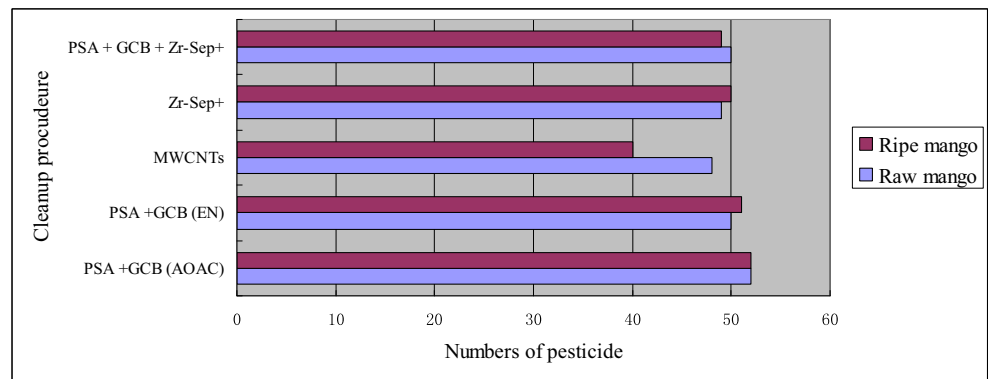


Fig. 5 Numbers of pesticide with recovery values between 70 and 120% analyzed by GC-MS/MS

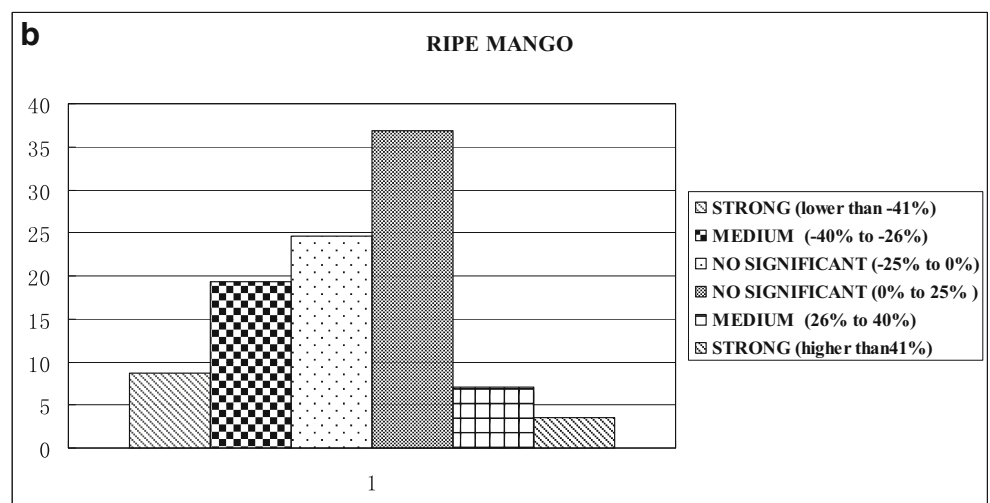
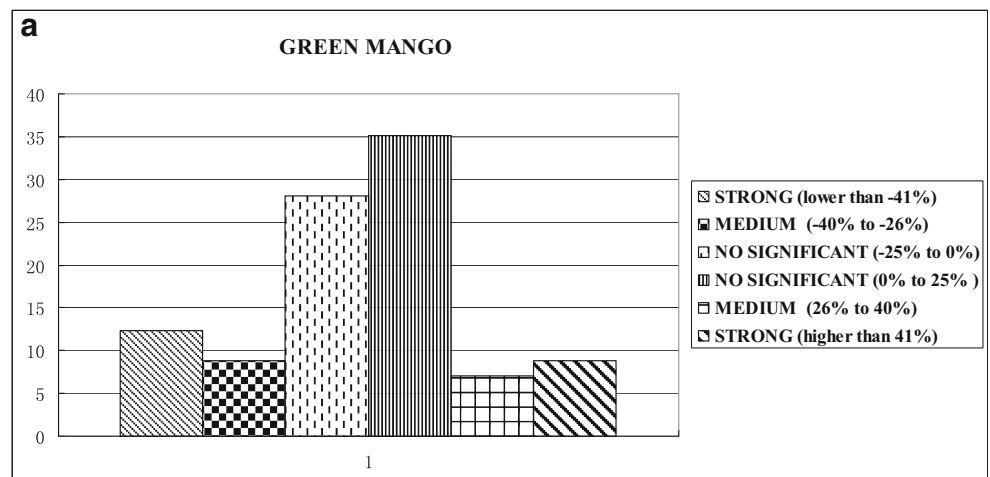


such as Zr-Sep⁺ and multiwalled carbon nanotubes. In addition, the proposed method has advantages in determining the highest number of pesticides ($n = 113$). Remarkably, the proposed method showed better accuracy, precision, and measurement uncertainty for green and ripe mango. Thus, it was confirmed that the proposed method is efficient for screening and quantitation of residues in different maturity level of mango matrices.

Real Sample Analysis

Forty-five samples from local markets were determined to validate the application of the established method. One blank sample fortified with 100 $\mu\text{g}/\text{kg}$ was used for quality control. It was demonstrated that a few of mango samples contain pesticide residues, including chlorpyrifos, imidacloprid, cypermethrin, difenoconazole, cyhalothrin, thiabendazole,

Fig. 6 **a** Percentage values of matrix effect (%ME) observed in green mango by UHPLC-MS/MS analysis. **b** Percentage values of matrix effect (%ME) observed in ripe mango by UHPLC-MS/MS analysis



azoxystrobin, and carbendazim. Chlorpyrifos was found in sample no. 7 (68 µg/kg), no. 10 (110 µg/kg), no. 43 (110 µg/kg), and no. 120 (120 µg/kg), at concentrations higher than the MRLs established by EU (50 µg/kg) in mangoes. Imidacloprid was detected in 20% of the samples at values lower than 200 µg/kg. But China did not set MRLs (maximum residue limits) for chlorpyrifos and imidacloprid in mangoes at present (China National Food Safety Standard 2016). The two insecticides were widely used in crop growth. Cypermethrin was detected in 17 samples at a trace level (< 200 µg/kg), which was lower than MRLs set by the China National Food Safety Standard (700 µg/kg) in mangoes. This is an insecticide widely used in fruits and vegetables. Sample no. 8 showed a positive result of difenoconazole (86 µg/kg), which was fungicide and exceeded the MRL of the China National Standard (70 µg/kg). Cyhalothrin was found in no. 37 (140 µg/kg) and no. 43 (50 µg/kg), but the concentrations were lower than MRLs of mangoes (200 µg/kg). Six samples were detected to contain thiabendazole and azoxystrobin, but the concentration level was very low (< 50 µg/kg). The MRLs of thiabendazole and azoxystrobin are 5 and 1 mg/kg in mangoes, respectively. Finally, carbendazim was detected in 40% of samples and the no. 23 sample (0.8 mg/kg) above the MRL (0.5 mg/kg). Carbendazim was the main degradation product of benomyl and thiophanate methyl. Thiabendazole, azoxystrobin, and carbendazim are usually applied in post-harvest on mangoes to protect them from decay caused by various fungal pathogens.

Conclusion

The proposed QuEChERS extraction method using acidified acetonitrile and ammonium acetate proved to be suitable for the extraction of 113 pesticides in green/ripe mangoes. The optimization conditions of pretreatment revealed that the use of ammonium acetate and 400 mg PSA + 400 mg GCB is sufficient for extraction and cleanup of 56 pesticides, which were analyzed by GC-MS/MS. At the same time, the use of ammonium acetate without cleanup is effective for 57 pesticides, which were analyzed by UHPLC-MS/MS. With the advantages of high sensitivity, simple maintenance, and strongly withstanding matrix interference, UHPLC-MS/MS enabled an unnecessary cleanup, which prevents from being more time-consuming and from susceptibility to analytical errors.

From the study, pesticides for GC-MS/MS analysis did not perform a significant matrix effect and the values of the matrix effect were in the range of $\pm 25\%$. However, for pesticides used in UHPLC-MS/MS analysis, the values of the matrix effect observed in the range -85 to 186% and -59 to 210% in raw and ripe mangoes samples, respectively. Therefore, the use of solvent solution standard is enough to quantify those

pesticides for GC-MS/MS. In order to compensate the matrix effect, matrix-matched standards were used to calculate the concentration of pesticides for UHPLC-MS/MS analysis.

The optimized QuEChERS extraction method combined with GC-MS/MS and UHPLC-MS/MS for the determination of 113 pesticides in raw/ripe mangoes has considerable superiorities in respect of being high-throughput, simple, fast, and cheap. This method gave very good results including recovery, precision, linearity, LOD, and LOQ. In conclusion, the modified method meets the China criteria, and thus is useful for routine analyses to trace level quantification of the pesticide residues from different maturity degrees of mango.

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Compliance with Ethical Standards

Conflict of Interest Pingping Li declares that she has no conflict of interest. Yun Duan declares that he has no conflict of interest. Huilin Ge declares that he has no conflict of interest. Yue Zhang declares that she has no conflict of interest. Xiaofang Wu declares that she has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Informed consent is not applicable for this study.

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