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Automatic single-step quick, easy, cheap, effective, rugged and safe sample preparation devices for analysis of pesticide residues in foods

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ABSTRACT

In this research, the manual two-step QuEChERS approach has been streamlined and automated into a one-step method using a cleanup tube fitted within an extraction tube. A novel automatic QuEChERS combination have been developed to simplify the QuEChERS procedures and improve sample preparation efficiency. This combination integrates QuEChERS procedures into a single run *via* the use of a vortex vibration-centrifuge device and a centrifuge filtration tube. To validate the efficiency of our automatic QuEChERS device, 270 pesticides were analyzed in plant origined foods including celery, tomatoes, leeks, eggplants, grapes, corn, green tea, and soybean oil using this automatic platform. The results were then compared with those obtained using the manual QuEChERS method. Different parameters were validated and compared including recovery, linearity, repeatability and limits of quantification (LOQ). Satisfactory results, comparable to results obtained using the manual QuEChERS method were obtained. The average recoveries ranged between 70% and 120% for most pesticides with associated relative standard deviations (RSDs) <20% (n = 5) indicating satisfactory accuracy and repeatability. An LOQ of 2 μg/kg was obtained for most pesticides present in celery and corn matrices, and the correlation coefficients (r^2) were >0.990 within a linearity range of 2–500 μg/kg. Compared to manual QuEChERS, this novel automatic QuEChERS device and combination could significantly improve the sample preparation efficiency for the multiresidue analysis of pesticides.

1. Introduction

Food crops are important sources of human nutrition. To increase the production of crops, pesticides are frequently applied in modern agriculture [1], playing an important role in keeping crops safe from weeds, insects, rodents and damage from other pests [2,3]. However, using pesticides inappropriately in agricultural production may lead to unacceptable levels of pesticides in the food material, which can pose potential threats to human health [4,5]. To fully ensure consumer protection, the European Union and most countries worldwide (for example, China, the United States and Japan) have established maximum pesticide residue levels (MRLs) for food merchandise. Thus, to ensure food safety, monitoring the level of pesticide residues in crops is crucial [6].

Multiresidue analysis in complicated matrices is considered a demanding task, owing to a wide range of physicochemical properties and the trace-level content of pesticides. In this context, an efficient and convenient sample preparation technique is necessary to remove interfering substances, so that accurate determination and quantification of analytes in complicated matrices may be achieved [7]. Different sample preparation techniques for the extraction of pesticides from different matrices have been explored. For instance, liquid-liquid extraction (LLE) [8], solid-phase extraction (SPE) [9,10], gel permeation chromatography (GPC) [11], solid-phase microextraction (SPME) [12], and matrix solid-phase dispersion (MSPD) [13] have all been used to extract pesticide residues. It is undeniable that these methods are effective, however their utility is limited, as they are solvent consuming, time consuming and require intense labor.

In response to this, a sample preparation approach known as QuEChERS (quick, easy, cheap, effective, rugged, and safe), developed by Anastassiades et al. [14,15], has obtained approval in the scientific community. The method consists of two steps, referred to as the salting out and clean-up steps. Generally, pesticides are extracted with acetonitrile, while salting out to remove the water, followed by clean-up using dispersive solid phase extraction (d-SPE) [6]. Since then, many studies have focused on modifications to the QuEChERS method in order to expand the scope of matrices covered [16–18].

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The QuEChERS procedure combined with LC–MS/MS or GC–MS/MS determination has been used successfully in multiresidue analyses for screening the presence of pesticides in vegetables, fruits, and cereals [7,19–22]. Zheng et al. [23] proposed a "one-step" QuEChERS method for pesticide residue analysis in freshly squeezed juices prepared from fruits and vegetables. Luo et al. [24] developed the use of magnetic graphene as a QuEChERS adsorbent for the determination of organochlorine pesticide residues in tobacco. Recent efforts have focused on the development of new devices or techniques combined with the QuEChERS extraction approach to optimize extraction procedures and improve efficiency. For example, a multiplug filtration clean-up (M-PFC) based on multiwalled carbon nanotubes, which used a multiplug filtration clean-up column coupled with a syringe, was proposed by Zhao et al. [25]. Additionally, Lehotay et al. developed an automated mini-cartridge solid-phase extraction (mini-SPE) clean-up coupled with LPGC–MS/MS analysis for diverse types of analytes and foods [26]. Although, the techniques above improved the experimental efficiency of pesticide determination to some extent, optimizations to fully achieve convenient operation and good repeatability of results are still required.

The aim of this study was to evaluate and validate an automatic QuEChERS procedure for sample preparation, and to demonstrate the feasibility of the automatic QuEChERS methodology when combined with liquid chromatography–tandem mass spectrometry (LC–MS/MS) and gas chromatography-triple quadrupole mass spectrometry (GC–MS/MS). The study compares the automatic method with the manual QuEChERS method in simultaneously determining the content of 270 pesticides in different matrices. After validation, the automatic method was successfully applied in real samples analysis.

2. Materials and methods

2.1. Materials and reagents

HPLC-grade acetonitrile, acetone, and ethyl acetate were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Water was freshly purified by a Milli-Q (Millipore, Billerica, MA, USA) system. QuEChERS extraction salt packets (Anhydrous $MgSO_4$, 4 g; sodium chloride, 1 g; sodium citrate, 1 g; sodium hydrogencitrate sesquihydrate, 0.5 g), dispersive solid-phase extraction salt and sorbent (PSA, C_{18} and GCB), polypropylene centrifuge tubes, 50 mL volume for initial extraction, and 15 mL volume for the d-SPE step in manual QuEChERS, and ceramic homogenizer were purchased from Agilent (Agilent Technologies, Lake forest, CA).

Pesticide standards, all >98% purity, were purchased from Chem Service (West Chester, PA, USA) and Dr. Ehrenstorfer (Ausberg, Germany). Stock standard solutions containing 5 mg/L of each pesticide and internal standard solutions (heptachlor epoxide, 1 μg/mL) for GC–MS/MS analysis were prepared in acetone and stored at −20 °C until use.

2.2. Automatic QuEChERS device method

The automatic QuEChERS method requires a vortex vibration-centrifuge device and a sample preparation tube (Benli Technologies, China). The sample preparation tube integrates an outer tube and an inner tube to realize the functions of a sample extraction tube and dispersive solid phase extraction (d-SPE) tube required in the manual QuEChERS methodology. The diagram of the sample preparation tube is given in Fig. 1. The vortex vibration-centrifuge device has vortex vibration and centrifuge functions employing an eccentric shaft to realize sample extraction and phase extraction. The diagram of this device has been given in Fig. S1 (see Supplementary material) and the operation mode of the automatic QuEChERS combination is shown in Supplementary Videos S1 and S2.

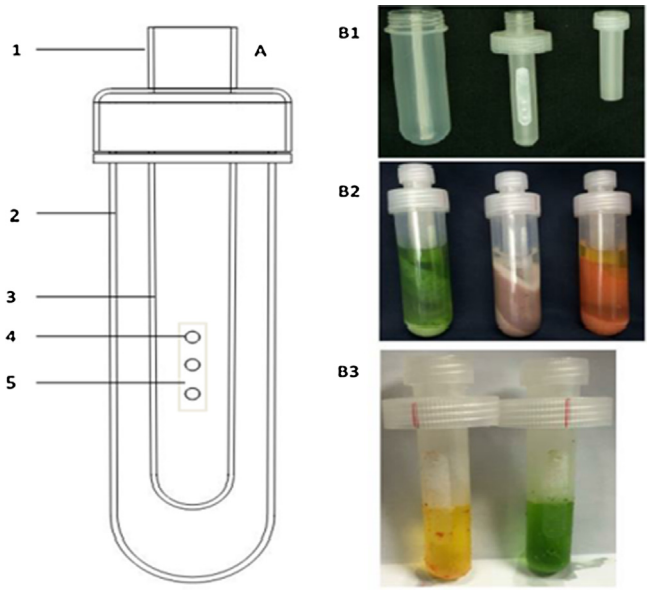

Fig. 1. Diagram of sample extractio tube. A: 1, screw cab; 2, outer tube, for sample extraction. Transfer sample into the outer tube, add extraction buffer salt and Zirconium beads; 3, inner tube, for dispersive solid phase extraction. Extract into the inner tube containging d-SPE sorbents and Zirconium beads; 4, holes on inner tube, to let extract pass through; 5, PTFE membrance, 0.22 μm, only extract (acetonitrile) can pass through the membrance under centrifugal force because of its hydrophobic characterisitc. B1: outer tube, inner tube and screw cab of the sample prapration tube. B2: sample after extraction. B3: final extract in the inner tube.

2.3. LC–MS/MS conditions

LC–MS/MS analysis was performed using a QTRAP 4500 system (Sciex) and UHPLC system (Waters). An HSS $T3C_{18}$ column (2.1 × 100 mm, 1.8 μm), obtained from Waters, was used for analyte separation with a constant flow rate of 0.3 mL/min. The injection volume was 5 μL. Mobile phase A was methanol, while mobile phase B was 2 mM ammonium acetate in water. The gradient elution was programmed as follows: initially phase B was 85% in 0–0.5 min and declined to 50% at 2.5 min, followed by a ramp to 5% within 10 min, held for 2 min, then returned to initial conditions by a 0.1 min ramp, and kept for 3 min to equilibrate the column, yielding a total run time of 15 min. MS determination was performed in positive mode combined with monitoring of the two most abundant MS/MS (precursor/product) ion transitions. The MS source conditions were as follows: curtain gas (CUR) 25 psi, collision gas (CAD) is medium, ion spray voltage (IS) of 5500 V, source temperature of 500 °C, ion source gas 1 of 50 psi, and ion source gas 2 of 50 psi. The QTRAP 4500 for LC–MS/MS analysis has sufficient sensitivity suitable for the determination of heat-labile pesticides and polar pesticides. To optimize the MS/MS conditions, precursor and product ions were chosen for each analyte. Generally, the transition with maximum intensity was used for quantification. In addition, collision tests were carried out to determine the most suitable declustering potential (DP), collision energy (CE), and collision cell exit potential (CXP) for each pesticide. Table 1 shows analyte-specific MS/MS conditions and LC retention times for LC-amenable analytes.

2.4. GC–MS/MS conditions

GC–MS/MS analysis was performed using an Agilent 7890A GC, coupled with a 7693 autosampler and a 7000C Triple Quadrupole

Table 1
Retention time (RT) and MRM condition of 133 pesticides for LC–MS/MS analysis[a].

Q1	Q3	RT(min)	Analyte	DP	EP	CE	CXP
238	181	3.7	3-Hydroxycarbofuran 1	65	10	14	12
238	163	3.7	3-Hydroxycarbofuran 2	65	10	20	10
184	143	2.1	Acephate1	50	10	10	9
184	125	2.1	Acephate2	50	10	26	9
223	126	3.7	Acetamiprid 1	70	10	27	11
223	99	3.7	Acetamiprid 2	70	10	47	11
270.2	148.2	7.9	Acetochlor 1	36	10	15	9
270.2	133.1	7.9	Acetochlor 2	36	10	45	9
270.1	238.1	7.9	Alachlor 1	46	10	15	9
270.1	162	7.9	Alachlor 2	46	10	25	9
208	116	4.4	Aldicarb 1	20	10	11	8
208	89	4.4	Aldicarb 2	20	10	22	8
240.1	148	2.6	Aldicarb Sulfone 1	25	10	17	11
240.1	86	2.6	Aldicarb Sulfone 2	25	10	24	11
207	89	2.5	Aldicarb sulfoxide 1	51	10	20	6
207	132	2.5	Aldicarb sulfoxide 2	51	10	10	6
228.1	186.2	7.0	Ametryn 1	100	10	25	5
228.1	96	7.0	Ametryn 2	100	10	35	5
216.1	174	6.0	Atrazine 1	71	10	23	9
216.1	104	6.0	Atrazine 2	71	10	39	9
188	103.9	4.0	Atrazine- desethyl1	85	10	33	10
188	145.9	4.0	Atrazine- desethyl2	75	10	25	10
174	68	3.4	Atrazine-desisopropyl1	70	10	40	10
174	104	3.4	Atrazine-desisopropyl2	75	10	30	10
318	132.2	6.5	Azinphos-methyl 1	29	10	21	6
318	160.2	6.5	Azinphos-methyl 2	29	10	13	6
404.1	372	6.7	Azoxystrobin 1	70	10	20	10
404.1	344.1	6.7	Azoxystrobin 2	70	10	34	10
326	148.1	8.6	Benalaxyl 1	80	10	28	14
326	91	8.6	Benalaxyl 2	80	10	55	14
338.2	70	7.9	Bitertanol 1	30	10	25	6
338.2	269	7.9	Bitertanol 2	30	10	15	4
261	205	5.1	Bromacil 1	65	10	21	6
261	188	5.1	Bromacil 2	65	10	41	6
306.2	201.1	9.5	Buprofezin 1	66	10	17	9
306.2	116.2	9.5	Buprofezin 2	66	10	21	9
312.1	238	9.9	Butachlor 1	54	10	15	9
312.1	162	9.9	Butachlor 2	54	10	32	9
202.1	145	5.3	Carbaryl 1	54	10	15	10
202.1	127	5.3	Carbaryl 2	54	10	40	10
192	160	4.1	Carbendazim 1	80	10	25	11
192	132	4.1	Carbendazim 2	80	10	41	11
222.1	165	5.0	Carbofuran 1	70	10	17	14
222.1	123.1	5.0	Carbofuran 2	70	10	29	14
236.1	142.9	5.4	Carboxin 1	70	10	21	10
236.1	87	5.4	Carboxin 2	70	10	33	10
483.9	452.9	6.5	Chlorantraniliprole 1	80	10	28	9
483.9	285.9	6.5	Chlorantraniliprole 2	80	10	28	9
309	156	8.3	Chlorbenzuron 1	75	10	20	10
309	139	8.3	Chlorbenzuron 2	75	10	44	10
293	204	7.0	Chlorbromuron 1	76	10	29	4
293	182	7.0	Chlorbromuron 2	76	10	25	4
358.9	99	8.6	Chlorfenvinphos 1	71	10	39	4
358.9	155.1	8.6	Chlorfenvinphos 2	71	10	17	4
540	383	10.4	Chlorfluazuron 1	110	10	30	6
540	158	10.4	Chlorfluazuron 2	110	10	27	6
350	198	10.0	Chlorpyrifos 1	82	10	29	9
350	97	10.0	Chlorpyrifos 2	82	10	49	9
324	125.1	9.0	Chlorpyrifos-methyl 1	65	10	28	12
321.9	125.1	9.0	Chlorpyrifos-methyl 2	65	10	25	12
240.1	125	6.6	Clomazone 1	80	10	27	8
240.1	89.1	6.6	Clomazone 2	80	10	65	8
250	169.1	3.5	Clothianidin 1	71	10	17	9
250	132	3.5	Clothianidin 2	71	10	21	9
363	227	8.6	Coumaphos 1	100	10	36	10
363	307	8.6	Coumaphos 2	100	10	25	10
523.2	281	10.5	Deltamethrin 1	55	10	23	14
523.2	506.1	10.5	Deltamethrin 2	55	10	16	14
305	169	8.6	Diazinon 1	80	10	27	11
305	153	8.6	Diazinon 2	80	10	28	11
221	109	4.9	Dichlorvos 1	70	10	23	11
221	127	4.9	Dichlorvos 2	70	10	25	13
238.1	127.1	3.3	Dicrotophos 1	62	10	25	10
238.1	112	3.3	Dicrotophos 2	62	10	17	10
268.1	226.1	6.9	Diethofencarb 1	66	10	14	6
268.1	180	6.9	Diethofencarb 2	66	10	25	6
406.1	251	8.9	Difenoconazole 1	120	10	37	7
406.1	337	8.9	Difenoconazole 2	120	10	23	7
311	158	8.0	Diflubenzuron 1	72	10	21	6
311	141.2	8.0	Diflubenzuron 2	72	10	47	6
230	125	3.7	Dimethoate 1	56	10	29	10
230	199	3.7	Dimethoate 2	56	10	13	10
388.1	301	7.1	Dimethomorph 1	115	10	29	6
388.1	165	7.1	Dimethomorph 2	115	10	43	6
326	70	8.9	Diniconazole 1	105	10	57	6
326	159	8.9	Diniconazole 2	105	10	38	6
330	121	7.8	Epoxiconazole 1	76	10	27	9
330	101	7.8	Epoxiconazole 2	76	10	63	9
385	199.1	9.9	Ethion 1	31	10	17	6
385	171	9.9	Ethion 2	31	10	23	4
243	131	7.9	Ethoprophos 1	51	10	29	6
243	97	7.9	Ethoprophos 2	51	10	41	6
360.1	141	10.3	Etoxazole 1	96	10	45	4
360.1	57.2	10.3	Etoxazole 2	96	10	45	4
293.1	265.1	8.5	Etrimfos 1	72	10	35	6
293.1	125	8.5	Etrimfos 2	72	10	24	6
392	238	8.5	Famoxadone 1	45	10	23	6
392	331	8.5	Famoxadone 2	45	10	15	4
312.1	92	7.0	Fenamidone 1	77	10	38	7
312.1	65	7.0	Fenamidone 2	77	10	71	7
304.2	217.1	8.1	Fenamiphos 1	77	10	31	15
304.2	202	8.1	Fenamiphos 2	77	10	45	15
331	81	7.7	Fenarimol 1	86	10	47	6
331	268	7.7	Fenarimol 2	86	10	31	6
337.1	124.9	7.9	Fenbuconazole 1	115	10	42	12
337.1	70	7.9	Fenbuconazole 2	115	10	43	12
208.1	95	6.8	Fenobucarb 1	65	10	21	9
208.1	152	6.8	Fenobucarb 2	65	10	13	9
254.1	72.1	8.2	Fenothiocarb 1	61	10	35	10
254.1	160.2	8.2	Fenothiocarb 2	61	10	14	10
304.3	147.1	11.4	Fenpropimorph 1	49	10	39	6
304.3	117	11.4	Fenpropimorph 2	49	10	71	6
279.1	169	8.4	Fenthion 1	78	10	23	10
279.1	247	8.4	Fenthion 2	78	10	18	10
454	368.1	8.1	Fipronil 1	50	10	33	6
454	290.1	8.1	Fipronil 2	50	10	42	6
384.1	282.1	9.6	Fluazifop-butyl 1	74	10	27	6
384.1	328	9.6	Fluazifop-butyl 2	74	10	23	6
376	349	7.6	Fluquinconazole 1	91	10	25	4
376	307	7.6	Fluquinconazole 2	91	10	33	4
324.1	262.1	7.2	Flutolanil 1	84	10	25	6
324.1	282.1	7.2	Flutolanil 2	84	10	17	6
247	109.1	8.6	Fonofos 1	50	10	25	6
247	201	8.6	Fonofos 2	50	4.5	20	6
284	104	5.7	Fosthiazate 1	63	10	28	7
284	228	5.7	Fosthiazate 2	63	10	15	7
314.1	70.1	8.6	Hexaconazole 1	94	10	45	6
314.1	159	8.6	Hexaconazole 2	94	10	40	6
460.9	158	9.1	Hexaflumuron 1	100	10	25	9
460.9	141	9.1	Hexaflumuron 2	100	10	65	9
253.1	171.1	5.1	Hexazinone 1	70	10	23	13
253.1	71.1	5.1	Hexazinone 2	70	10	43	13
297.1	159	8.5	Imazalil 1	60	10	31	9
297.1	201	8.5	Imazalil 2	60	10	23	9
256.1	175	3.4	Imidacloprid 1	60	10	26	13
256.1	209	3.4	Imidacloprid 2	60	10	23	13
528.1	203	9.0	Indoxacarb 1	71	10	51	9
528.1	56	9.0	Indoxacarb 2	71	10	55	9
330.1	245	8.0	Iprodione 1	85	10	21	6
330.1	288	8.0	Iprodione 2	85	10	16	6
314	162	7.5	Isazofos 1	70	10	22	9
314	120	7.5	Isazofos 2	70	10	40	9
291.1	231.1	7.3	Isoprothiolane 1	35	10	16	6
291.1	189	7.3	Isoprothiolane 2	35	10	30	6
314.1	105	8.7	Isoxathion 1	59	10	21	6
314.1	170	8.7	Isoxathion 2	59	10	19	7
331	127	7.3	Malathion 1	64	10	17	9
331	99	7.3	Malathion 2	64	10	31	9
299.1	148.1	7.5	Mefenacet 1	35	10	19	6
299.1	120.1	7.5	Mefenacet 2	35	10	35	6
280.2	220	6.2	Metalaxyl 1	65	10	18	11

Table 1 (*Continued*)

Q1	Q3	RT(min)	Analyte	DP	EP	CE	CXP
280.2	192.3	6.2	Metalaxyl 2	65	10	24	11
142	125	1.7	Methamidophos 1	54	10	18	9
142	94	1.7	Methamidophos 2	54	10	19	9
163	106	2.9	Methomyl 1	38	10	13	9
163	88	2.9	Methomyl 2	38	10	13	9
284.1	251.9	8.1	Metolachlor 1	54	10	19	6
284.1	176	8.1	Metolachlor 2	54	10	33	6
188.1	126.2	7.5	Molinate 1	61	10	17	6
188.1	55.1	7.5	Molinate 2	61	10	35	6
224.1	127	3.1	Monocrotophos 1	71	10	21	6
224.1	98	3.1	Monocrotophos 2	71	10	17	6
289.1	70	7.4	Myclobutanil 1	80	10	35	6
289.1	125	7.4	Myclobutanil 2	80	10	46	6
272	129.3	7.9	Napropamide 1	80	10	21	10
272	171	7.9	Napropamide 2	80	10	26	10
214	109	2.3	Omethoate 1	56	10	36	6
214	182.9	2.3	Omethoate 2	56	10	16	6
279.1	219.2	4.5	Oxadixyl 1	68	10	17	6
279.1	132.1	4.5	Oxadixyl 2	68	10	41	6
294	70	7.2	Paclobutrazol 1	90	10	50	9
294	125	7.2	Paclobutrazol 2	90	10	55	9
276.1	220	5.8	Paraoxon 1	69	10	19	6
276.1	248.1	5.8	Paraoxon 2	69	10	13	6
292	236	8.2	Parathion 1	80	10	20	7
292	264	8.2	Parathion 2	80	10	15	7
284	159	8.3	Penconazole 1	81	10	39	4
284	70	8.3	Penconazole 2	81	10	29	4
282.1	212	10.1	Pendimethalin 1	45	10	15	6
282.1	194	10.1	Pendimethalin 2	45	10	25	6
408.2	183.1	11.0	Permethrin 1	50	10	22.3	9
408.2	355.2	11.0	Permethrin 2	50	10	11.5	9
261	75	8.8	Phorate 1	51	10	21	10
261	199	8.8	Phorate 2	51	10	10	10
293	96.9	5.9	Phorate sulfone1	65	10	50	10
293	114.7	5.9	Phorate sulfone2	65	10	35	10
276.9	96.9	5.7	Phorate sulfoxide1	60	10	45	10
276.9	114.7	5.7	Phorate sulfoxide2	55	10	28	10
368	182	8.8	Phosalone 1	71	10	20	6
368	322	8.8	Phosalone 2	71	10	13	6
318	160	6.6	Phosmet 1	61	10	17	10
318	133	6.6	Phosmet 2	61	10	49	11
299.1	129	8.7	Phoxim 1	67	10	16	10
299.1	77	8.7	Phoxim 2	67	10	46	10
239.2	72	5.9	Pirimicarb 1	20	10	36	6
239.2	182	5.9	Pirimicarb 2	20	10	21	6
334.2	198.1	9.9	Pirimiphos-ethyl 1	39	10	27	6
334.2	182.1	9.9	Pirimiphos-ethyl 2	39	10	27	6
306.1	164.1	8.9	Pirimiphos-methyl 1	75	10	29	6
306.1	108	8.9	Pirimiphos-methyl 2	75	10	40	6
376.2	308	8.8	Prochloraz 1	65	10	17	6
376.2	70.1	8.8	Prochloraz 2	65	10	43	6
373	302.9	9.5	Profenofos 1	80	10	25	12
373	345.2	9.5	Profenofos 2	80	10	18	12
242.1	158	7.8	Prometryne 1	80	10	31	11
242.1	200.1	7.8	Prometryne 2	80	10	24	11
218.1	127.1	6.9	Propanil 1	76	10	37	4
218.1	162.1	6.9	Propanil 2	76	10	21	4
368	231	10.2	Propargite 1	46	10	17	9
368	175	10.2	Propargite 2	46	10	21	9
230.1	146	7.0	Propazine 1	74	10	29	6
230.1	188.1	7.0	Propazine 2	74	10	19	6
342.1	159	8.5	Propiconazole 1	86	10	43	9
342.1	69.1	8.5	Propiconazole 2	86	10	33	9
210.1	111	5.0	Propoxur 1	33	10	19	6
210.1	168.1	5.0	Propoxur 2	33	10	11	6
256	173.1	7.3	Propyzamide 1	54	10	31	6
256	190	7.3	Propyzamide 2	54	10	19	7
345	241	10.8	Prothiofos 1	60	10	26	6
347	243	10.8	Prothiofos 2	60	10	26	6
361.1	138.1	8.8	Pyraclofos 1	86	10	49	6
361.1	257	8.8	Pyraclofos 2	86	10	28	6
374.1	222.1	8.9	Pyrazophos	56	10	29	6
374.1	194	8.9	Pyrazophos 2	56	10	43	4
341	189	7.4	Pyridaphenthion 1	71	10	29	6
341	205	7.4	Pyridaphenthion 2	71	10	35	4
200	107	7.0	Pyrimethanil 1	91	10	34	10
200	82	7.0	Pyrimethanil 2	91	10	37	10

Table 1 (*Continued*)

Q1	Q3	RT(min)	Analyte	DP	EP	CE	CXP
322.1	96	9.9	Pyriproxyfen 1	60	10	23	11
322.1	185	9.9	Pyriproxyfen 2	60	10	31	11
299	163	8.3	Quinalphos 1	66	10	31	11
299	147	8.3	Quinalphos 2	66	10	29	11
308	162	10.0	Quinoxyfen 1	61	10	57	6
308	197	10.0	Quinoxyfen 2	61	10	43	6
411.2	71.1	10.6	Spirodiclofen 1	46	10	25	6
411.2	313.1	10.6	Spirodiclofen 2	46	10	17	4
323	115	8.4	Sulfotep 1	70	8.5	43	6
323	171.1	8.4	Sulfotep 2	70	8.5	21	6
323	219	10.1	Sulprofos 1	81	10	21	4
323	247	10.1	Sulprofos 2	81	10	17	4
308.1	70	8.4	Tebuconazole 1	90	10	49	7
308.1	125	8.4	Tebuconazole 2	90	10	47	7
334.2	117	9.7	Tebufenpyrad 1	71	10	47	6
334.2	145	9.7	Tebufenpyrad 2	71	10	37	4
242.2	186.1	8.0	Terbutryn 1	49	10	25	6
242.2	68.1	8.0	Terbutryn 2	49	10	57	6
367	127	8.2	Tetrachlorvinphos 1	66	10	19	6
365	127	8.2	Tetrachlorvinphos 2	66	10	19	6
372	159	7.7	Tetraconazole 1	66	10	39	6
372	70	7.7	Tetraconazole 2	66	10	47	4
292	211	3.0	Thiamethoxam 1	60	10	18	15
292	181	3.0	Thiamethoxam 2	60	10	32	15
258.1	125	8.9	Thiobencarb 1	66	10	25	6
258.1	89	8.9	Thiobencarb 2	66	10	67	6
301	268.9	8.8	Tolclofos-methyl 1	59	10	23	6
301	175	8.8	Tolclofos-methyl 2	59	10	35	6
294	197	7.4	Triadimefon 1	81	10	21	6
294	225	7.4	Triadimefon 2	81	10	17	6
314	119.1	7.5	Triazophos 1	70	10	47	9
314	162	7.5	Triazophos 2	70	10	25	9
190	163.1	4.2	Tricyclazole 1	70	10	32	6
190	136	4.2	Tricyclazole 2	70	10	38	6
292.1	124.9	8.0	Uniconazole 1	90	10	40	9
292.1	70	8.0	Uniconazole 2	90	10	55	9
288	146	3.7	Vamidothion 1	56	10	17	4
288	118	3.7	Vamidothion 2	56	10	31	4

[a] Compound-dependent parameters: DP, declustering potential; EP, entrance potential; CE, collision energy; CXP, collision cell exit potential.

MS (Agilent Technologies, Palo Alto, CA, USA), equipped with MassHunter software (B.07.00, Agilent) for quantitation. The injector, ion source, and transfer line temperatures were all set to 280 °C. Analytes were separated on an HP-5 MS UI capillary column (30 m × 0.250 mm i.d., 0.25 μm film thickness) from Agilent Technologies. The column was set at a constant flow rate of 1 mL/min using helium as the carrier gas. The injection volume was 1 μL in splitless mode. The purge flow rate to split vent was set at 30 mL/min for 1 min (20 mL/min gas saver after 2 min). The oven temperature program was as follows: the initial temperature was 60 °C (for 1 min) and increased to 120 °C at 40 °C/min, ramped to 310 °C at 5 °C/min, and then held for 6 min. The total run time was 40.5 min. The optimal two ion transitions (primary and secondary transitions of a precursor to product) for the multiple reaction monitoring (MRM) of each pesticide were determined via collision tests (Table 2). Identification of pesticides in fortified samples by GC–MS/MS was determined by comparing the expected retention time and the ratio of the two transition (primary/secondary) results to matrix-matched standards, following the criteria for identification established by the FDA and the European Union.

2.5. Sample preparation and extraction procedure

Pesticide-free samples for fortification experiments were purchased from an organic vegetable farm and were minced by a homogenizer (except soybean oil). To evaluate the automatic QuEChERS method, a comparison between the automatic and manual method was carried out.

Table 2
Retention times and MRM parameters of 137 pesticides for GC–MS/MS.

Pesticides	t_R(min)	TS	MRM1	CE	MRM2	CE
Aclonifen	24.91	48	212.1 –> 182.2	10	264.1 –> 194.2	15
Acrinathrin	30.64	63	207.8 –> 181.1	10	181 –> 152	30
Aldrin	19.58	33	262.9 –> 192.9	35	254.9 –> 220	20
Anilofos	28.78	59	225.9 –> 184.0	5	225.9 –> 157	10
Atraton	14.92	18	169.0 –> 154.1	5	211 –> 169.1	5
Azinphos-ethyl	30.56	63	132.0 –> 77.1	15	160 –> 77.1	20
Beflubutamid	21.67	39	176.1 –> 91.1	10	221 –> 193.1	5
Benfluralin	14.04	16	292.0 –> 264.0	5	292 –> 206	10
BHC-alpha	14.34	16	216.9 –> 181.0	5	218.9 –> 183	5
BHC-beta	15.41	19	181.0 –> 145.0	15	216.9 –> 181.1	5
BHC-delta	16.55	21	181.1 –> 145.1	15	217 –> 181.1	5
BHC-gamma	15.60	19	181.0 –> 145.0	15	216.9 –> 181	5
Bifenthrin	28.26	57	181.2 –> 165.2	25	181.2 –> 166.2	10
Biphenyl	8.29	6	154.1 –> 153.1	15	153.1 –> 152.1	15
Boscalid	33.30	66	140.0 –> 112.0	10	140 –> 76	25
Bromfenvinfos	23.01	43	266.9 –> 159.1	15	268.9 –> 161.1	15
Bromophos	20.59	36	330.8 –> 315.8	15	328.8 –> 313.8	15
Bromophos-ethyl	22.22	41	358.7 –> 302.8	15	302.8 –> 284.7	15
Bromopropylate	28.06	56	185.0 –> 157.0	15	183 –> 155	15
Bupirimate	23.98	45	272.9 –> 193.1	5	272.9 –> 108	15
Butamifos	22.98	43	285.9 –> 202.0	15	200 –> 92	10
Carbophenothion	25.85	50	199 –> 143	10	153.0 –> 96.9	10
Chlordane-trans	21.98	40	271.7 –> 236.9	15	372.8 –> 265.8	15
Chlordimeform	13.48	14	151.9 –> 117.1	10	195.9 –> 181	5
Chlorfenson	22.84	43	175.0 –> 111.0	10	302 –> 175	10
Chlorobenzilate	24.60	46	139.1 –> 111.0	10	251.1 –> 139.1	15
Chloroneb	10.59	9	191.0 –> 113.0	10	191 –> 141	10
Chlorpropham	13.35	14	153.0 –> 90.0	25	153 –> 125.1	10
Chlorthiophos	25.27	48	324.8 –> 268.9	10	296.8 –> 268.9	5
Crotoxyphos	21.89	40	127.0 –> 109.0	15	104 –> 103	15
Cyanazine	20.02	34	225.0 –> 189.2	15	212 –> 123.1	15
Cycloate	13.01	13	154.1 –> 83.1	5	154.1 –> 72.1	5
Cyflufenamid	24.36	46	118.1 –> 90.0	10	118.1 –> 89	25
Cyfluthrin	32.90	66	226.0 –> 206.0	15	162.9 –> 127	5
Cyhalothrin (lambda)	30.21	62	197.0 –> 141.0	10	208 –> 181	5
Cypermethrin	33.33	66	163.0 –> 91.0	10	163 –> 127	5
Cyproconazole	24.17	45	139.0 –> 111.0	15	222 –> 125.1	15
Cyprodinil	20.90	37	225.2 –> 224.3	10	224.2 –> 208.2	20
DDD-o,p'	23.70	44	235.0 –> 165.2	20	237 –> 165.2	20
DDD-p,p'	24.91	48	234.9 –> 165.1	20	236.9 –> 165.2	20
DDE-o,p'	22.23	41	246.0 –> 176.2	30	248 –> 176.2	30
DDE-p,p'	23.40	43	246.1 –> 176.2	30	315.8 –> 246	15
DDT-o,p'	25.01	48	235.0 –> 165.2	20	237 –> 165.2	20
DDT-p,p'	26.23	51	235.0 –> 165.2	20	237 –> 165.2	20
DEF	23.43	43	202.0 –> 147.0	5	169 –> 57.1	5
Deltamethrin	36.44	72	250.7 –> 172.0	5	252.9 –> 172	15
Desmetryn	17.63	25	213.0 –> 58.1	10	213 –> 171.2	5
Dichlofenthion	17.78	26	278.9 –> 222.9	15	222.9 –> 204.9	15
Dichlorobenzonitrile	7.72	5	171.0 –> 100.0	25	171 –> 136.1	15
Diclofop-methyl	26.89	54	253.0 –> 162.1	15	339.9 –> 252.9	10
Dicloran	14.79	18	206.1 –> 176.0	10	160.1 –> 124.1	10
Dicrotofos	13.78	15	127 –> 95	15	127.0 –> 109.0	15
Dieldrin	23.37	43	262.9 –> 193.0	35	277 –> 241	5
Dimepiperate	21.55	39	144.9 –> 112.1	10	119 –> 91	10
Diphenylamine	12.75	12	169.0 –> 168.2	15	168 –> 167.2	15
Dipropetryn	19.59	33	255.1 –> 222.1	10	255.1 –> 180.1	20
Disulfoton sulfone	22.49	41	213.0 –> 96.9	10	152.9 –> 97	10
Disulfoton sulfoxide	24.74	47	125.0 –> 97.0	5	125 –> 65	35
Ditalimfos	22.71	42	130.0 –> 102.1	10	148 –> 130.1	10
Edifenphos	25.99	50	172.9 –> 109.0	5	201 –> 109	10
endosulfan ii	24.50	46	206.9 –> 172.0	15	194.9 –> 124.9	25
Endrin	24.15	45	262.8 –> 193.0	35	244.8 –> 173	30
EPN	28.09	56	169.0 –> 141.1	5	169 –> 77.1	25
Ethalfluralin	13.60	14	275.9 –> 202.1	15	315.9 –> 275.9	10
Ethofumesate	19.31	32	206.9 –> 161.1	10	161 –> 105.1	10
Etridiazole	9.58	8	183.0 –> 140.0	10	211.1 –> 183	10
Famphur	25.83	50	218.0 –> 109.0	15	218 –> 79	30
Fenamiphos sulfone	27.85	56	319.8 –> 292.0	10	171 –> 107	5
Fenhexamid	26.17	51	177.1 –> 78.0	10	97.1 –> 55.1	10
Fenitrothion	19.17	31	277.0 –> 260.0	5	277.1 –> 109	15
Fenpropathrin	28.46	58	207.9 –> 181.0	5	264.9 –> 210	10
Fensulfothion	24.75	47	291.8 –> 156.0	15	291.8 –> 108.8	15
Fenthion sulfone	24.97	48	309.9 –> 105.0	10	135.9 –> 92	10
Fenthion sulfoxide	24.76	47	278.0 –> 109.0	15	278 –> 169	15
Fenvalerate	35.04	69	224.9 –> 119.0	5	167 –> 125.1	5
Flucythrinate	33.74	67	156.9 –> 107.1	15	198.9 –> 157	10

Table 2 (*Continued*)

Pesticides	t_R(min)	TS	MRM1	CE	MRM2	CE
Fludioxonil	23.39	43	248.0 –> 154.1	20	248 –> 182.1	10
Fluorodifen	23.07	43	190.0 –> 126.1	10	190 –> 75	20
Fluridone	34.47	68	328.0 –> 258.9	15	328.9 –> 328.1	15
Formothion	17.29	24	170.0 –> 93.0	5	197.9 –> 92.9	10
Hexachlorobenzene	14.61	17	283.8 –> 213.9	30	283.8 –> 248.8	15
Iprobenfos	17.14	23	203.9 –> 91.0	5	121.9 –> 121	15
Isocarbophos	20.24	35	135.9 –> 108.0	15	135.9 –> 69	30
Isofenphos	21.56	39	212.9 –> 121.1	10	212.9 –> 185.1	5
Isofenphos oxon	20.28	35	229.0 –> 200.9	10	229 –> 121	25
Isofenphos-methyl	20.97	37	199.0 –> 121.0	10	241.1 –> 199.1	10
Isoprocarb	11.14	10	121.0 –> 77.1	20	136 –> 121.1	10
Kresoxim-methyl	24.04	45	116.0 –> 89.0	15	116 –> 63	30
Leptophos	29.41	61	171.0 –> 77.1	15	154.9 –> 77.1	15
Mecarbam	21.60	39	130.9 –> 74.0	5	158.9 –> 131	5
Mepanipyrim	22.59	41	223.2 –> 222.2	10	222.2 –> 207.2	15
Mephosfolan	21.44	39	196.0 –> 139.9	15	168 –> 139.9	5
Methidathion	22.08	40	144.9 –> 85.0	5	144.9 –> 58.1	15
Methoprene	21.91	40	153.0 –> 111.1	5	111.1 –> 55	15
Methoprotryne	23.89	45	256.0 –> 212.1	15	256 –> 170.1	25
Methoxychlor	26.68	53	227.1 –> 121.1	10	227.1 –> 91.1	35
Metribuzin	17.84	26	198.0 –> 82.0	15	198 –> 55	30
Mevinphos	9.08	7	127.0 –> 109.0	10	127 –> 95	15
Monolinuron	15.29	19	214.0 –> 61.0	15	126 –> 99	15
Nitrofen	24.14	45	202.0 –> 139.1	20	282.9 –> 253	10
o,p'-Dicofol	20.01	34	251.0 –> 139.0	15	139 –> 111	15
Oxadiazon	23.64	44	174.9 –> 112.0	15	174.9 –> 76	35
Oxyfluorfen	23.86	45	252.0 –> 196.0	20	252 –> 146	30
Paraoxon-methyl	16.51	21	229.9 –> 106.1	5	108.9 –> 79	5
Parathion-methyl	18.10	27	262.9 –> 109.0	10	232.9 –> 109	10
Pentachloroaniline	17.34	24	262.8 –> 192.0	20	264.9 –> 194	20
Pentachloronitrobenzene	15.79	20	236.9 –> 118.9	25	236.9 –> 142.9	30
Permethrin	31.78	64	183.1 –> 168.1	10	183.1 –> 153	10
Phosphamidon I	16.41	21	127.0 –> 95.0	10	127 –> 109	10
Phosphamidon II	17.82	26	127.0 –> 109.0	10	127 –> 95	15
Piperonyl butoxide	27.16	55	176.1 –> 103.1	25	176.1 –> 131.1	15
Piperophos	28.30	57	140.0 –> 98.1	10	320 –> 122	10
Pretilachlor	23.43	43	262.0 –> 202.0	20	162.1 –> 132.2	20
Procymidone	21.87	40	96.0 –> 67.1	10	96 –> 53.1	15
Profluralin	16.08	20	317.9 –> 199.0	15	317.9 –> 54.8	10
Prometryn	18.62	30	226.0 –> 184.2	10	199 –> 184.1	5
Pronamide	16.01	20	173.0 –> 145.0	15	175 –> 147	15
Propaphos	22.21	41	220.1 –> 140.1	10	220.1 –> 125.1	25
Propetamphos	15.96	20	138.0 –> 110.0	10	138 –> 64	15
Propisochlor	18.59	30	162.0 –> 120.1	15	162 –> 147.1	15
Pyridaben	31.73	64	147.2 –> 117.1	20	147.2 –> 132.2	10
Ronnel	18.66	30	285.0 –> 269.9	15	286.9 –> 272	15
Simazine	15.10	19	201.1 –> 173.1	5	201.1 –> 186.2	5
Tebupirimfos	17.16	23	233.9 –> 110.1	15	260.8 –> 137.2	15
Tecnazene (TCNB)	12.44	12	260.9 –> 203.0	10	214.9 –> 179	10
Terbufos	15.87	20	230.9 –> 129.0	20	230.9 –> 175	10
Terbufos sulfone	21.20	38	152.9 –> 96.9	10	198.9 –> 96.9	20
Terbuthylazine	15.88	20	228.9 –> 173.1	5	172.9 –> 138.1	5
Tetradifon	28.98	60	226.9 –> 199.0	10	158.9 –> 131	10
Tetramethrin	28.24	57	164.0 –> 77.1	25	164 –> 107.1	10
Thiometon	14.60	17	125.0 –> 47.0	15	125 –> 79	10
Thionazin	12.48	12	143.0 –> 79.0	10	175 –> 79	10
Triadimenol	21.64	39	168.0 –> 70.0	10	128 –> 65	25
Triallate	16.84	23	268.0 –> 184.1	20	142.9 –> 83	15
Trichloronat	20.42	35	296.8 –> 268.9	10	298.8 –> 270.9	10
Trifloxystrobin	26.43	52	116.0 –> 89.0	15	131 –> 89	30
Vinclozolin	18.12	27	187.0 –> 124.0	20	197.9 –> 145	15

For the automatic QuEChERS method, a portion of sample was weighed into a centrifuge outer tube and fortified with the appropriate standard mixture to obtain the standard concentration. The sample was then allowed to stand for 0.5 h. After which, 10 mL of acetonitrile was added into the centrifuge tube. For dry samples, before addition of acetonitrile, 10 mL of purified water was first added into the centrifuge tube, followed by shaking of the centrifuge tube by hand for several seconds to hydrate the sample. After letting the sample stand for a further 0.5 h, 10 zirconium beads and the QuEChERS extraction salt packet were added into the outer tube, and then the inner tube containing the dispersive solid-phase extraction adsorbents and 10 zirconium beads was inserted. After these steps, the sample was ready for process.

Compared with the manual QuEChERS method, the automatic QuEChERS method integrate all the extraction and clean-up procedures into one single run. First, the centrifuge tube was vibrated for 2 min at 168 rcf followed by centrifugation for 5 min at 2688 rcf. The sample was then vibrated for 3 min at 168 rcf followed by further centrifugation for 3 min at 2688 rcf. The specific process is shown in Fig. 2. Finally, 1 mL of the supernatant in inner tube was filtered through a syringe filter (0.22 μm) for LC–MS/MS analysis. In addition, 1 mL of the supernatant was transferred into a 10 mL glass

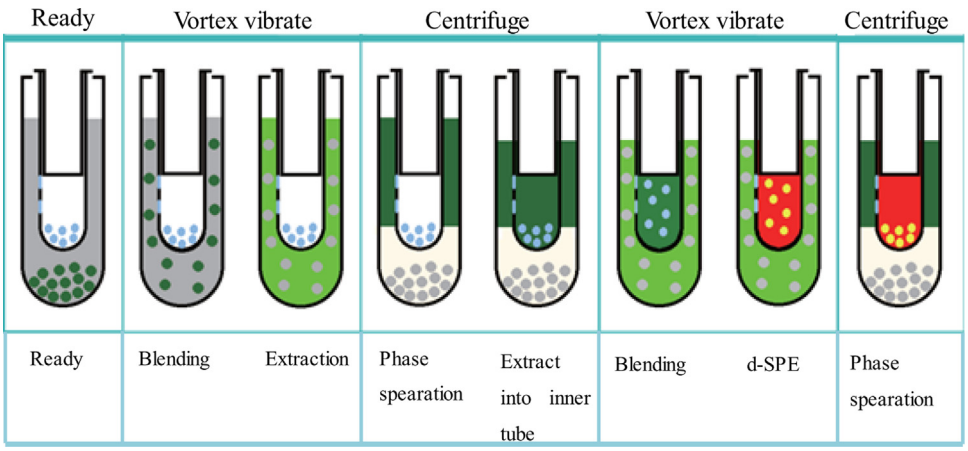

Fig. 2. Flow diagram of the automatic QuEChERS approach.

centrifuge tube containing 50 μL of internal standard solution. This solution was evaporated to dryness under a gentle stream of nitrogen in a 35 °C water bath. Finally, the residue was redissolved in 1 mL of ethyl acetate, and filtered through a syringe filter (0.22 μm) for GC–MS/MS analysis.

For the manual QuEChERS method, a portion of sample was weighed into a 50 mL centrifuge tube and fortified with the appropriate amount of the standard mixture to obtain standard concentrations. The sample was then allowed to stand for 0.5 h. After this period, 10 mL of acetonitrile was added into the centrifuge tube. In the case of dry samples, 10 mL of purified water was first added into the centrifuge tube, followed by shaking of the centrifuge tube by hand for several seconds to hydrate the sample, after which acetonitrile was added. Then, a QuEChERS extraction salt packet and ceramic homogenizer were added and the tube was immediately sealed and violently shaken by hand for 1 min. After shaking, the tube was centrifuged for 5 min at 3944 rcf and 6 mL of the supernatant was transferred into a 15 mL centrifuge tube containing dispersive solid-phase extraction adsorbents. Finally, the extract was vortexed for 1 min and centrifuged for 5 min at 3944 rcf before proceeding to the next steps, which were the same as in the procedure for the automatic QuEChERS method. The information of sample weight and d-SPE adsorbents for different matrices is given in table S1 (see Supplementary material).

2.6. Validation of the method

To determine the accuracy and precision of our automatic method, recovery studies were performed for each sample matrix in five replicates for each of the three fortification levels. Recoveries were calculated by the peak area ratios of the sample to the matrix-matched standards. Linearity was evaluated by analyzing matrix-matched standards in celery blank matrices at eight levels (2, 5, 10, 20, 50, 100, 200 and 500 μg/kg) to reduce quantitative errors. Solvent-based standards were also analyzed to estimate the impact of the matrix. The limits of quantification (LOQ) for each pesticide was set as the lowest concentration level meeting an acceptable mean recovery within the range of 70–120% and precision RSD less than or equal to 20% [27].

3. Results and discussion

3.1. Optimization of sample extraction procedure

The manual QuEChERS method has a two-step sample preparation process, which are salting out (extraction) and dispersive solid phase extraction (clean-up), respectively [27]. In addition, to prevent formation of crystalline agglomerates during $MgSO_4$ hydration, it is necessary to immediately seal the tube and shake vigorously used of a mechanical shaker after adding the salt extraction packet. The method is acknowledged to be effective; however, there are some disadvantages, as the extraction is labor intensive and time consuming. To avoid relatively complex procedures, the automatic QuEChERS method was developed, allowing for the rapid and high throughput analysis of pesticides. The optimization of extraction time was explored to get the best results in the shortest possible time from complicated matrices. Two representative matrices, corn and green tea, were tested in the experiments. Using the automatic QuEChERS methodology, vibration times of 1, 2, and 3 min for the first stage of vibration at 168 rcf were subsequently assessed. The recovery values for different vibration times are presented in Fig. S2. Results showed that, 2 min of vortex vibration was sufficient to obtain satisfactory recoveries. In addition, the recoveries did not increase observably, when the time of vortex vibration was increased to 3 min. Given this, the time of shaking in the first step was set to 2 min so that the best recovery was obtained with minimal waiting time.

A comparison between manual and automatic QuEChERS procedures was performed to validate the performance in different matrixes, resulting in the boxplot of the data in Fig. 3. The results indicate that the recoveries of the automatic method were as satisfactory as those obtained with the manual method and were even better for some pesticides. Thus, it is worth mentioning that the automatic QuEChERS method decreases labor and saves time while the efficiency of the automatic QuEChERS method was higher than that of the manual QuEChERS method.

3.2. Matrix effect

The matrix effect poses a great threat to the accuracy of experimental results that the suppression or enhancement of signal responses via the co-elution of matrix components [28]. In general, matrix effects are closely related to the chemical properties of the analyte and the sample preparation procedure, which are assessed by comparison between the slopes in the matrix calibration solutions and the slopes in pure solvent. The matrix effect is calculated according to the following equation [29]:

$$ME(\%) = \frac{m_{matrix} - m_{solvent}}{m_{solvent}} \times 100$$

Where ME is the matrix effect and m_{matrix} and $m_{solvent}$ are the slopes of calibration curves obtained in the matrix and in the solvent, respectively. Mild matrix effects (suppression or enhancement of 0–20%) are negligible. However, if the matrix effect has

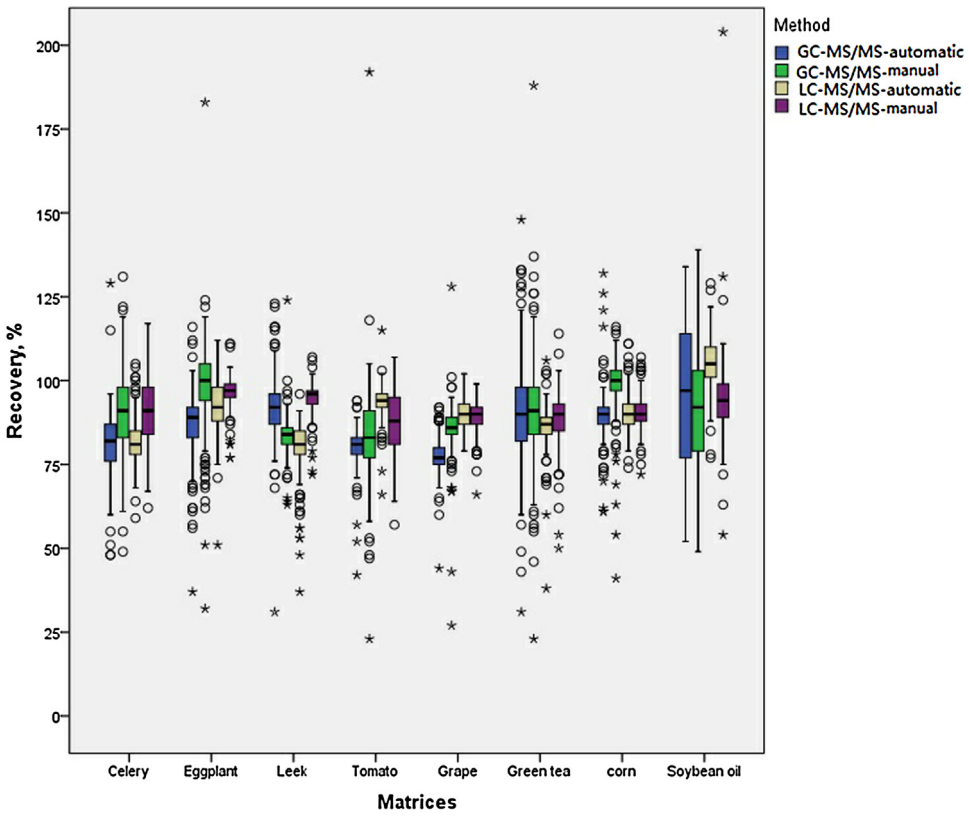

Fig. 3. Boxplot of the recovery values obtained with the manual method (GC–MS/MS-manual, LC–MS/MS-manual) and automatic method (GC–MS/MS-automatic, LC–MS/MS-automatic) at spiking levels of 100 μg/kg in eight matrices.

medium (suppression or enhancement of 20–50%) or high values (suppression or enhancement of >50%), then steps must be taken to eliminate or decrease the influence of the matrix. Matrix-matched calibration standards are usually used to reduce the quantitative error caused by matrix effects.

Fig. S3 and Tables S2–S3 (see Supplementary material) present the matrix effect values of celery. As can be seen from results, the matrix effects of the automatic method were similar to those obtained from the manual method. Most of the pesticides analyzed by LC–MS/MS exhibited matrix suppression effects, while most of the pesticides analyzed by GC–MS/MS exhibited matrix enhancement effects. For the automatic method, approximately 48% of the pesticides exhibited low/negligible matrix effects, 24% exhibited medium matrix effects, and 28% exhibited high matrix effects. While for the manual method, approximately 55% of the pesticides exhibited low/negligible matrix effects, 20% exhibited medium matrix effects, and 25% exhibited high matrix effects. The results indicate that matrix-matched calibration standards are indispensable for accurate quantification by LC–MS/MS and GC–MS/MS.

3.3. Method validation

In this study, to evaluate the performance of the automatic QuEChERS method, the recoveries, LOQ, and linearity were determined.

Recoveries were determined for five replicates at three spiking levels to validate the method's accuracy. The results of mean recoveries and RSDs for different matrices are presented in Tables S4–S19 (see Supplementary material), and indicate that the recoveries were generally in the range of 70–120% with a relative standard deviation (RSD) below 20%. It is obvious that the recoveries of soybean oil were relatively low, due to its high fat content, but the results were still defined as acceptable according to the guidelines for drafting standard methods for the determination of pesticide residues. Thus, in this study, the reliability of the automatic QuEChERS method was validated and the accuracy was satisfactory.

LOQs were set based on the recovery and RSD results and defined as the lowest validated spike level that met the requirements of recovery and RSD as described in SANTE/11945/2015 [30]. The LOQs derived from fortified studies ranged from 2 to 10 μg/kg for 270 pesticides in celery and corn (Tables S20–S23, see Supplementary material). As can be seen from the results in celery, 252 out of 270 pesticides had LOQs of 2 μg/kg for the manual method, while 245 out of 270 pesticides had LOQs at 2 μg/kg for the automatic method. In corn, 253 out of 270 pesticides had LOQs at 2 μg/kg for the manual method and 235 out of 270 pesticides had LOQs at 2 μg/kg for the automatic method.

Superb linearity guarantees accurate quantification, and was examined over the concentration range of 2–500 μg/L. As presented in the results, the coefficients of determination (r^2) were higher or equal to 0.990 for the majority of pesticides.

3.4. Application to real samples

To further validate the feasibility of this method, 15 real samples of celery, leeks, and tomatoes obtained from two local supermarkets were analyzed respectively using the automatic and manual QuEChERS methods described above. In five celery samples, 14 pesticides were detected. While for five leek samples, 16 out of 270 pesticides were detected. Lastly, for five tomatoes samples, 9 pesticides were detected. The results are in good agreement for automatic and manual QuEChERS methods (Table S24, see Supplementary material).

4. Conclusions

A rapid and high throughput automatic QuEChERS method for the multiresidue analysis of 270 pesticides in celery, eggplant,

tomato, leek, green tea, corn, grape, and soybean oil has been developed using an automatic QuEChERS device combined with LC–MS/MS and GC–MS/MS. The automated QuEChERS method allowed for the extraction and clean-up procedures to be performed in one centrifuge tube in a single run and yielded satisfactory validation parameters, including recovery, accuracy, precision and LOQ. The study has demonstrated the feasibility of a rapid, high throughput analysis of pesticides by using the automatic QuEChERS methodology, which minimizes manual involvement and thus, this method presents a considerable advancement in pesticide analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2017.09.027.

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