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A Rapid, Efficient, Reliable Method for Simultaneous Determination of Pesticide Residues in Green Chilli by Gas Chromatography-Mass Spectrometry

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This study describes a rapid, efficient and reliable method for the simultaneous determination of 42 pesticide residues in green chilli using gas chromatography single quadrupole mass spectrometry with selected ion monitoring (GC-SQ/MS-SIM) mode. QuEChERS (quick-easy-cheap-effective-rugged-safe) acetonitrile-based extraction technique was used prior to GC-MS analysis, followed by cleanup with primary-secondary amine (PSA). Linearity ($r^2 > 0.99$) within 50-1000 µg/kg with negligible matrix interferences was achieved by method optimization. The percentage recovery evaluated at 50, 100 and 250 µg/kg level of spiked concentration was observed to range between 75-127% with RSD (< 9.1%) for the majority of analytes. The expanded uncertainty was measured below 48% for all target residues. The limit of detection and limit of quantification ranged between 1-63 µg/kg and 4-150 µg/kg, respectively. The developed method was observed to be specific, accurate, reproducible and user friendly for determining different pesticides in green chilli crops.

Keywords: Food matrices, Recovery, Limit of detection, Limit of quantification, QuEChERS.

INTRODUCTION

The safety of commercially growing vegetables and fruits from various pests is an important concern currently [1]. Cultivars grown by fertilizers are protected by effective pesticides for efficient crop production, but this is associated with harmful effects not only on human health but on the ecosystem too [2,3]. Pesticides are toxic compounds and these bioaccumulate in biological system to take part in many physical, chemical and biological processes. Due to physico-chemical characteristics and extensive use, pesticides are today found in surface and groundwater and cause a potential risk for the drinking water and crop irrigation [4,5]. Pesticides are listed as 'priority pollutants' by the United States Environmental Protection Agency (USEPA), World Health Organization (WHO), Codex Alimentarius, *etc.* owing to their associated risks not only from the environmental perspectives but also from the human health view point as these pose risks such as metabolic disorder and reproductive toxicity [6-8]. In India, over 280 pesticides have been commercially registered and around 46 pesticides are currently banned for import, production and usage, whereas eight pesticides have been withdrawn as per Government guidelines for the pesticide industry S.O 915(E) dated 15th Jun, 2006 [9,10].

Green chilli also known as 'wonder spice' is one of the most frequently used spices globally [11]. It is reported to contain vitamin A, vitamin C, tocopherol, neutral and acidic antioxidant phenolic compounds *i.e.* capsaicinoids and microelements (K, Mn, Fe and Mg) [12]. Owing to high susceptibility of green chilli crop to insect pests (mites, thrips, aphids, borers *etc.*), farmers tend to spray bulk of pesticides (as insecticides, miticides and insect growth regulators) for shielding purposes. This is harmful both to the consumers' health as well as the ecosystem [2,13,14]. The concern necessities the use of a rapid, reliable and effective analytical method for providing accurate information about types and quantity of pesticides used and related risk management [15,16].

The present study has used the 'quick-easy-cheap-effective-rugged-safe (QuEChERS)' method for extracting multilevel pesticide residue in green chilli samples prior to gas chromatography-mass spectrometry (GC-MS) analysis. Injecting more sample volumes into GC coupled with the 'single quadrupole mass spectrometer and selected ion monitoring-SIM provides compensated sensitivity, improved the signal-noise ratio (S/N) and achieved the limit of quantitation (LOQs) in compliance to regulatory requirements [17,18]. This study has developed a rapid, efficient, reliable method for simultaneous determination of 42 pesticide residues in different green chilli matrices using GC-MS.

EXPERIMENTAL

The standard pesticides, AccuStandard (USA) were of purity > 99.9%. Primary secondary amine (PSA, Bondesil, 40 µm), Agilent Technologies (USA). Methanol (LCMS grade), acetone (residue grade), anhydrous Na_2SO_4 and NaCl (ACS certified) were procured from Thermo-Fisher Scientific, India. Millipore water was purchased from Fisher Scientific.

The stock solutions (1000 mg/L) of different pesticide residue standards were prepared as per their respective solvents (*viz.* acetone, MeOH, ACN, *etc.*) and stored at 5 ºC. Further dilutions of individual stock standards (200 mg/L) were prepared in acetone. Working mixture solution (5 mg/L) was prepared from intermediate solutions. The freshly prepared working mixture solution was used for validation, confirmation and quantification. Matrix matched standards were prepared by adding known quantities of standard (50, 100, 250, 500, 750 and 1000 µg/L) mixture in the blank green chilly extract [19].

Analytical balance (Shimadzu AUX220, Japan), homogenizer (Tulip, Japan), rotary evaporator (Heidolph Instruments, Germany), centrifuge (Thermo Fisher Scientific Inc., USA) and TurboVap LV Evaporator (Zymark, USA) were used. GC-MS (Perkin-Elmer, USA) with analytical capillary column *viz.* DB-5ms, 5% phenyl 95% dimethyl-polysiloxane (30 m × 0.25 mm i.d. × 0.25 µm) was used for pesticide residues analysis.

The oven temperature was initially set at 80 ºC and then increased at 15 ºC/min up to 200 ºC, kept for 5 min on hold and then increased again at 8 ºC/min to 250 ºC. It was then finally increased by 10 ºC/min and maintained for 5 min. The run time (total) was 29 min. The injector was set at 250 ºC. The flow of the carrier gas helium (99.999%) was 1 mL/min. The MS was operated in electron impact ionization mode at 70 eV of collision energy and electron multiplier voltage 400 V. The temperature of ion source and detector interface, respectively set at 240 and 250 ºC. A full scan (range 50-280 *m/z*) for qualitative analysis was performed in SIM mode. The method selectivity was estimated by examining the presence of co-extractant in blank samples.

The modified 'QuEChERS' extraction method was applied in this study [20]. The homogenized sample was weighed (10 g), post which 10 mL acetonitrile, 4 g $MgSO_4$ and 1 g NaCl were added, after which vortexing was done for 1 min and centrifugation at 5000 rpm was done for 5 min. Subsequently, 5 mL of supernatant was added into a cleanup tube containing 50 mg PSA and 300 mg $MgSO_4$. The tube was vortexed and centrifuged for 6 min at 5000 rpm. The supernatant was then evaporated near to dryness using a Turbovap system. Acetone (1 mL) was added for final residues reconstitution for GC-MS analysis.

Selectivity, linearity, precision, limit of quantification, limits of detection and recovery were evaluated for method validation [19]. To overcome the adverse matrix effect, dilutions for calibration curves were prepared by spiking blank green chilly samples with definite amounts of pesticides.

The matrix effect was calculated by the following equation:

$$\text{Matrix effect (\%)} = \frac{\text{Peak area of post extraction spike}}{\text{Peak area of standard}} \times 100$$

The expanded uncertainty at 95% confidence level was obtained using the medium level concentration of the linear range organochlorines (OCs) (50 µg/L), organophosphates (OPs) (100 µg/L) and pyrethroids (250 µg/L) [21].

RESULTS AND DISCUSSION

The temperature gradient for pesticide residues analysis on GC-MS was optimized to achieve the best resolution between peaks in the shortest analysis time. Different oven temperature programmes and flow rates were checked to verify the separation of standard mixture within an acceptable runtime. Table-1 shows the molecular weight and ions used for the quantitative analysis and retention time of each pesticide under optimal separation conditions. Chromatogram of pesticide standard mixture revealed a clear decrease in total run time when initial oven temperatures were set at 50, 80, 150 and 180 ºC, however, 80 ºC was adopted as optimal initial oven temperature. The programme temperature rate (10 ºC/min) provided an increase in speed analysis without a decrease in peak separation. The carrier gas flow was evaluated at different flow rates *i.e.* 0.5, 0.75, 1.0, 1.5 and 2.0 mL/min for corresponding chromatographic separation and S/N of each pesticide. Maximum results were obtained at 1.0 mL/min. Mass spectrometer was autotuned with perflurotributylamine (PFTBA) as mass calibration reference standard in EI-mode. The calibration result showed that residual range was between -0.2 to +0.2 Da, which is similar to the study performed by Ferrer *et al.* [22].

The full scan was performed for identification of retention time and mass confirmation of pesticide by the NIST library. Optimization of SIM mode was used for good signal intensity, 5-10 points along with the peak were considered for selection of ions of each pesticide. The dwell time was adjusted accordingly. Qualitative and quantitative estimation of pesticide residues were carried out using fragmented ion with high abundance as base peak along with *m/z* ratio > 3 after background noise removal. The characteristic ions were selected to avoid matrix interference. Meanwhile, a target ion and three qualifier ions were selected with tolerance levels within ± 15% for confirmation and quantification of each pesticide residues (Table-1).

QuEChERS is a multi-residue method efficient for broad-spectrum pesticides analysis using less solvent volume and optimum extraction period [23,24]. The present extraction procedure was devoid of acetic acid and found no deviation in the recovery of pesticide as compared to the previously used QuEChERS method [1]. Fig. 1 revealed matrix interferences examined by monitoring SIM chromatograms for individual pesticide at expected retention time window for each compound in green chilli blank matrix spiked at 100 µg/L. The present method may be considered as SIM mode minimizing the signal of interfering compounds. Moreover, the abundant ions were taken care for quantification, which revealed no interfering

TABLE-1
PARAMETERS FOR QUANTITATION OF PESTICIDE RESIDUES IN GREEN CHILLI SAMPLE BY GC-MS/SIM

Pesticide	Chemical group	Class	t_r^a	Quantification ion	Qualifying ion		
					1	2	3
Dichlorovos	Organophosphate	Insecticide	5.36	109 (100)	185(28)	79(27)	187(19)
4-Bromo-2-chlorophenol	Organophosphate	Insecticide	5.57	208 (100)	206(78)	63(42)	210(24)
Monocrotophos	Organophosphate	Insecticide	9.34	127 (100)	67(51)	97(27)	58(23)
Phorate	Organophosphate	Insecticide	9.46	75 (100)	121(30)	97(24)	260(14)
α-BHC	Organochlorine	Insecticide	9.63	183 (100)	181(98)	219(87)	217(67)
Dimethoate	Organophosphate	Insecticide	9.91	87 (100)	93(53)	125(45)	58(16)
β-BHC	Organochlorine	Insecticide	10.22	219 (100)	181(94)	109(91)	183(91)
γ-BHC	Organochlorine	Insecticide	10.39	111 (100)	109(95)	181(83)	183(74)
Diazinone	Organophosphate	Insecticide	10.71	179 (100)	137(98)	152(70)	199(47)
Fluchloralin	Dinitroaniline	Herbicide	10.79	306 (100)	326(91)	63(73)	264(49)
δ-BHC	Organochlorine	Insecticide	10.99	109 (100)	219(95)	183(90)	181(89)
Phosphamidon	Organophosphate	Insecticide	11.94	127 (100)	264(46)	72(37)	109(23)
Chlorpyrifos-methyl	Organophosphate	Insecticide	12.29	286 (100)	125(95)	288(78)	79(29)
Methyl parathion	Organophosphate	Insecticide	12.30	109 (100)	263(86)	125(82)	79(36)
Alachlor	Chloroacetanilide	Herbicide	12.58	160 (100)	188(57)	146(20)	237(15)
Heptachlor	Organochlorine	Insecticide	12.65	100 (100)	272(80)	274(65)	270(41)
Fenitrothion	Organophosphate	Insecticide	13.31	277 (100)	125(85)	109(71)	260(60)
Malathion	Organophosphate	Insecticide	13.75	125 (100)	173(93)	93(93)	127(86)
Aldrin	Organochlorine	Insecticide	14.01	66 (100)	263(53)	79(45)	293(24)
Chlorpyrifos	Organophosphate	Insecticide	14.19	97 (100)	197(90)	199(88)	314(47)
Pendimethalin	Dinitroaniline	Herbicide	15.39	252 (100)	281(23)	162(18)	191(13)
Heptachlor epoxide	Organochlorine	Insecticide	15.43	81 (100)	353(94)	355(72)	351(48)
Quinalphos	Organophosphate	Insecticide	15.79	146 (100)	298(57)	157(46)	156(43)
o,p′-DDE	Organochlorine	Insecticide	16.39	246 (100)	248(62)	318(39)	316(32)
α-Endosulfan	Organochlorine	Insecticide	16.64	241 (100)	239(91)	195(88)	237(86)
Butachlor	Chloroacetanilide	Herbicide	16.77	176 (100)	57(96)	160(86)	188(48)
Profenofos	Organophosphate	Insecticide	17.29	337 (100)	339(98)	97(79)	139(71)
p,p′-DDE	Organochlorine	Insecticide	17.40	246 (100)	318(68)	248(63)	316(56)
o,p′-DDD	Organochlorine	Insecticide	17.66	235 (100)	237(66)	165(46)	199(19)
β-Endosulfan	Organochlorine	Insecticide	18.39	195 (100)	197(88)	241(86)	237(73)
p,p′-DDD	Organochlorine	Insecticide	18.65	235 (100)	237(62)	165(41)	199(13)
o,p′-DDT	Organochlorine	Insecticide	18.76	235 (100)	237(64)	165(27)	236(15)
Ethion	Organophosphate	Insecticide	18.82	231 (100)	97(46)	153(40)	125(32)
Triazophos	Organophosphate	Insecticide	19.20	161 (100)	77(87)	97(75)	162(65)
Edifenphos	Organophosphate	Insecticide	19.56	109 (100)	173(68)	65(31)	310(31)
p,p'-DDT	Organochlorine	Insecticide	19.73	235 (100)	237(65)	165(43)	199(13)
Fenpropathrin	Pyrethroid	Insecticide	21.29	97 (100)	55(78)	181(55)	125(31)
λ-Cyhalothrin	Pyrethroid	Insecticide	22.39	181 (100)	197(70)	208(43)	141(27)
Cyfluthrin	Pyrethroid	Insecticide	23.97	163 (100)	165(63)	206(56)	91(37)
α-Cypermethrin	Pyrethroid	Insecticide	24.46	163 (100)	181(89)	165(64)	91(41)
Fenvalerate	Pyrethroid	Insecticide	25.38	125 (100)	167(78)	225(69)	419(49)
Deltamethrin	Pyrethroid	Insecticide	26.44	253 (100)	181(88)	251(50)	255(46)

t_r^a = Retention time of the pesticides (min)

compounds in residual determination. Fig. 2 showed quantitation process of pesticides by GC-MS for *p,p′*-DDE in green chilli samples indicating extracted ion chromatogram, mass spectrum, NIST library search, linearity of matrix matched calibration, quantification and qualifier ion ratio and selected ion chromatogram. Linearity was evaluated by means of calibration curves in 50-1000 µg/L range in matrix-matched green chilli. Determination coefficient (r^2) observed for pesticides in matrix-matched calibration curves was greater than 0.99 (Table-2). This result evidenced the study of Paz *et al.* [25] which showed a good linearity ($r^2 \geq 0.9916$) and recovery (69-110%) using QuEChERS method for OCs residue analysis in Brazilian fruit pulps.

The LOD-LOQ values ranged between 1-63 µg/kg and 4-150 µg/kg, respectively (Table-2). The observed values were below the prescribed maximum residue levels (MRLs) fulfilling the regulatory requirements and were found similar to the previously performed study [24].

Recovery concentration was determined by spiking of organochlorines (50 µg/L), organophosphates (100 µg/L) and synthetic pyrethroids (250 µg/L) corresponding to the lowest and the highest concentration of linear range. Recovery obtained for each pesticide in green chilly matrix ranged between 75-117% except for chlorpyrifos (122%) and fenithrion (127%), which was acceptable according to the SANTE/11813/2017 guidelines (Table-2). The precision was observed to be within

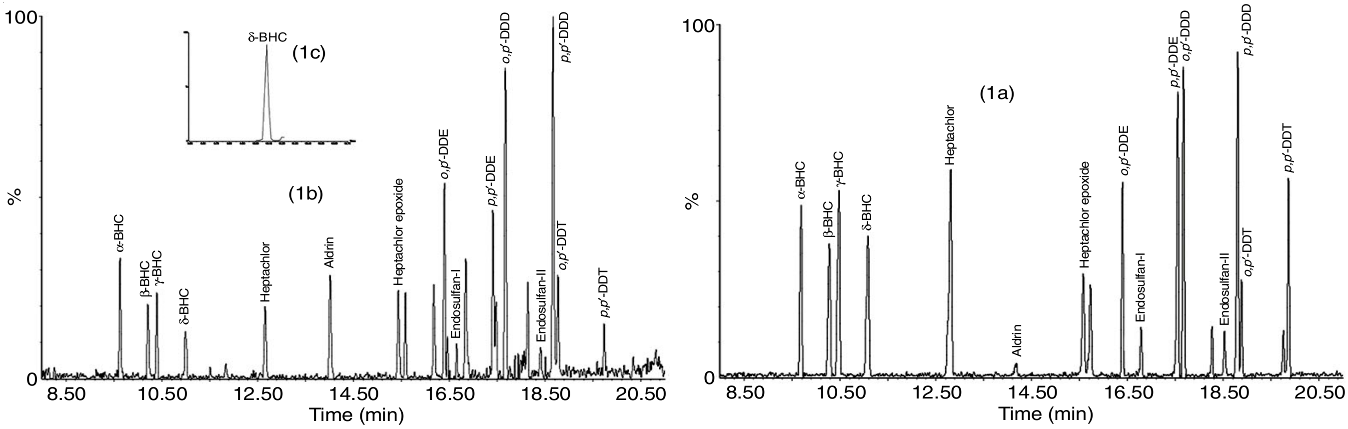
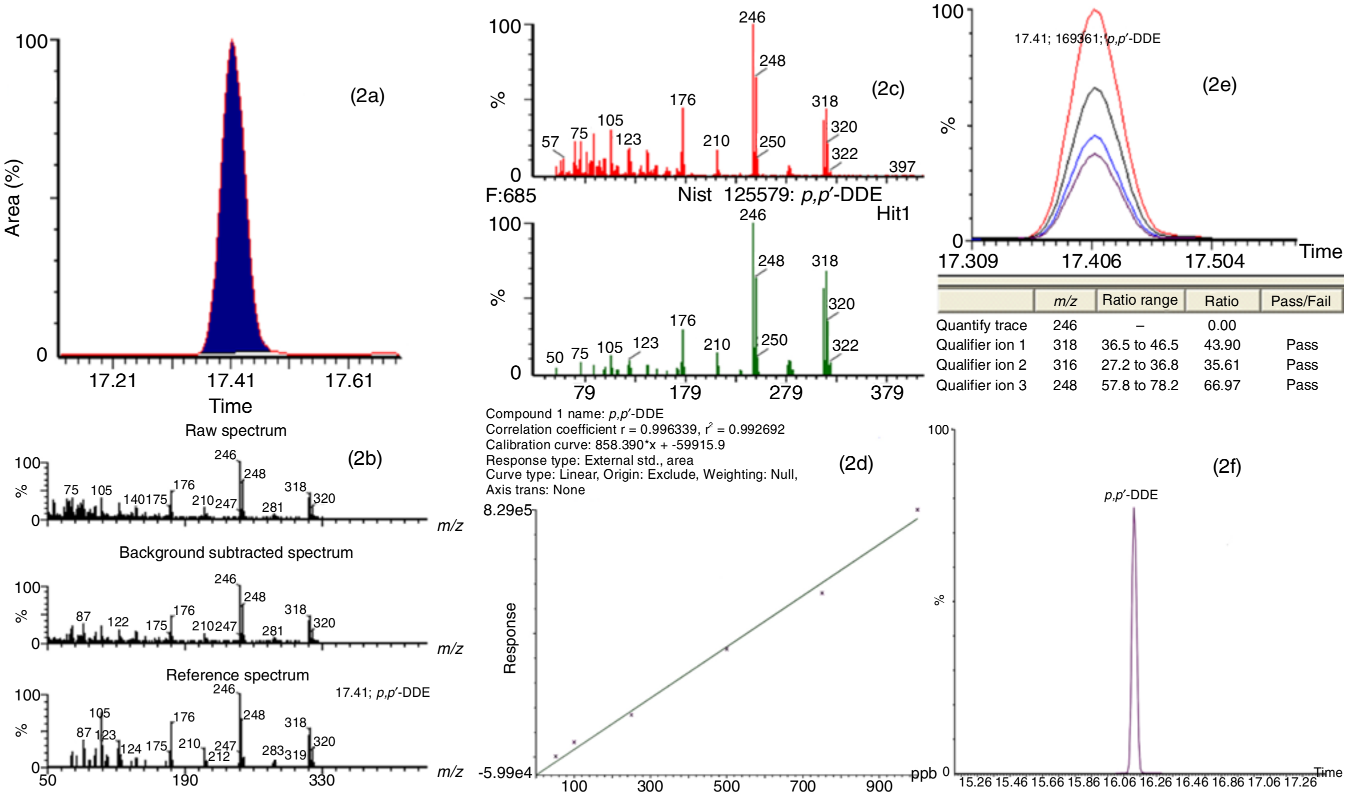


Fig. 1. GC-MS typical representative chromatogram of pesticides. (a) Standard chromatogram (TIC) of pesticides at 100 µg L^{-1}, (b) Spiked chromatogram (TIC) of pesticides in green chilli sample at 100 µg kg^{-1}, (1c) Selected ion chromatogram (SIM) of δ-BHC in green chilli sample at 50 µg kg^{-1}



Compound 1 name: *p,p'*-DDE
Correlation coefficient r = 0.996339, r^2 = 0.992692
Calibration curve: 858.390*x + -59915.9
Response type: External std., area
Curve type: Linear, Origin: Exclude, Weighting: Null,
Axis trans: None

	m/z	Ratio range	Ratio	Pass/Fail
Quantify trace	246	–	0.00	
Qualifier ion 1	318	36.5 to 46.5	43.90	Pass
Qualifier ion 2	316	27.2 to 36.8	35.61	Pass
Qualifier ion 3	248	57.8 to 78.2	66.97	Pass

Fig. 2. GC-MS typical quantitation process of pesticides (*p,p′*-DDE, representative pesticide) in green chilli sample. (a) Extracted ion chromatogram, (b) Review of mass spectrum, (c) NIST library search, (d) Linearity of matrix matched calibration, (e) Quantification and qualifier ion ratio, (f) Selected ion chromatogram (SIM) of *p,p′*-DDE

satisfactory range (0.4-9.1%) of SANTE/11813/2017 guidelines [19].

Previous studies reported that matrix effect mediated a signal enhancement produced for interaction of analyte functional groups such as OH, NH_3 and PO_4 with active surfaces of GC-MS injector, column and detector [26,27]. Costa *et al.* [28] reported that compounds containing oxygen, phosphorous (organophosphate) functional groups were more susceptible towards the matrix effect. Matrix matched calibration curve play an important role in reducing the matrix effect along with signal suppression and enhancement during analysis [29]. In present study, majority of pesticides were not markedly changed by the matrix effect. However, some of the pesticides showed signal enhancement. Moreover, application of SIM mode revealed that there were no significant matrix effects in characteristic target as well as qualifier ions [30].

In present study, uncertainty was calculated using all parameters including accuracy, precision, repeatability, recovery and calibration curves for each pesticide. Uncertainty was estimated at confidence level 95% (k = 2) for concentration of organochlorines (50 µg/kg), organophosphates (100 µg/kg) and synthetic pyrethroids (250 µg/kg) (Table-2). The uncer-

TABLE-2
GC-MS METHOD PERFORMANCES OF PESTICIDE RESIDUES IN GREEN CHILLI SAMPLES

Pesticides	t_r[a]	Calibration		LOD[c]	LOQ[d]	RSD[e]	Recovery[f]	U (%)[g]
		r^2[b]	Equation					
Dichlorovos	5.36	0.9985	Y = 232.354 * x + -36849.1	3	11	2.8	91 ± 3	18
4-Bromo-2-chlorophenol	5.57	0.9993	Y = 265.968 * x + -42944.4	1	4	7.2	81 ± 12	21
Monocrotophos	9.34	0.9963	Y = 133.912 * x + -99046.3	15	46	7.8	87 ± 9	20
Phorate	9.46	0.9914	Y = 86.3362 * x + -7551.01	12	41	3.6	113 ± 4	26
α-BHC	9.63	0.9937	Y = 682.171 * x + -39806.3	2	7	6.6	90 ± 6	6
Dimethoate	9.91	0.9929	Y = 159.915 * x + -37931.2	9	30	4.3	103 ± 4	10
β-BHC	10.22	0.9920	Y = 593.670 * x + -42377.2	3	11	2.5	99 ± 3	16
γ-BHC	10.39	0.9926	Y = 542.804 * x + -36217.0	3	10	2.4	95 ± 2	6
Diazinone	10.71	0.9922	Y = 250.796 * x + -50118.0	3	10	3.5	111 ± 4	5
Fluchloralin	10.79	0.9925	Y = 222.154 * x + -23022.2	5	17	8.3	75 ± 6	26
δ-BHC	10.99	0.9912	Y = 440.316 * x + -36267.2	3	10	2.1	108 ± 1	5
Phosphamidon	11.94	0.9901	Y = 543.335 * x + -115210	5	17	1.0	103 ± 1	9
Chlorpyrifos-methyl	12.29	0.9942	Y = 642.454 * x + -101766	2	7	4.5	105 ± 3	48
Methyl parathion	12.30	0.9905	Y = 468.626 * x + -91842.2	2	7	3.0	117 ± 1	10
Alachlor	12.58	0.9972	Y = 403.684 * x + -44125.9	4	14	9.1	83 ± 7	32
Heptachlor	12.65	0.9928	Y = 460.372 * x + -43375.9	3	10	2.1	103 ± 1	5
Fenitrothion	13.31	0.9861	Y = 52.8351 * x + -7282.48	17	57	4.0	127 ± 2	42
Malathion	13.75	0.9931	Y = 372.220 * x + -72233.5	6	20	2.8	116 ± 2	32
Aldrin	14.01	0.9964	Y = 840.588 * x + -42071.0	10	34	2.6	104 ± 3	6
Chlorpyrifos	14.19	0.9905	Y = 117.488 * x + -26982.5	4	14	1.6	122 ± 6	26
Pendimethalin	15.39	0.9947	Y = 147.800 * x + -31221.0	13	45	4.5	112 ± 8	48
Heptachlor epoxide	15.43	0.9910	Y = 436.303 * x + -20743.2	12	40	3.6	92 ± 3	38
Quinalphos	15.79	0.9910	Y = 238.434 * x + -48672.3	9	30	6.4	108 ± 2	7
o,p′-DDE	16.39	0.9914	Y = 976.603 * x + -68751.2	2	7	2.7	104 ± 3	18
α-Endosulfan	16.64	0.9917	Y = 174.625 * x + -15350.3	17	57	4.5	121 ± 1	6
Butachlor	16.77	0.9914	Y = 674.562 * x + -65315.7	2	7	7.9	97 ± 8	48
Profenofos	17.29	0.9960	Y = 112.601 * x + -24586.9	25	85	0.4	110 ± 1	42
p,p′-DDE	17.40	0.9927	Y = 858.390 * x + -59915.9	2	7	5.8	103 ± 3	4
o,p′-DDD	17.66	0.9923	Y = 1896.55 * x + -125765	1	4	2.8	107 ± 1	12
β-Endosulfan	18.39	0.9930	Y = 108.726 * x + -11138.1	20	67	5.1	116 ± 6	6
p,p′-DDD	18.65	0.9940	Y = 1862.05 * x + -120284	1	4	0.7	114 ± 1	4
o,p′-DDT	18.76	0.9923	Y = 395.823 * x + -26832.5	3	10	3.7	105 ± 1	15
Ethion	18.82	0.9979	Y = 342.033 * x + -57889.9	3	10	1.7	108 ± 2	7
Triazophos	19.20	0.9960	Y = 385.022 * x + -56845.3	6	21	1.2	94 ± 2	12
Edifenphos	19.56	0.9950	Y = 260.807 * x + -46119.3	4	14	3.2	92 ± 3	18
p,p′-DDT	19.73	0.9952	Y = 283.112 * x + -24984.7	4	14	5.5	106 ± 4	21
Fenpropathrin	21.29	0.9911	Y = 646.793 * x + -5617.08	7	23	8.0	79 ± 6	48
λ-Cyhalothrin	22.39	0.9960	Y = 514.347 * x + -28914.9	15	50	5.8	100 ± 6	48
Cyfluthrin	23.97	0.9959	Y = 178.375 * x + -5728.05	21	69	3.8	104 ± 4	35
α-Cypermethrin	24.46	0.9954	Y = 547.054 * x + -20942.2	17	57	3.1	95 ± 3	48
Fenvalerate	25.38	0.9960	Y = 287.789 * x + -24867.7	23	75	4.6	100 ± 5	48
Deltamethrin	26.44	0.9978	Y = 118.124 * x + -20611.3	63	150	1.8	117 ± 2	32

[a]Retention time (min), [b]Linearity, [c]Limit of detection (μg/kg), [d]Limit of quantification (μg/kg), [e]Relative standard deviation (seven replicates), [f]Recovery (seven replicates), [g]Uncertainty measurement.

tainty ranged between 4-48% for all pesticides. Chlorpyrifos-methyl, pendimethalin, butachlor, fenpropathrin, l-cyhalothrin, α-cypermethrin and fenvalerate showed highest uncertainty values. The contribution of accuracy and repeatability was the highest towards uncertainty measurement as compared to purity of the reference standard which contributed the least. It was however found to be within uncertainty acceptance criteria (< 50%) of SANTE/11813/2017 guideline [19].

This validated method was also applied to 55 samples procured from local market, Ahmedabad, India. The samples were chosen according to the consumption and the pesticides were selected according to the recommended usage in green chillies [31-33]. Pesticides were detected below LOQ in these samples however, ethion was found to be positive in 3 samples (range, 217-229 μg/kg) but below MRL values [34]. Table-3 depicts a comparison of the current method and other methods performed previously, wherein non-significant variance in recovery, LOD and LOQs was obtained. The present method was observed to be simpler than other methods and has advantage in terms of efficiency, recovery percentage, analysis time as well as cost-effectiveness.

Conclusion

An analytical method for determining 42 pesticides in chilly matrix using modified QuEChERS extraction method followed by GC-SQ/MS-SIM analysis was developed and

TABLE-3
OVERVIEW OF MULTI-RESIDUE METHODS FOR THE ANALYSIS OF DIFFERENT PESTICIDE IN CHILLI SAMPLES

Analytes	Sample amount	Extraction		Sorbents in clean-up	Analytical technique	Recovery (%)	LODs	LOQs	Ref.
		Solvents	Salts						
Spiromesifen	10 g	Acetonitrile	NaCl, $MgSO_4$	PSA GCB	UHPLC	84.14-95.20	0.05 µg/g	0.015 µg/g	[35]
23 pesticides	15 g	Acetonitrile	NaCl, $MgSO_4$	PSA	GC-MS	79-108	–	–	[36]
47 pesticides	10 g	Acetonitrile	NaCl, $MgSO_4$	Sin-QuEChERS cartridge	LC-MS/MS GC-MS/MS	70-120	–	0.01 mg/kg	[37]
Tebuconazole	15 g	Acetonitrile	NaCl, $MgSO_4$	PSA	GC-MS	94-104	0.017 mg/kg	0.05 mg/kg	[38]
80 pesticides	15 g	Acetonitrile	$MgSO_4$, CH_3COONa	PSA	LC-MS/MS GC-MS/MS	70.5-126.6	0.0004-0.0023 mg/kg	0.0008-0.0047 mg/kg	[39]
Chlorantraniliprole	15 g	Acetonitrile	NaCl, $MgSO_4$	PSA	GC-MS/MS	72-91	0.005 mg/kg	0.01 mg/kg	[40]
42 pesticides	10 g	Acetonitrile	NaCl, $MgSO_4$	PSA	GC-MS-SIM	75-127	1-63 µg/kg	4-150 µg/kg	Present study

validated. Optimized conditions permitted the separation of all analytes with high resolution. Post application of modified QuEChERS in chilly matrix, a proper validation *viz.* linearity, recovery and precision was performed and the expanded uncertainty was observed to be lying within the acceptable range. The developed method was found to be specific, accurate, reproducible and user friendly for different pesticides in green chilli crops.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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