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# Multivariate optimization and validation of 200 pesticide residues in the banana matrix by GC-MS/MS†

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GC-MS/MS has been observed from past studies to be an appropriate choice for designing a simple, efficient and sensitive analytical technique. Accordingly, the linearity and working range, Method Limit of Detection (MLOD), Method Limit of Quantification (MLOQ), accuracy, precision (intra-day and inter-day), Matrix Effect (ME) and selectivity were analyzed for the assessment of 200 pesticide residues [organophosphorus pesticides (OPP), organochlorine pesticides (OCP), organonitrogen pesticides (ONP), synthetic pyrethroid pesticides (SPP), and herbicide methyl esters (HME)] in the banana matrix. The procedure involved QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction and clean-up with Multi-Walled Carbon Nanotubes (MWCNTs) and Primary Secondary Amine (PSA) wherein the factors were optimized using the Plackett–Burman and central composite designs. The performance of the method in order to quantitate 200 pesticides at trace levels was evaluated by matrix-matched calibration. The linearity was observed to range from 1 to 100  $\mu\text{g L}^{-1}$  with determination coefficient ( $r^2$ ) > 0.99. Recovery studies were conducted at 2 levels, 10  $\mu\text{g kg}^{-1}$  and 25  $\mu\text{g kg}^{-1}$ , and the values obtained were in the range of 71–116% and 72–119%, respectively. The Relative Standard Deviation (RSD) was observed to be less than 20% in line with the recommended guidelines (SANTE/11312/2021). The MLOD and MLOQ were found to be in the range of 0.45–6.33  $\mu\text{g kg}^{-1}$  and 1.44–9.59  $\mu\text{g kg}^{-1}$  respectively. The developed method was applied satisfactorily to analyse banana samples cultivated in different regions of Gujarat, India.

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## Introduction

Banana, an edible fruit belonging to the genus *Musa* is known for its nutritional as well as medicinal benefits. It is not just high in calories, providing about 90–100 kcal per 100 g of edible portion, but it also has an abundance of necessary elements.<sup>1</sup> Banana plantations thrive in hot, wet and tropical climates, due to which they are more susceptible to pest infestations and fungal infection, especially from *Thrips hawaiiensis*, *Hypomeces* spp., *Macrophoma musae*, *Pyricularia grisea*, *Mycosphaerella musicola*, etc.<sup>2</sup> It is to prevent these infestations as well as to increase the yield of bananas that agricultural professionals have over time made liberal use of pesticides.<sup>3</sup>

However, it is imperative to note that repeated usage of pesticides increases the possibility of pesticide resistance and pest resurgence, in addition to retention of residues, and the resultant ecological damage. Depending on their type and interaction, potential pesticides build up in the fatty tissues of human beings and over a period of time damage the endocrine, nervous, and immune systems, sometimes even causing cancer. Serious illnesses such as kidney disease, Parkinson's disease, Alzheimer's disease etc.<sup>1,3–5</sup> too have been linked to exposure to them. In order to mitigate these and many other adverse health effects, various organizations have proposed maximum residue levels (MRLs) so as to regulate exposure to pesticide residues in foods.<sup>1,3</sup> Development of specific and sensitive analytical methods aids in assessing multi-pesticide residues which in turn aids in evaluating MRLs for regulatory purposes. The present study is an attempt towards achieving the same for the banana matrix.

Chromatographic techniques combined with Nitrogen-Phosphorus Detection (NPD),<sup>6</sup> Flame Ionization Detection (FID),<sup>6</sup> Diode-Array Detection (DAD),<sup>6</sup> Electron Capture Detection (ECD),<sup>6</sup> Mass Spectrometry (MS),<sup>6,7</sup> etc. have been to date commonly employed for specific pesticide residue analysis.

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Herein, the number of target analytes is limited, but sensitivity and confirmation too frequently fall short of trace level (sub ppb level) estimations. Gas chromatographic methods coupled with tandem mass spectrometry (MS/MS) detection have of late emerged as an excellent alternative for detecting pesticide residues at extremely low levels with exceptional sensitivity and specificity.<sup>6,8,9</sup> In view of this, it is critical to emphasize that use of the multiple reaction monitoring (MRM) mode and electron impact ionization shortens the time of chromatographic analysis or separation and even improves the signal-to-noise ratios (S/N) thereby improving specificity and sensitivity.<sup>9,10</sup>

Determination of pesticide residues at trace levels in food matrices is challenging due to a host of factors. These include the physicochemical features of the pesticides being estimated as well as the voluminous quantity of interferents which can lead to adverse outcomes post chromatography.<sup>1,4,11,12</sup> Over the last few years numerous procedures involving Solid Liquid Extraction (SLE),<sup>12</sup> Solid Phase Extraction (SPE),<sup>12</sup> Matrix Solid-Phase Dispersion (MSPD),<sup>12</sup> Solid-Phase Micro Extraction (SPME),<sup>12</sup> Pressurized Liquid Extraction (PLE),<sup>12</sup> Stir Bar Sorptive Extraction (SBSE)<sup>12</sup> and Microwave Assisted Extraction (MAE)<sup>10</sup> have been developed and employed for extraction and clean-up, for residual pesticide analysis in fruits.<sup>10</sup> Although these techniques have been proven to be quite effective, some of them used large amounts of solvents whereas some had high run times making these studies difficult to perform when extraction of a small range of pesticides was needed, or sometimes when multi-residue analysis<sup>7,10</sup> was to be carried out.

The QuEChERS method developed in 2003 brought about a revolutionary change in the sample preparation method for pesticide residue analysis. This approach based on acetonitrile-based extraction and salt-assisted partitioning<sup>14</sup> involved use of different sorbents for extraction procedures. Whilst magnesium sulphate ( $\text{MgSO}_4$ ) is used in this technique to lower the aqueous phase and increase partitioning of pesticides into an organic layer, the fat globules were broken down using sodium acetate (Na acetate). Cleaning up with primary secondary amine (PSA) in dispersive solid phase extraction (d-SPE) further improved the production of cleaner extracts.<sup>15,16</sup> This in turn increased the capacity for removing sugars, organic and fatty acids and polar pigments, as well as aiding in eliminating matrix co-extractants, which could interfere with pesticide residue analysis. The QuEChERS technique incorporates multiwalled carbon nanotubes (MWCNTs) due to their advantageous physico-chemical properties, such as high porosity, surface area, and chemical stability. Furthermore, MWCNTs exhibit favourable stacking interactions between  $\pi$ - $\pi$  molecules and a strong affinity for polycyclic molecules, making them valuable in this context.<sup>16-18</sup> Whilst the  $\text{C}_{18}$  silica sorbent is employed for samples with known fat content, graphitic carbon black (GCB) is used in this technique to remove pigments such as chlorophylls and carotenoids because of their affinity for planar molecules. Usage of citrate salts is also occasionally done whenever method modification is required so as to enhance recovery of sensitive and pH-dependent pesticides or when complicated matrices<sup>1,12</sup> are investigated. Over the last few years the QuEChERS method has seen optimization and validation for a host of matrices *viz.*

vegetables, fruits, fruit juices, cereals, fatty foods<sup>1,12,15</sup> *etc.* However, during a literature review it was observed that only limited studies reported the amalgamation of d-SPE and MWCNT extraction methods for estimation of multi-class pesticide residues, especially for the banana matrix.

The Central Insecticides Board and Registration Committee (CIBRC) of India has registered under its ambit numerous pesticides, insecticides, fungicides and herbicides, the usage of which is prevalent in the country. Whilst some of these are regularly applied to bananas, others are used in broader agricultural contexts and often result in residues in banana samples *via* runoff, drift, or soil contamination. In order to encompass this wide spectrum of pesticides, it became pertinent to develop a method for a mixture with a vast spectrum of residues. Development and validation of such a method would help facilitate a comprehensive assessment of pesticide residues, thereby enabling detection of pesticide residues in banana to assist in implementation of risk mitigation strategies, and help promote sustainable agricultural practices.

With these objectives in mind, the current study has integrated the use of d-SPE and MWCNTs along with a central composite design (CCD) for optimisation of the QuEChERS method for determination of 200 pesticide residues in banana by GC-MS/MS in MRM mode.

## Materials and methods

### Chemicals and apparatus

For the purpose of this study nine groups of certified reference standard pesticide mixtures of OPP, OCP, ONP, SPP and HME (totalling 200 pesticides) at a concentration of  $100 \text{ mg L}^{-1}$  and 81–99% purity were obtained from RESTEK (Bellefonte, PA 16823, USA). An individual stock standard solution of each group of pesticides was prepared at a concentration of  $50 \text{ mg L}^{-1}$  in toluene and the mixtures were stored at a temperature of  $-20^\circ \text{C}$  in amber glass volumetric flasks. A total of 200 mixtures of working standard solutions were prepared at different concentrations [ $50 \text{ mg L}^{-1}$  (main stock),  $5 \text{ mg L}^{-1}$  (intermediate stock) and  $1 \text{ mg L}^{-1}$  (working standard solution)] by appropriate dilution of the stock solutions. These were used for method optimization, validation, quantification and analysis of actual samples.

HPLC grade acetonitrile (J.T. Baker, New Jersey 8865, USA), reagent plus grade acetic acid, reagent plus grade anhydrous magnesium sulphate (purity  $\geq 99.5\%$ ), MWCNTs (with a diameter of 50–90 nm and  $>95\%$  carbon basis) and activated charcoal (100–400 mesh) were used (Sigma Aldrich, Louis, MO 63103, USA). Emparta® ACS grade ethyl acetate (Merck Life Science, Rahway, NJ 07065, USA), pesticide residue grade toluene (Fisher Scientific, Loughborough LE11 5RE – UK), ExcelR grade acetone and sodium acetate from Qualigens (Maharashtra, India) and PSA from Agilent Technologies (Santa Clara, CA 95051, USA) were used for this study.

A high volume homogenizer (Robot Coupe BLIXER® 6 V.V.); analytical balance – Shimadzu AUX (220); refrigerated centrifuge (SORVALL Legend X1R, Thermo Scientific, Waltham, MA 02451, USA); Zymark Turbovap LV (Marshall Scientific); Cryocube F740hi (Eppendorf); and micropipettes (Eppendorf) were

Table 1 Instrumental conditions adopted for the GC-MS/MS system

Parameters	Conditions		
Column	SH-I-5SilMS, $L$ 30 m $\times$ ID 0.25 $\mu$ m $\times$ dF 0.25 $\mu$ m		
Injector port temperature	280 $^{\circ}$ C		
Interface temperature	280 $^{\circ}$ C		
Ion-source temperature	230 $^{\circ}$ C		
Injection mode	Splitless		
Column flow	1.0 mL min $^{-1}$		
Purge flow	3 mL min $^{-1}$		
Solvent cut time (on delay)	4 min		
Collision gas	Argon (99.9999%)		
Carrier gas	Helium (99.9999%)		
Detector gain	+0.70 kV		
Ionization voltage	1.3 kV		
	Rate (°C min $^{-1}$ )	Temp. (°C)	Time (min)
Column temperature program	—	60	1
	15	190	5
	10	300	4
Total run time	28 min		
Injection volume	1 $\mu$ L		
Quantitation and confirmation mode	MRM		
Split ratio	20.0		

used for this study. Gas chromatography-triple quadrupole mass spectrometry (Nexis, GC 2030 and GC-MS-TQ8050NX, Shimadzu, Kanagawa 210-0821, Japan) was used for quantification and conditioning. The parameters adopted for GC-MS/MS are as described in Table 1.

### Sample processing

Samples of banana fruit ( $n = 25$ ) were selected at random in the months of February–March 2023 from the local markets of Ahmedabad, Gujarat. A representative portion of the sample was blended using a high-volume homogenizer and mixed thoroughly. The homogenised samples were stored in 50 mL polytetrafluoroethylene (PTFE) tubes at  $-20$   $^{\circ}$ C. Prior to

initiation of the experiment, these samples were thawed at 5  $^{\circ}$ C overnight. Details of the extraction and d-SPE clean-up procedure are as shown in Fig. 1.

### Multivariate optimization

In line with the aim of the study a multivariate approach was chosen for optimizing the factors involved in the extraction process. The variables selected for optimization were sample weight (g), as well as the weight of MWCNTs (mg), MgSO<sub>4</sub> (mg), PSA (mg), and activated charcoal (mg). For the purpose of optimization and representation these variables have been referred to as A, B, C, D, and E respectively in Table S1,<sup>†</sup> so as to be able to depict the interrelationships and interactions among multiple variables simultaneously. The process of multivariate optimisation involved two processes: (i) a Plackett–Burman (P–B) design (for screening), depicted in Tables S1 and S2,<sup>†</sup> followed by (ii) a central composite design (CCD) (for optimization) as shown in Table S3<sup>†</sup> for obtaining an effective and optimized extraction process for analysing multi-pesticide residues using the Minitab18.1<sup>®</sup> statistical software trial version (Minitab Inc., State College, USA).

Herein, a mixture of 200 pesticides was used for the analysis. Accordingly, the average recovery of these pesticides was used as the response in this optimization. This was done so as to develop an efficient extraction method by using a mixture of pesticides.

### Method validation

The developed method was validated in order to establish its reliability and suitability for quantification of multi-pesticide analytes in the banana matrix. The validation procedures were assessed as per SANTE guidelines.<sup>12,19</sup> The linearity and working range, MLOD, MLOQ, accuracy, precision (intra-day and inter-day), selectivity and ME were evaluated. The investigation of ME involved comparing the calibration curves generated in solvent with those created in the matrix-matched solvent. This was achieved by adding the standard to the solvent and matrix-matched solvent, respectively, to assess the differences if any in the matrix effect. For the purpose of linearity, pesticide mixtures were evaluated at 8 levels (*viz.* 1, 2.5, 5, 10, 25, 50, 75 and 100  $\mu$ g L $^{-1}$ ). Accuracy and precision were evaluated by examining seven replicates of a blank banana matrix spiked at concentrations of 10, 25, and 50  $\mu$ g L $^{-1}$  before sample extraction. The assessment was based on predefined acceptance criteria: recovery rates between 70% and 120% and a Relative Standard Deviation (RSD) of less than 20%. Inter-day precision was assessed and observed to be 25  $\mu$ g L $^{-1}$ . Post this seven spiked samples were examined for intra-day precision. The MLOD and MLOQ were evaluated by extracting seven replicates of the sample spiked with a mixture of pesticides at a concentration of 10  $\mu$ g L $^{-1}$ . The selectivity was evaluated based on extraction and analysis of a 'blank' and 'reagent blank'.

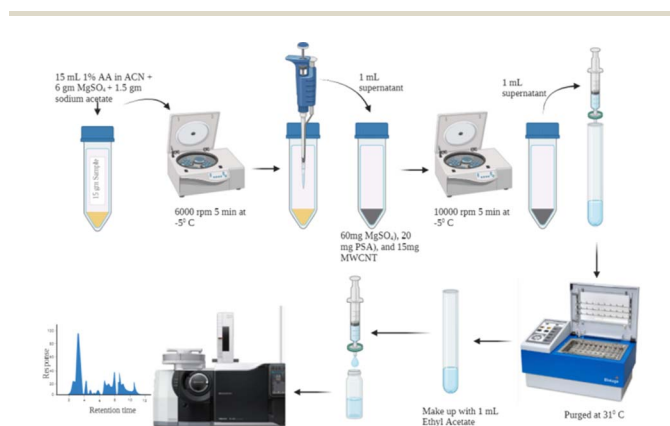


Fig. 1 Schematic diagram of the extraction procedure.

## Results and discussion

### Optimization of GC-MS/MS

GC-MS/MS parameters were optimized through Solution ver. 4.45 software and Microsoft Excel™ based files (MRM Optimization Tool and pesticide database ver. 1.03). For optimization of MS parameters, all compounds were first monitored in full scan mode in the range of 45–550 *m/z* using the Shimadzu SMART MRM Optimization Tool. The three most intense transitions for each pesticide and their optimal Collision Energies (CE) were selected for MRM mode. The working parameters of the GC-MS/MS have been tabulated in Tables 1 and 3 respectively.

The MRM mode was used, since it has been observed to be very specific, selective, and sensitive.<sup>20</sup> It was also observed that the peaks obtained were precisely separated and that retention times (RTs) too were within a deviation of  $\pm 0.2$  min from the estimated retention durations. Based on the separation obtained, the total ion chromatogram was used for screening whereas MRM was used for quantitation of pesticide residues in banana samples.

### Plackett–Burman (P–B) design

Sample preparation was optimized using the Plackett–Burman design and was used to screen for the most significant parameters. A permutation of the five effective parameters *viz.* (a) sample wt: 5–15 g; (b) MWCNTs wt: 5–15 mg; (c) MgSO<sub>4</sub> wt: 30–60 mg; (d) PSA wt: 20–40 mg and (e) activated charcoal wt: 0–5 mg was carried out to investigate their potential impact on sample preparation. The effectiveness was investigated in 15 runs at 3 levels (–1, 0, +1) using Analysis of Variance (ANOVA) at the 95% confidence level (*p* value < 0.05). Systematic random sampling was carried out for the samples for the said procedure so as to avoid bias. Results obtained from the P–B design have been depicted in the form of a Pareto chart in Fig. 2. The results indicated that, for sample preparation of the target analytes, sample weight and quantity of MWCNT were the only significant variables amongst all the parameters. It was also observed that MWCNTs were more significant as compared to PSA during the clean-up step, due to their ability to remove pigments and

matrix interfering substances whilst at the same time maintaining pH for improving method sensitivity.<sup>21</sup> The weight of (c) MgSO<sub>4</sub>, (d) PSA and (e) activated charcoal had no significant impact on the response and hence their values were fixed based on the response they produced during the screening design. Accordingly, (c) weight of MgSO<sub>4</sub> and (d) weight of PSA were fixed at 60 mg and 20 mg respectively. The smaller quantity of MgSO<sub>4</sub> was chosen since it tended to agglomerate at higher quantities and also produced an exothermic reaction, which could in turn cause loss of thermally sensitive pesticides.<sup>22</sup> It was also noticed that, as the amount of activated charcoal increased, recovery of analytes decreased indicating that use of activated charcoal as an adsorbent led to the deterioration of recovery of pesticide analytes in the matrix. Rather, higher recovery and efficiency were observed without including this adsorbent in this method.

Further, so as to deduce the optimum values of the two most significant factors the central composite design was utilised.

$$\text{Recovery} = 87.93 + 0.407a - 0.369b - 0.0083c - 0.0164d - 0.462e + 1.31C_tP_t$$

where *a* is the sample weight (g), *b* is the weight of MWCNTs (mg), *c* is the weight of MgSO<sub>4</sub> (mg), *d* is the weight of PSA (mg) and *e* is the weight of activated charcoal (mg).

### Central composite design (CCD)

The two significant factors obtained from the screening design were further optimized using a CCD and were studied at different levels of low (–1), medium (0), and high (+1) as well as at the axial points (– $\alpha$ , + $\alpha$ ). The ANOVA test was employed in order to elicit a response and to ascertain the optimum value for each factor at a 95% (*p* value < 0.05) confidence level (Table 2). It was observed that the interaction between the sample weight and weight of MWCNTs had a significant impact on the extraction efficiency with *p*-values of 0.01 and 0.05 respectively. The ‘lack of fit’ observed in this model was statistically not significant with a *p*-value of 0.5, indicating that the model satisfactorily captured the relationship between design and data.

The two-level full factorial CCD for 2 factors consisted of 13 randomized experimental runs including the center points. The randomized runs were performed so as to aid in mitigating the influence of a host of unpredictable and uncontrollable variables in the multi-residual extraction procedure experimental runs as shown in Table S3.† [The design of these runs consisted of 1 base block with cube point 4, a center point in cube 5 and the axial point 4.] The randomized runs were produced in line with the following equation *viz.*

$$N = 2^k + 2k + C_p$$

where *k* is the number of factors, *N* is the total number of runs, and *C<sub>p</sub>* is the number of centre points.<sup>23</sup>

The three-dimensional surface plot depicted in Fig. 3 portrays the influence of the two significant factors *viz.* wt of MWCNTs and wt of the sample on recovery. The surface plot also revealed that maximal recovery of pesticide residues could

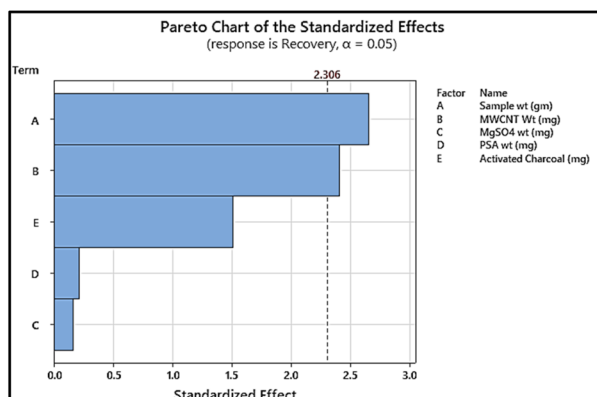


Fig. 2 Pareto chart (P–B design) for the sample, MWCNT, MgSO<sub>4</sub>, PSA and activated charcoal.

Table 2 Analysis of variance (ANOVA) for the central composite design<sup>a</sup>

Source	DF	Adj. SS	Adj. MS	f-Value	P-Value
Model	5	1025.42	205.083	3.9	0.052
Linear	2	916.82	458.408	8.72	0.013
Sample wt (g)	1	628.33	628.333	11.95	0.011
MWCNTs wt (mg)	1	288.48	288.483	5.49	0.052
Square	2	17.4	8.699	0.17	0.851
Sample wt (g) × sample wt (g)	1	13.16	13.157	0.25	0.632
MWCNT wt (mg) × MWCNT wt (mg)	1	2.46	2.461	0.05	0.835
2-Way interaction	1	91.2	91.202	1.74	0.229
Sample wt (g) × MWCNT wt (mg)	1	91.2	91.202	1.74	0.229
Error	7	367.96	52.656		
Lack-of-fit	3	147.28	49.092	0.89	0.519
Pure error	4	220.68	55.17		
Total	12	1393.37			

<sup>a</sup> DF – degree of freedom; adj. SS – adjusted sum of square; adj. MS – adjusted mean square.

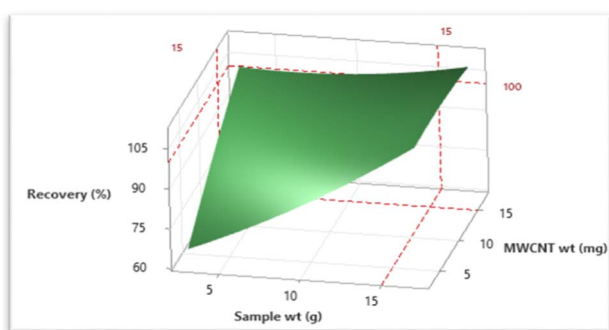


Fig. 3 Surface plot of recovery vs. MWCNTs vs. sample.

be achieved with an increase in sample weight and also by maintaining the weight of MWCNTs at a higher value. The main effects plot (Fig. 4) for recovery showcases a graphical representation depicting the optimal values for each independent variable which could maximize recovery. The analysis revealed that there existed a positive correlation between the increase in the weight of MWCNTs and sample weight which in turn led to an improvement in recovery of target analytes. Overall, gradual enhancements in the recovery of analytes were observed as the weights of the MWCNTs and the sample were increased.

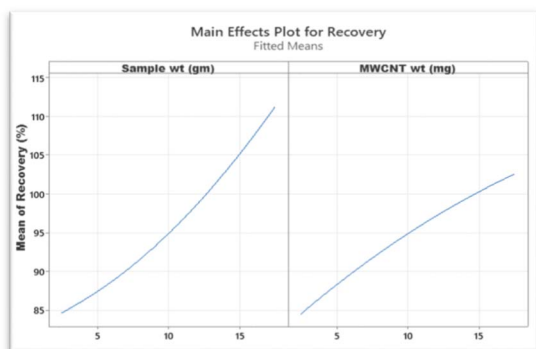


Fig. 4 Factorial plot for the sample and MWCNTs.

However, post reaching a threshold level (*viz.* wt of MWCNTs: 15 mg and wt of sample: 15 g) a further increase in their weights did not significantly enhance analyte recovery.

A regression equation for recovery of target analytes was also derived using a CCD since this equation could aid in prediction of response variables based on values of the factors and their resultant interaction within the experimental range.

The resultant equation obtained was:

$$\text{Recovery} = 49.2 + 2.58x + 3.59y + 0.055x \times x - 0.024y \times y - 0.191x \times y$$

where  $x$  is the sample weight (g) and  $y$  is the weight of MWCNTs (mg).

The regression analysis coefficients were observed to offer insights into both the direction and magnitude of the impacts of the factors, including their interactions on the response variables. The results obtained led to the identification of optimal conditions for the efficient and effective extraction of pesticides *viz.*: a sample weight of 15 g, weight of MWCNTs: 15 mg, weight of  $\text{MgSO}_4$ : 60 mg, and weight of PSA: 20 mg.

QuEChERS in conjunction with MWCNTs and PSA was selected for sample extraction chiefly due to its simplicity, ease of use, and associated benefits.<sup>16,17,24</sup> It is important to note here that the associated minimalism played a key role in influencing the results positively. These have been described below in method validation as well as in Table 4.

## Method validation

Performance of the developed method was evaluated by validating several parameters, *viz.* linearity, recovery, precision, accuracy, matrix effect, MLOD and MLOQ. These parameters were assessed in order to determine the efficiency of the developed and validated method for determination of multi-pesticide residue in banana samples. Fig. 5 shows the chromatogram generated for quantitative analysis of 200 pesticide residues in MRM mode whereas the blank chromatogram is presented in Fig. 6. Parameters and validation parameters for all the pesticide residues analysed are summarized in Tables 3 and 4.

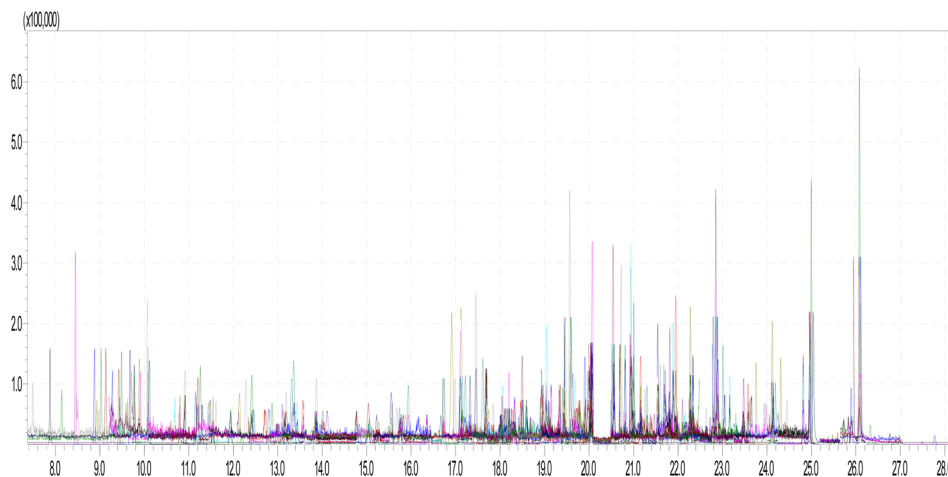


Fig. 5 Typical GC-MS/MS-MRM chromatogram of pesticide residues in banana spiked at  $10 \mu\text{g L}^{-1}$ .

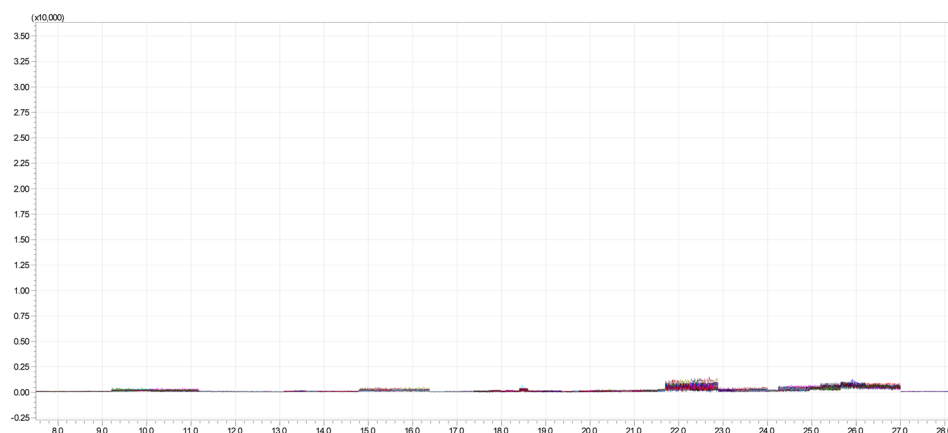


Fig. 6 GC-MS/MS chromatogram of a blank sample.

### Linearity and working range

Linearity of the method was assessed by analysing the relationship between the concentration of the analytes and their corresponding response signals. A linear curved graph was obtained during the matrix match calibration over the concentration range of  $1\text{--}100 \mu\text{g L}^{-1}$ , indicating a strong linearity of 0.995 in the range of 0.990–0.999.

Studies of a similar kind have been reported for estimating 733 pesticide residues in fruits and vegetables. The correlation co-efficient of  $r^2 \geq 0.995$  was recorded for 96.1% of the pesticides by LC-Q-TOFMS and 92.4% by GC-Q-TOFMS.<sup>4</sup> Another study wherein 31 compounds were analysed by GC-MS/MS<sup>1</sup> reported a linearity of 0.995 in the range of 0.9570–0.9992.

### Selectivity

In line with the SANTE guidelines, selectivity of a method is verified by identification and confirmation at the Screening Detection Limit (SDL).<sup>19</sup> The procedure is referred to as selective, when the analyte is detected in tests and is not obscured by the presence of other chemicals. Hence, accordingly, analysis

was done on blank banana samples in order to check for interference peaks, if any. Further, in order to verify the presence, if any, of other compounds which could interfere in peak detection, blank and spiked samples were also compared.

With the exception of one instance, every pesticide was accurately identified in the examined samples. None reported any interference. In the sole instance wherein interference was observed, six pesticides (2-phenyl phenol, captafol, captan, choroneb, endrin aldehyde and triadimenol) were reported in the banana matrix. Hence, these six compounds could be considered as not complying with the validation parameters of the SANTE guidelines. This could be attributed to ion enhancement. Since this was observed only for 06 out of the 200 pesticides, the study can be deemed reliable since the results are within the permissible range.

### Method limit of detection (MLOD)

The MLOD of this method was determined by using seven replicates ( $n = 7$ ) of pesticide fortified solutions at a concentration of  $10 \mu\text{g L}^{-1}$ . The MLOD of the method was observed to

Table 3 Parameters for GC-MS/MS – chemical class, RT and MRM transition<sup>a</sup>

Compound name	Chemical class	RT <sup>b</sup>	Quantitation		Confirmation			
			MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>
(E)-Chlorfenvinphos	OPP	18.315	323.00 > 267.00	16	267.00 > 159.00	18	267.00 > 203.00	12
(Z)-Chlorfenvinphos	OPP	19.425	323.00 > 267.00	16	267.00 > 159.00	18	267.00 > 203.00	12
2,3,5,6-Tetrachloroaniline	ONP	11.195	228.90 > 158.00	18	230.90 > 158.00	22	230.90 > 160.00	18
2,4'-Methoxychlor	OCP	21.940	227.10 > 121.10	16	121.10 > 78.00	22	121.10 > 91.00	12
2-Phenylphenol	HME	10.060	170.10 > 141.10	24	141.10 > 115.10	18	170.10 > 115.10	28
3,4-Dichloroaniline	ONP	9.270	161.00 > 99.00	22	161.00 > 90.00	18	161.00 > 126.00	14
4,4'-Dichlorobenzophenone	OCP	17.445	139.00 > 111.00	14	139.00 > 75.00	26	249.90 > 139.00	16
4,4'-Methoxychlor olefin	OCP	21.540	238.10 > 223.10	12	308.00 > 238.10	16	238.10 > 195.10	20
Acetquinocyl	HME	26.000	342.20 > 188.10	14	188.10 > 131.10	22	188.10 > 160.10	8
Acetochlor	ONP	15.210	174.10 > 146.10	12	223.10 > 132.10	22	223.10 > 147.10	10
Acrinathrin-1	SPP	24.085	181.10 > 152.10	26	289.10 > 93.00	14	181.10 > 127.10	28
Alachlor	ONP	15.580	188.10 > 160.10	10	188.10 > 132.10	18	160.10 > 132.10	10
Aldrin	OCP	17.975	262.90 > 191.00	34	262.90 > 193.00	28	292.90 > 219.90	26
Allethrin-3,4	SPP	18.450	123.10 > 81.10	10	136.10 > 93.10	14	123.10 > 95.10	8
Allidochlor	ONP	7.875	132.10 > 56.00	8	138.10 > 96.00	6	132.10 > 49.00	24
Alpha-BHC	OCP	12.130	180.90 > 144.90	16	218.90 > 182.90	8	218.90 > 144.90	20
Alpha-endosulfan	OCP	14.810	194.90 > 160.00	8	194.90 > 125.00	24	194.90 > 123.00	22
Anthraquinone	SPP	17.110	180.10 > 152.10	14	208.10 > 180.10	10	208.10 > 152.10	22
Atrazine	ONP	12.700	215.10 > 58.00	14	215.10 > 173.10	6	200.10 > 104.10	18
Azinphos-ethyl	OPP	24.295	132.10 > 77.00	14	160.10 > 132.10	4	160.10 > 77.00	18
Azinphos-methyl	OPP	23.640	160.10 > 132.10	6	160.10 > 77.00	20	132.10 > 77.00	14
Benfluralin	ONP	11.535	292.10 > 264.00	8	292.10 > 160.00	22	292.10 > 206.00	12
Beta-BHC	OCP	12.785	180.90 > 144.90	16	218.90 > 182.90	8	218.90 > 144.90	20
Beta-endosulfan	OCP	20.800	194.90 > 160.00	8	194.90 > 125.00	24	194.90 > 123.00	22
Bifenthrin	SPP	22.845	181.10 > 166.10	12	181.10 > 179.10	12	181.10 > 153.10	8
Biphenyl	ONP	8.870	154.10 > 128.10	22	154.10 > 115.10	24	152.10 > 126.10	24
Bromfenvinfos-methyl	OPP	18.340	294.90 > 109.00	16	296.90 > 109.00	16	294.90 > 266.90	6
Bromfenvinphos	OPP	19.425	266.90 > 159.00	14	268.90 > 161.00	16	322.90 > 266.90	12
Bromophos	OPP	17.655	330.90 > 315.90	14	328.90 > 313.90	18	330.90 > 285.90	28
Bromophos-ethyl	OPP	18.910	358.90 > 302.90	16	302.90 > 284.90	18	358.90 > 330.90	10
Bromopropylate	HME	22.895	340.90 > 182.90	18	340.90 > 184.90	20	340.90 > 157.00	30
Bupirimate	ONP	20.090	273.10 > 108.10	16	273.10 > 193.10	8	316.10 > 208.10	10
Captan	ONP	22.300	79.00 > 77.00	14	79.00 > 51.00	20	183.10 > 79.00	18
Captan	ONP	18.520	149.10 > 79.10	14	149.10 > 105.10	4	149.10 > 70.00	18
Carbophenothion	OPP	21.525	157.00 > 45.00	18	341.90 > 157.00	14	341.90 > 199.00	8
Carfentrazone-ethyl	HME	21.455	340.10 > 312.10	14	312.10 > 151.10	24	340.10 > 151.10	28
Chlorbenside	OCP	18.930	125.00 > 89.00	16	125.00 > 99.00	18	127.00 > 89.00	18
Chlorfenapyr	ONP	20.325	247.10 > 227.00	16	139.00 > 102.00	12	247.10 > 200.00	24
Chlorfenson	OCP	19.580	175.00 > 111.00	12	175.00 > 75.00	28	301.90 > 175.00	8
Chlorobenzilate	HME	20.712	139.00 > 111.00	16	251.00 > 139.00	14	139.00 > 75.00	26
Chloroneb	OCP	9.885	206.00 > 191.00	12	206.00 > 141.00	20	193.00 > 113.00	18
Chlorothalonil	ONP	13.625	263.90 > 168.00	24	263.90 > 228.80	18	265.90 > 168.00	22
Chlorpropham	HME	11.430	127.10 > 65.00	22	213.10 > 171.10	6	127.10 > 92.00	18
Chlorpyrifos	OPP	16.975	196.90 > 168.90	14	313.90 > 257.90	14	313.90 > 285.90	8
Chlorpyrifos-methyl	OPP	15.265	285.90 > 93.00	22	287.90 > 93.00	22	285.90 > 270.90	14
Chlorthal-dimethyl	HME	17.145	298.90 > 220.90	24	300.90 > 222.90	26	300.90 > 272.90	14
Chlorthiophos	OPP	20.300	256.90 > 239.00	14	256.90 > 193.00	22	256.90 > 165.00	26
Chlozolinate	HME	18.245	330.90 > 258.90	6	258.90 > 188.00	14	330.90 > 186.00	20
cis-Chlordane	OCP	19.325	374.80 > 265.90	26	372.80 > 263.90	28	372.80 > 265.90	22
cis-Nonachlor	OCP	20.940	406.80 > 299.90	24	406.80 > 109.00	22	406.80 > 334.90	16
Clomazone	ONP	12.860	204.10 > 107.00	20	204.10 > 78.00	26	204.10 > 68.00	24
Coumaphos	OPP	24.950	362.00 > 109.00	16	362.0 > 109.0	14	362.00 > 226.00	14
Cycloate	ONP	11.255	154.20 > 83.10	8	154.20 > 55.00	18	154.20 > 72.00	6
Cyfluthrin	SPP	25.355	163.10 > 127.10	6	163.10 > 91.00	14	226.10 > 206.10	14
Cypermethrin	SPP	25.715	163.10 > 127.10	6	163.10 > 91.00	14	181.10 > 152.10	22
Cyprodinil	ONP	18.035	224.10 > 208.10	16	224.10 > 197.10	22	224.10 > 131.10	14
Delta-BHC	OCP	14.003	180.90 > 144.90	16	218.90 > 182.90	8	218.90 > 144.90	20
Deltamethrin	SPP	27.760	180.90 > 151.90	22	252.90 > 93.00	20	252.90 > 171.90	8
Di-allate	ONP	11.905	234.10 > 150.00	20	234.10 > 192.10	14	128.00 > 86.00	4
Diazinon	OPP	13.355	304.10 > 179.10	10	179.10 > 137.10	18	179.10 > 122.10	24
Dichlofluanid	ONP	16.660	223.90 > 123.10	8	167.10 > 124.10	10	167.10 > 97.00	22

Table 3 (Contd.)

Compound name	Chemical class	RT <sup>b</sup>	Quantitation		Confirmation			
			MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>
Dichlobenil	ONP	8.445	171.00 > 136.00	13	171.00 > 100.00	25	136.00 > 100.00	10
Dicloran	ONP	12.460	206.00 > 176.00	10	176.00 > 148.00	12	206.00 > 124.00	24
Dieldrin	OCP	20.015	276.90 > 241.00	8	262.90 > 193.00	34	262.90 > 228.00	24
Dimethachlor	ONP	15.015	197.10 > 148.10	10	197.10 > 120.10	22	199.10 > 148.10	10
Diphenamid	ONP	17.675	167.10 > 152.10	20	239.10 > 167.10	8	239.10 > 72.00	16
Diphenylamine	ONP	11.141	169.10 > 66.00	24	167.10 > 139.10	28	169.10 > 77.00	28
Disulfoton	OPP	13.790	153.00 > 97.00	10	153.00 > 125.00	6	186.00 > 153.00	6
Edifenphos	OPP	21.595	173.00 > 109.00	10	310.00 > 173.00	14	310.00 > 109.00	26
Endosulfan ether	OCP	14.820	240.90 > 205.90	16	238.90 > 203.90	16	240.90 > 203.90	18
Endosulfan sulfate	OCP	21.705	271.80 > 236.90	18	386.80 > 252.90	16	386.80 > 288.80	10
Endrin	OCP	20.565	262.90 > 191.00	30	262.90 > 193.00	28	244.90 > 173.00	32
Endrin aldehyde	OCP	21.150	249.80 > 214.90	26	344.90 > 244.90	16	344.90 > 242.90	14
Endrin ketone	OCP	22.760	316.90 > 244.90	20	314.90 > 242.90	18	316.90 > 101.00	16
EPN	OPP	22.860	169.10 > 140.90	8	156.90 > 77.00	24	169.10 > 77.00	22
Ethalfuralin	ONP	11.293	276.00 > 202.00	18	316.10 > 276.00	10	276.00 > 248.00	10
Ethion	OPP	20.910	153.00 > 97.00	14	230.90 > 129.00	24	153.00 > 125.00	6
Ethylan	OCP	20.545	223.00 > 167.00	12	223.00 > 179.00	22	223.00 > 193.00	28
Etofenprox	ONP	26.050	163.10 > 135.10	10	163.10 > 107.10	18	135.10 > 107.10	10
Etridiazole	ONP	9.420	210.90 > 182.90	10	182.90 > 139.90	18	210.90 > 139.90	22
Fenamiphos	OPP	19.455	303.10 > 195.10	8	288.10 > 260.10	6	303.10 > 154.10	18
Fenarimol	ONP	24.180	251.00 > 139.00	14	330.00 > 139.00	8	251.00 > 111.00	26
Fenchlorphos	OPP	15.930	284.90 > 269.90	16	286.90 > 271.90	18	284.90 > 239.90	26
Fenitrothion	OPP	16.425	277.00 > 260.00	6	277.00 > 109.10	14	260.00 > 125.10	12
Fenpropathrin	ONP	23.045	181.10 > 152.10	22	265.10 > 210.10	12	181.10 > 127.10	28
Fenson	OCP	17.600	141.00 > 77.00	16	267.90 > 141.00	6	267.90 > 77.00	20
Fenthion	OPP	17.100	278.00 > 109.00	20	278.00 > 169.00	14	278.00 > 125.00	20
Fenvalerate	SPP	26.755	225.10 > 119.10	20	225.10 > 147.10	10	419.10 > 225.10	6
Fipronil	ONP	18.150	366.90 > 212.90	30	368.90 > 214.90	30	366.90 > 254.90	22
Fluazifop- <i>P</i> -butyl	HME	20.515	282.10 > 91.00	18	282.10 > 238.10	18	383.10 > 282.10	14
Fluchloralin	ONP	13.425	306.00 > 264.00	8	326.00 > 63.00	16	328.00 > 65.00	16
Flucythrinate	SPP	25.885	199.10 > 157.10	10	157.10 > 107.10	12	199.10 > 107.10	22
Fludioxonil	ONP	19.625	248.00 > 127.00	26	248.00 > 154.00	20	182.00 > 127.00	16
Fluquinconazole	ONP	24.980	340.00 > 298.00	20	340.00 > 313.00	14	342.00 > 300.00	22
Fluridone	ONP	26.310	328.10 > 259.00	24	328.10 > 313.00	22	328.10 > 127.00	24
Flusilazole	ONP	20.040	233.10 > 165.10	14	206.10 > 151.10	16	233.10 > 152.10	14
Flutolanil	ONP	19.545	173.00 > 145.00	14	173.00 > 95.00	26	281.10 > 173.00	12
Flutriafol	ONP	19.385	219.10 > 123.10	14	219.10 > 95.00	28	164.10 > 95.00	28
Folpet	ONP	18.690	259.90 > 130.00	14	261.90 > 130.00	18	261.90 > 233.90	10
Fonofos	OPP	13.335	137.10 > 109.10	8	246.00 > 137.10	6	246.00 > 109.10	18
Gamma-BHC	OCP	13.115	180.90 > 144.90	16	218.90 > 182.90	8	218.90 > 144.90	20
Heptachlor	OCP	15.870	271.80 > 236.90	20	273.80 > 238.90	16	271.80 > 117.00	32
Heptachlor- <i>exo</i> -epoxide	OCP	18.295	352.80 > 262.90	14	354.80 > 264.90	20	352.80 > 316.90	10
Hexachlorobenzene	OCP	12.275	283.80 > 248.80	24	283.80 > 213.80	28	285.80 > 250.80	22
Hexazinone	ONP	21.880	171.10 > 71.00	16	171.10 > 85.00	16	128.10 > 83.00	10
Iodofenphos	OPP	19.585	376.90 > 361.80	22	376.90 > 331.80	32	378.90 > 363.80	24
Iprodione	ONP	22.660	314.00 > 245.00	12	314.00 > 56.00	22	316.00 > 247.00	12
Isazofos	OPP	13.815	257.00 > 162.00	8	257.00 > 119.00	18	285.00 > 161.00	12
Isodrin	OCP	17.990	192.90 > 157.00	20	192.90 > 123.00	26	262.90 > 192.90	28
Isopropalin	ONP	17.840	280.10 > 238.10	8	280.10 > 133.10	18	280.10 > 165.10	16
Lambda-cyhalothrin	SPP	23.925	181.10 > 152.10	24	163.10 > 91.00	22	163.10 > 127.00	14
Lenacil	ONP	21.670	153.10 > 136.10	14	153.10 > 82.10	16	153.10 > 110.10	16
Leptophos	OPP	23.605	376.90 > 361.90	24	374.90 > 359.90	24	376.90 > 268.90	36
Linuron	ONP	16.620	248.00 > 61.00	16	248.0 > 61.0	16	250.00 > 61.00	16
Malathion	OPP	16.730	173.10 > 99.00	14	173.10 > 127.00	6	158.10 > 125.00	10
Metalaxyl	HME	15.810	249.20 > 190.10	8	206.10 > 132.10	20	249.20 > 146.10	22
Metazachlor	ONP	18.065	209.10 > 132.10	18	133.10 > 117.10	24	211.10 > 132.10	20
Methacrifos	OPP	9.770	208.00 > 180.00	8	240.00 > 208.00	4	208.00 > 110.00	18
Methoxychlor	ONP	23.000	227.10 > 169.10	24	227.10 > 121.10	14	227.10 > 141.10	28
Metolachlor	ONP	16.905	162.10 > 133.10	16	238.10 > 162.10	12	238.10 > 133.10	26
Mevinphos	OPP	9.125	127.00 > 109.00	12	192.00 > 127.00	12	127.00 > 95.00	18
MGK 264	ONP	17.735	164.10 > 93.00	10	111.10 > 82.00	8	164.10 > 80.00	24



Table 3 (Contd.)

Compound name	Chemical class	RT <sup>b</sup>	Quantitation		Confirmation			
			MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>
Mirex	OCP	24.095	271.80 > 236.80	18	273.80 > 238.80	18	271.80 > 234.80	18
Myclobutanil	ONP	19.965	179.10 > 125.00	14	179.10 > 152.00	8	150.00 > 123.00	18
<i>N</i> -(2,4-Dimethylphenyl)formamide	ONP	9.667	149.10 > 121.10	6	149.10 > 106.10	16	120.10 > 77.00	18
Nitralin	ONP	22.295	316.10 > 274.00	8	274.00 > 169.00	12	274.00 > 216.00	8
Nitrofen	ONP	20.470	202.00 > 139.00	24	282.90 > 253.00	12	282.90 > 162.00	24
Norflurazon	ONP	21.555	145.00 > 95.00	18	303.00 > 145.00	22	145.00 > 75.00	28
<i>o,p'</i> -DDD	OCP	20.055	235.00 > 165.00	24	237.00 > 165.00	28	235.00 > 199.00	16
<i>o,p'</i> -DDE	OCP	19.035	246.00 > 176.00	30	248.00 > 176.00	28	246.00 > 211.00	22
<i>o,p'</i> -DDT	OCP	21.010	235.00 > 165.00	24	237.00 > 165.00	28	235.00 > 199.00	16
Oxadiazon	ONP	19.902	258.00 > 175.00	8	302.00 > 175.00	14	258.00 > 112.00	28
Oxyfluorfen	ONP	20.100	252.00 > 196.00	22	361.00 > 300.00	14	361.00 > 317.00	6
<i>p,p'</i> -DDD	OCP	20.935	235.00 > 165.00	24	237.00 > 165.00	28	235.00 > 199.00	16
<i>p,p'</i> -DDE	OCP	19.900	246.00 > 176.00	30	317.90 > 248.00	24	246.00 > 211.00	22
<i>p,p'</i> -DDT	OCP	21.805	235.00 > 165.00	24	237.00 > 165.00	28	235.00 > 199.00	16
Parathion	OPP	17.210	139.00 > 109.00	8	291.10 > 109.00	14	291.10 > 137.00	6
Parathion-methyl	OPP	15.480	263.00 > 109.00	14	125.00 > 47.00	12	125.00 > 79.00	8
Pebulate	ONP	9.485	128.10 > 57.00	6	128.10 > 72.00	4	161.10 > 128.10	6
Penconazole	ONP	18.185	248.10 > 157.10	26	159.10 > 123.10	22	248.10 > 192.10	14
Pendimethalin	ONP	18.015	252.10 > 162.10	10	252.10 > 191.10	8	252.10 > 208.10	6
Pentachloroaniline	ONP	14.750	262.90 > 191.90	22	264.90 > 193.90	18	264.90 > 191.90	18
Pentachloroanisole	OCP	12.410	264.80 > 236.80	16	279.90 > 236.80	26	279.90 > 264.80	12
Pentachlorobenzene	OCP	10.107	249.90 > 214.90	18	249.90 > 178.90	28	249.90 > 176.90	26
Pentachlorobenzonitrile	ONP	13.090	274.80 > 239.80	18	272.80 > 202.90	30	274.80 > 204.90	32
Permethrin	SPP	24.805	183.10 > 153.10	14	163.10 > 127.10	6	183.10 > 168.10	14
Phenothrin	SPP	23.340	123.10 > 81.00	8	183.10 > 153.10	14	183.10 > 168.10	14
Phorate	OPP	11.935	260.00 > 75.00	8	231.00 > 129.00	24	231.00 > 175.00	12
Phosalone	OPP	23.565	182.00 > 111.00	14	182.00 > 138.00	8	182.00 > 102.00	14
Phosmet	OPP	22.785	160.00 > 77.00	24	160.00 > 133.00	14	160.00 > 105.00	18
Piperonyl butoxide	OPP	22.275	176.10 > 131.10	12	176.10 > 117.10	20	176.10 > 103.10	24
Pirimiphos ethyl	OPP	17.995	304.10 > 168.10	12	318.10 > 166.10	12	318.10 > 182.10	12
Pirimiphos-methyl	OPP	16.340	290.10 > 125.00	22	290.10 > 233.10	12	305.10 > 180.10	8
Pretilachlor	ONP	19.720	262.10 > 202.10	10	238.10 > 162.10	10	238.10 > 146.10	10
Prochloraz	ONP	25.030	180.10 > 138.10	12	180.10 > 69.00	20	180.10 > 95.00	20
Procymidone	ONP	18.615	283.00 > 96.00	10	285.00 > 96.00	10	283.00 > 68.00	24
Prodiamine	ONP	16.450	321.10 > 279.10	6	321.10 > 203.10	10	321.10 > 205.10	14
Profenofos	OPP	19.775	338.90 > 268.90	18	336.90 > 266.90	14	338.90 > 310.90	6
Profluralin	ONP	13.015	318.10 > 199.10	16	318.10 > 55.00	22	330.10 > 69.00	20
Propachlor	ONP	10.905	120.00 > 77.00	20	176.10 > 57.00	8	120.00 > 92.00	8
Propanil	ONP	15.065	217.00 > 161.00	10	160.90 > 99.00	24	160.90 > 90.00	22
Propargite	ONP	22.130	135.10 > 107.10	16	135.10 > 77.00	24	135.10 > 95.00	14
Propisochlor	ONP	15.735	162.10 > 120.10	14	162.10 > 147.10	14	162.10 > 144.10	12
Propyzamide	ONP	13.300	172.90 > 144.90	16	172.90 > 109.00	26	172.90 > 74.00	28
Prothiofos	OPP	19.675	266.90 > 238.90	10	309.00 > 238.90	14	266.90 > 220.90	20
Pyraclofos	OPP	24.440	194.00 > 138.00	22	360.10 > 194.00	14	360.10 > 139.00	14
Pyrazophos	OPP	24.125	221.10 > 193.10	12	221.10 > 149.10	14	221.10 > 177.10	16
Pyridaben	ONP	25.005	147.10 > 117.10	22	147.10 > 132.10	14	147.10 > 119.10	10
Pyridaphenthion	OPP	22.625	340.00 > 199.10	8	199.10 > 92.00	16	199.10 > 77.00	24
Pyrimethanil	ONP	13.555	198.10 > 183.10	14	198.10 > 118.10	28	198.10 > 158.10	18
Pyriproxyfen	ONP	23.745	136.10 > 78.00	20	136.10 > 96.00	14	226.10 > 186.10	14
Quinalphos	OPP	18.490	146.10 > 118.00	10	146.10 > 91.00	24	157.10 > 129.00	14
Quintozene	ONP	12.980	264.80 > 236.80	10	294.80 > 236.80	16	294.80 > 264.80	12
Resmethrin	SPP	22.195	143.10 > 128.10	10	171.10 > 143.10	6	171.10 > 128.10	12
Sulfotep	OPP	11.605	322.00 > 202.00	10	322.00 > 174.00	18	322.00 > 294.00	4
Sulprofos	OPP	21.300	156.00 > 141.00	18	322.00 > 156.00	8	156.00 > 108.00	28
Tau-fluvalinate	SPP	26.890	250.10 > 55.00	18	250.1 > 55.0	16	250.10 > 200.10	16
Tebuconazole	ONP	22.095	250.10 > 125.10	22	125.10 > 89.00	18	250.10 > 153.10	12
Tebufenpyrad	ONP	23.155	333.10 > 171.10	20	333.10 > 276.10	8	318.10 > 131.10	18
Tecnazene	ONP	10.790	260.90 > 202.90	14	202.90 > 142.90	22	202.90 > 85.00	24
Tefluthrin	SPP	13.855	177.00 > 127.10	16	177.00 > 137.10	16	197.00 > 141.10	14
Terbacil	ONP	13.740	161.00 > 144.00	14	161.00 > 88.00	20	117.00 > 76.00	8
Terbufos	OPP	13.175	231.00 > 128.90	26	231.00 > 174.90	14	231.00 > 202.90	8

Table 3 (Contd.)

Compound name	Chemical class	RT <sup>b</sup>	Quantitation		Confirmation			
			MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>	MRM transition <sup>c</sup>	CE <sup>d</sup>
Terbutylazine	ONP	13.165	229.10 > 173.10	6	214.10 > 71.00	16	214.10 > 132.10	8
Tetradifon	OCP	23.455	226.90 > 199.00	16	355.90 > 159.00	18	355.90 > 228.90	12
Tetramethrin	SPP	22.715	164.10 > 107.10	14	164.10 > 77.00	22	164.10 > 135.10	8
THPI (tetrahydrophthalimide)	ONP	9.755	151.10 > 79.00	18	151.10 > 123.10	4	151.10 > 77.00	28
Tolclofos-methyl	OPP	15.550	264.90 > 249.90	14	264.90 > 93.00	24	264.90 > 219.90	22
Tolyfluanid	ONP	18.280	238.00 > 137.10	14	181.10 > 138.10	10	181.10 > 94.10	18
trans-Chlordane	OCP	18.960	374.80 > 265.90	26	372.80 > 263.90	28	372.80 > 265.90	22
Transfluthrin	SPP	15.670	163.10 > 127.10	6	163.10 > 143.10	16	163.10 > 91.00	12
trans-Nonachlor	OCP	19.410	406.80 > 299.90	24	406.80 > 334.90	16	406.80 > 109.00	22
Triadimefon	ONP	17.315	208.10 > 181.00	10	208.10 > 111.00	22	208.10 > 127.00	14
Triadimenol	ONP	18.580	168.10 > 70.00	10	128.10 > 65.00	22	128.10 > 100.10	14
Tri-allate	ONP	14.100	268.10 > 184.00	20	270.10 > 186.00	20	268.10 > 226.00	14
Triazophos	OPP	21.255	161.00 > 134.00	8	161.00 > 106.00	14	257.00 > 162.00	8
Tricyclazole	ONP	19.705	189.00 > 161.90	12	189.00 > 135.00	18	161.90 > 135.00	8
Triflumizole	ONP	18.672	206.10 > 179.10	14	278.10 > 73.00	6	206.10 > 186.10	8
Trifluralin	ONP	11.470	306.10 > 264.10	8	264.10 > 160.10	18	264.10 > 206.10	8
Vinclozolin	ONP	15.410	212.00 > 172.00	16	285.00 > 212.00	12	212.00 > 145.00	24

<sup>a</sup> OPP: organophosphorus pesticides; OCP: organochlorine pesticides; ONP: organonitrogen pesticides; SPP: synthetic pyrethroid pesticides; HME: herbicide methyl esters. <sup>b</sup> R.T.: retention time. <sup>c</sup> MRM: multiple reaction monitoring (*m/z*). <sup>d</sup> CE: collision energy.

range between 1 and 6  $\mu\text{g kg}^{-1}$  for 194 compounds while for the remaining 6 compounds (chloroneb, 2-phenylphenol, captan, triadimenol, endrin aldehyde, and captafol) it was found to be at higher than 10  $\mu\text{g kg}^{-1}$  levels. A study conducted in 2013 in Brazil for the banana matrix reported the LOD ranging between 5.0 and 7.5  $\mu\text{g kg}^{-1}$  for 128 pesticide residues.<sup>3,13</sup>

#### Method limit of quantification (MLOQ)

The MLOQ for the current method was reported to be in the range of 1–10  $\mu\text{g kg}^{-1}$  for 191 compounds. The remaining 9 compounds (dichlobenil, biphenyl, chloroneb, 2-phenylphenol, captan, triadimenol, endrin aldehyde, acequinocyl and captafol) could not be quantified accurately due to matrix interference being observed at lower concentrations (<25  $\mu\text{g kg}^{-1}$ ). On correlating the current study with other studies,<sup>1,3</sup> it was observed that the LOQs obtained in this study were less than 10  $\mu\text{g kg}^{-1}$  for a majority of pesticides, with the exception of fenamiphos and mevinphos for which the obtained LOQ was 25  $\mu\text{g kg}^{-1}$ . The values of MLOD and MLOQ obtained in this study have been detailed in Table 4. A comparison of the obtained MLOQ values with the established MRLs for specific pesticides indicated that the MLOQs obtained by this method were comparatively lower.

#### Recovery, accuracy and precision

Mean recovery rates were obtained by spiking the standards at 2 levels, *viz.* 10 and 25  $\mu\text{g kg}^{-1}$  before sample extraction. The mean recovery rates for 191 pesticide residues varied between 71 and 117% when fortified at 10  $\mu\text{g kg}^{-1}$  before sample extraction. The recovery range for some of the pesticides *viz.* dichlobenil, biphenyl, chloroneb, 2-phenylphenol *etc.* was observed to be outside the prescribed range despite the RSD

being within the range. When the standards were spiked at 25  $\mu\text{g kg}^{-1}$ , the method recovery was observed to be in the range of 72–120% for 190 pesticide residues. Precision of the method was assessed by calculating the RSD of seven replicate measurements at specific concentrations. Additionally, to evaluate the precision across different levels, intraday ( $CV_I$ ) and interday ( $CV_R$ ) studies were conducted. The average RSD yield (2–10%) of the developed method was found to be below 20% for all the compounds in the  $CV_I$  study. In the  $CV_R$  study, the RSD for all compounds ranged between 1 and 20%, and was observed to be below 20% except for three pesticide residues where it exceeded 20%. The obtained responses were satisfactory, as the precision and recovery data from the developed method fulfilled the requirements of 70–120% recovery along with RSD values being  $\leq 20\%$  for the pesticides in accordance with the SANTE guidelines.<sup>19</sup>

#### Matrix effect

The results of the matrix effect analysis indicated that of all the analyzed compounds 145 of the total 200 pesticide residues fell within the range of –20% to +20%, as prescribed by the SANTE guidelines.<sup>19</sup> This was suggestive of the fact that the sample matrix had minimal impact on the measurement of the majority of compounds as most of these values were close to the repeatability limit (Table 4). Only 6 compounds showed strong matrix effects *i.e.* beyond the –50 to +50% range of matrix effects. However, the RSD for these compounds was well within the acceptable limit except for captafol. These findings demonstrate a strong level of accuracy and reliability in the analysis, indicating that interference from the matrix on most compounds was minimal. When ME was below –20%, it indicated ion suppression as the sample matrix was causing

Table 4 Analytical method performance for pesticide residues in banana by GC-MS/MS

Compound name	$r^{2a}$	Precision <sup>b</sup>		Spiking level <sup>c</sup> ( $\mu\text{g kg}^{-1}$ )		MLOD <sup>d</sup>	MLOQ <sup>e</sup>	% ME <sup>f</sup>
		CV <sub>(r)</sub>	CV <sub>(R)</sub>	10	25			
(E)-Chlorfenvinphos	0.999	3	1	100	109	1	2	13.9
(Z)-Chlorfenvinphos	0.999	4	5	96	112	2	7	16.5
2,3,5,6-Tetrachloroaniline	0.999	2	2	99	112	1	3	11.1
2,4'-Methoxychlor	0.997	2	2	90	101	1	2	12.0
2-Phenylphenol	0.999	2	6	211	221	13	42	128.2
3,4-Dichloroaniline	0.999	4	8	101	116	1	5	19.7
4,4'-Dichlorobenzophenone	0.998	3	2	97	113	1	3	18.0
4,4'-Methoxychlor olefin	0.999	3	3	100	113	1	3	20.1
Acequinocyl	0.995	12	22	59	53	2	6	-43.7
Acetochlor	0.999	2	11	107	114	3	8	21.5
Acrinathrin-1	0.994	4	6	88	102	3	9	20.2
Alachlor	0.999	3	16	91	109	1	4	15.1
Aldrin	0.991	4	6	96	110	2	8	27.0
Allethrin-3,4	0.999	10	31	107	88	3	9	-8.6
Allidochlor	0.999	2	1	102	116	1	4	15.5
Alpha-BHC	0.999	1	4	92	109	1	3	8.1
Alpha-endosulfan	0.997	15	19	94	99	3	9	-9.8
Antraquinone	0.998	2	3	105	111	1	3	20.6
Atrazine	0.997	4	5	99	116	3	9	13.9
Azinphos-ethyl	0.996	12	2	104	114	2	6	34.7
Azinphos-methyl	0.994	7	4	97	97	2	6	22.2
Benfluralin	0.998	2	1	97	111	1	4	20.4
Beta-BHC	0.999	4	3	103	112	1	4	12.5
Beta-endosulfan	0.998	8	7	102	107	3	9	6.8
Bifenthrin	0.999	3	1	100	113	1	2	19.5
Biphenyl	0.999	3	1	698	320	6	20	212.0
Bromfenvinfos-methyl	0.997	3	5	87	106	2	6	16.5
Bromfenvinphos	0.999	3	1	89	106	1	4	8.1
Bromophos	0.998	2	3	108	113	1	3	18.0
Bromophos-ethyl	0.998	4	5	96	113	2	5	19.8
Bromopropylate	0.997	3	3	110	116	1	4	24.3
Bupirimate	0.999	5	6	99	111	2	6	14.1
Captafol	0.993	70	47	328	273	18	58	125.3
Captan	0.992	21	36	ND	99	15	46	16.0
Carbophenothion	0.998	3	3	101	111	1	5	23.3
Carfentrazone-ethyl	0.999	2	4	103	112	1	5	16.2
Chlorbenside	0.998	4	2	106	106	1	3	9.2
Chlorfenapyr	0.996	13	14	91	103	3	9	12.7
Chlorfenson	0.999	2	3	101	113	1	2	18.2
Chlorobenzilate	0.997	3	3	103	115	1	2	20.0
Chloroneb	0.997	3	1	1295	490	19	62	371.4
Chlorothalonil	0.995	4	8	53	72	1	3	-24.3
Chlorpropham	0.999	2	1	108	114	1	4	16.7
Chlorpyrifos	0.999	3	5	108	109	2	5	9.6
Chlorpyrifos-methyl	0.999	4	2	98	113	2	5	19.4
Chlorthal-dimethyl	0.998	1	3	93	112	1	3	15.3
Chlorthiophos	0.996	4	16	105	110	2	7	16.0
Chlozolinate	0.995	7	3	112	178	2	7	80.8
cis-Chlordane	0.994	10	3	90	106	2	5	6.3
cis-Nonachlor	0.999	4	5	98	111	2	5	16.8
Clomazone	0.999	2	4	92	110	1	2	12.2
Coumaphos	0.996	4	3	112	107	1	4	20.3
Cycloate	0.999	1	2	100	113	1	3	14.3
Cyfluthrin	0.998	16	11	100	101	2	8	19.7
Cypermethrin	0.997	16	21	100	98	2	7	15.8
Cyprodinil	0.999	3	2	105	114	1	4	20.3
Delta-BHC	0.998	2	6	98	111	1	4	11.0
Deltamethrin	0.994	2	4	88	109	2	7	26.8
Di-allate	0.999	3	3	101	111	1	3	9.4
Diazinon	0.995	5	5	111	120	2	8	38.6

Table 4 (Contd.)

Compound name	$r^{2a}$	Precision <sup>b</sup>		Spiking level <sup>c</sup> ( $\mu\text{g kg}^{-1}$ )		MLOD <sup>d</sup>	MLOQ <sup>e</sup>	% ME <sup>f</sup>
		CV <sub>(r)</sub>	CV <sub>(R)</sub>	10	25			
Dichlofluanid	0.999	4	9	72	95	2	6	-3.0
Dichlobenil	0.999	3	3	381	179	5	15	77.2
Dicloran	0.995	3	2	99	111	1	4	3.0
Dieldrin	0.999	6	7	114	110	2	7	10.1
Dimethachlor	0.997	2	3	97	111	1	2	13.0
Diphenamid	0.998	3	5	102	112	2	7	15.6
Diphenylamine	0.999	2	2	108	110	1	3	15.6
Disulfoton	0.998	11	25	80	93	3	8	-5.7
Edifenphos	0.996	2	1	86	96	1	4	9.1
Endosulfan ether	0.997	2	2	100	119	2	6	22.7
Endosulfan sulfate	0.995	3	3	93	106	1	4	20.4
Endrin	0.993	2	9	85	108	2	7	10.2
Endrin aldehyde	0.995	15	53	191	98	38	121	7.1
Endrin ketone	0.992	10	9	98	106	2	6	22.4
EPN	0.996	5	5	108	108	3	9	21.3
Ethalfuralin	0.998	2	4	99	109	1	4	15.8
Ethion	0.999	1	1	102	111	1	3	18.0
Ethylan	0.998	1	1	97	112	1	2	19.0
Etofenprox	0.999	2	2	102	115	1	2	15.3
Etridiazole	0.999	1	3	94	106	1	2	14.2
Fenamiphos	0.999	4	6	110	103	2	7	11.4
Fenarimol	0.999	2	2	106	116	1	4	21.3
Fenclorophos	0.997	3	2	101	117	1	4	15.2
Fenitrothion	0.998	3	2	116	119	2	6	23.3
Fenpropathrin	0.994	7	9	102	109	2	8	16.1
Fenson	0.999	2	4	99	114	1	2	16.0
Fenthion	0.999	2	4	115	123	1	2	25.9
Fenvalerate	0.997	3	4	96	113	1	4	20.8
Fipronil	0.997	3	4	103	116	3	8	22.3
Fluazifop- <i>P</i> -butyl	0.999	2	1	100	113	1	3	18.7
Fluchloralin	0.997	5	6	89	100	2	6	2.5
Flucythrinate	0.997	5	4	107	119	2	6	33.1
Fludioxonil	0.998	5	5	104	109	1	4	14.5
Fluquinconazole	0.999	2	3	104	110	1	2	16.2
Fluridone	0.993	7	7	108	120	3	9	49.8
Flusilazole	0.997	3	4	92	110	2	5	17.3
Flutolanil	0.998	3	2	105	112	1	4	20.6
Flutriafol	0.992	2	3	108	117	2	5	10.9
Folpet	0.990	11	9	71	75	1	3	-7.7
Fonofos	0.999	2	2	103	113	1	3	16.2
Gamma-BHC	0.997	1	1	99	111	1	4	14.6
Heptachlor	0.998	3	2	95	108	1	3	7.5
Heptachlor- <i>exo</i> -epoxide	0.998	4	6	107	130	3	9	27.3
Hexachlorobenzene	0.997	2	4	109	115	1	2	16.8
Hexazinone	0.999	2	2	99	113	1	3	19.5
Iodofenphos	0.997	3	3	90	108	1	4	25.4
Iprodione	0.994	5	10	88	97	3	9	12.6
Isazofos	0.999	4	18	105	115	2	5	18.8
Isodrin	0.993	4	4	100	112	1	2	16.6
Isopropalin	0.994	2	1	110	115	1	3	34.1
Lambda-cyhalothrin	0.996	7	2	102	87	1	3	-6.7
Lenacil	0.997	6	5	105	113	1	3	24.9
Leptophos	0.997	2	3	101	110	1	4	18.4
Linuron	0.998	4	4	88	113	3	8	10.7
Malathion	0.998	2	3	94	110	3	9	18.4
Metalaxyl	0.996	5	9	99	114	3	8	14.5
Metazachlor	0.997	3	2	101	113	1	4	23.5
Methacrifos	0.999	1	2	101	113	1	3	12.5
Methoxychlor	0.997	4	3	85	93	1	4	4.0
Metolachlor	0.999	2	2	97	111	1	2	14.5

Table 4 (Contd.)

Compound name	$r^{2a}$	Precision <sup>b</sup>		Spiking level <sup>c</sup> ( $\mu\text{g kg}^{-1}$ )		MLOD <sup>d</sup>	MLOQ <sup>e</sup>	% ME <sup>f</sup>
		CV <sub>(r)</sub>	CV <sub>(R)</sub>	10	25			
Mevinphos	0.999	1	1	99	108	1	3	11.5
MGK 264	0.997	4	16	100	113	2	6	19.4
Mirex	0.998	2	2	98	110	1	2	14.9
Myclobutanil	0.995	2	2	99	110	1	3	12.2
N-(2,4-Dimethylphenyl)formamide	0.998	4	4	108	111	3	8	10.4
Nitralin	0.995	12	9	81	83	2	6	-14.8
Nitrofen	0.997	2	3	101	112	1	3	17.3
Norflurazon	0.997	5	2	100	109	1	4	17.2
<i>o,p'</i> -DDD	0.998	2	2	97	115	1	3	19.1
<i>o,p'</i> -DDE	0.998	2	2	100	111	1	2	12.8
<i>o,p'</i> -DDT	0.997	2	5	88	98	1	4	9.3
Oxadiazon	0.997	4	2	100	112	2	5	19.9
Oxyfluorfen	0.993	7	6	93	108	3	9	43.0
<i>p,p'</i> -DDD	0.999	1	2	101	114	1	2	20.9
<i>p,p'</i> -DDE	0.998	1	4	96	110	1	4	13.1
<i>p,p'</i> -DDT	0.997	4	3	86	96	0	1	8.9
Parathion	0.998	5	4	111	115	2	8	18.9
Parathion-methyl	0.998	5	4	109	109	2	6	21.2
Pebulate	0.999	1	2	102	112	1	4	11.4
Penconazole	0.998	3	4	103	114	1	4	16.6
Pendimethalin	0.994	5	2	113	113	1	4	32.8
Pentachloroaniline	0.997	2	2	94	113	2	7	13.1
Pentachloroanisole	0.998	2	3	100	114	1	3	15.3
Pentachlorobenzene	0.998	2	3	96	111	1	3	14.5
Pentachlorobenzonitrile	0.999	2	4	111	119	1	4	20.4
Permethrin	0.998	4	6	94	111	2	7	15.6
Phenothrin	0.997	3	7	94	108	3	9	12.9
Phorate	0.997	1	5	113	114	3	8	15.7
Phosalone	0.997	4	4	101	109	2	6	19.1
Phosmet	0.995	4	4	91	97	1	3	13.1
Piperonyl butoxide	0.999	2	2	107	115	1	3	22.0
Pirimiphos ethyl	0.998	3	4	107	116	2	6	24.2
Pirimiphos-methyl	0.996	3	2	107	112	1	3	16.2
Pretilachlor	0.996	2	2	93	112	2	6	20.8
Prochloraz	0.998	7	9	106	109	2	7	20.4
Procymidone	0.998	4	3	95	113	1	3	14.2
Prodiamine	0.999	3	5	100	117	2	5	25.5
Profenofos	0.991	4	4	91	104	1	5	7.8
Profluralin	0.995	2	9	101	117	3	9	42.4
Propachlor	0.999	3	2	94	109	1	4	11.4
Propanil	0.998	11	3	107	106	3	10	12.6
Propargite	0.991	21	7	94	95	2	8	3.0
Propisochlor	0.997	2	3	104	127	3	9	30.9
Propyzamide	0.998	2	1	106	114	1	5	18.7
Prothiofos	0.998	2	3	99	113	1	3	21.3
Pyraclofos	0.994	7	4	105	102	2	7	11.0
Pyrazophos	0.998	5	3	94	108	1	3	22.5
Pyridaben	0.998	4	9	108	110	3	9	23.4
Pyridaphenthion	0.998	3	6	107	114	2	6	29.3
Pyrimethanil	0.998	4	7	87	108	3	9	9.0
Pyriproxyfen	0.998	6	9	96	105	3	9	11.1
Quinalphos	0.999	3	4	100	116	2	7	22.2
Quintozene	0.997	17	13	98	112	2	5	26.8
Resmethrin	0.994	6	18	99	106	2	7	8.1
Sulfotep	0.999	3	4	98	113	1	4	17.0
Sulprofos	0.997	2	3	117	115	1	3	20.3
Tau-fluvalinate	0.993	3	3	100	107	1	4	25.8
Tebuconazole	0.999	3	1	100	112	1	2	14.8
Tebufenpyrad	0.999	3	3	94	112	1	3	14.7
Tecnazene	0.999	4	4	106	115	1	3	15.5

Table 4 (Contd.)

Compound name	$r^{2a}$	Precision <sup>b</sup>		Spiking level <sup>c</sup> ( $\mu\text{g kg}^{-1}$ )		MLOD <sup>d</sup>	MLOQ <sup>e</sup>	% ME <sup>f</sup>
		CV <sub>(r)</sub>	CV <sub>(R)</sub>	10	25			
Tefluthrin	0.997	2	3	78	111	1	4	13.2
Terbacil	0.997	2	33	104	115	3	9	19.6
Terbufos	0.999	2	2	112	127	2	7	27.6
Terbuthylazine	0.998	9	8	104	110	1	4	9.1
Tetradifon	0.998	3	1	87	108	3	8	9.3
Tetramethrin	0.999	6	7	100	111	2	8	17.9
THPI (tetrahydrophthalimide)	0.995	3	7	107	116	2	6	20.8
Tolclofos-methyl	0.998	4	2	92	110	2	5	11.6
Tolyfluanid	0.998	5	8	73	93	1	4	-3.9
<i>trans</i> -Chlordane	0.995	5	3	92	106	1	2	12.4
Transfluthrin	0.999	6	3	99	111	1	3	8.1
<i>trans</i> -Nonachlor	0.992	2	12	88	103	2	7	29.1
Triadimefon	0.997	5	10	84	113	2	7	12.5
Triadimenol	0.997	13	10	73	97	22	71	1.8
Tri-allate	0.999	1	3	97	112	3	9	9.8
Triazophos	0.996	3	6	105	113	2	5	32.6
Tricyclazole	0.997	15	14	100	101	3	8	10.7
Triflumizole	0.992	3	4	92	115	1	4	10.2
Trifluralin	0.999	3	1	102	111	1	2	18.6
Vinclazolin	0.996	7	4	105	111	2	5	24.5

<sup>a</sup>  $r^2$ : linearity. <sup>b</sup> Precision: CV<sub>(R)</sub>: between-day precision ( $n = 7$ ), CV<sub>(r)</sub>: within-day precision ( $n = 7$ ). <sup>c</sup> % recovery ( $n = 7$ ) calculated from spiking concentration. <sup>d</sup> MLOD: method limit of detection ( $\mu\text{g kg}^{-1}$ ). <sup>e</sup> MLOQ: method limit of quantification ( $\mu\text{g kg}^{-1}$ ). <sup>f</sup> % ME: matrix effect (%).

a decrease in the signal intensity of the analyte and when it was above 20%, it indicated ion enhancement, suggestive of the fact that the sample matrix was causing an increase in the signal intensity of the analyte.

Several recent studies (Table S4†) carried out over the last 3 years have investigated various methodologies for pesticide analysis. A study conducted by Mohammed Almutairi *et al.* analysed 294 pesticides with the QuEChERS-dSPE method.<sup>25</sup> A similar study using the QuEChERS-dSPE-GC-QMS method was also carried out by Hiago de O. Gomes *et al.* but only for three pesticides. The LOD, LOQ, recovery and RSD in this study were reported to be 0.01–0.05 mg kg<sup>-1</sup>, 0.03–0.10 mg kg<sup>-1</sup>, 74.78% and 99.98% and <20 respectively.<sup>26</sup> Saihao Ren *et al.* investigated the presence of single compound fluopyram using GC-MS/MS in a range of crops that included tomato, cucumber, cowpea, pepper, eggplant, potato, banana, grape, and citrus. The extraction method employed was QuEChERS, with the clean-up using PSA, C18, and MWCNTs-NH<sub>2</sub>. The recovery for this study ranged from 87.02% to 101.42%, RSD was 9.25%, and ME ranged from -1.41% to 17.67%.<sup>27</sup> Ahmed S. Affy *et al.* conducted an analysis for 49 pesticides encompassing commodities such as tomato, cucumber, zucchini, *etc.* This analysis utilized the QuEChERS dSPE + GCB method in conjunction with GC-MS/MS. Key parameters such as LOD (0.0005–0.0024 mg kg<sup>-1</sup>), LOQ (0.0011–0.0047 mg kg<sup>-1</sup>), recovery (78–107%), RSD (<20%), and  $r^2$  (0.99) were determined. However, it is pertinent to note that only 49 pesticides were extracted.<sup>28</sup> Xiao Shu *et al.* conducted a study on hawk tea utilizing the EMR-lipid material-QuEChERS

for the extraction of 186 pesticides. MgSO<sub>4</sub>, PSA, and MWCNTs were employed for clean-up and quantification was performed using a GCMS-TQ8050 triple-quadrupole mass spectrometer, with parameters including LOD (0.001–0.02 mg kg<sup>-1</sup>), LOQ (0.005–0.05 mg kg<sup>-1</sup>), recovery (70–120%), RSD (0.3–14.4%), and  $r^2$  (0.99). However, it is significant to note that the authors validated and estimated their results using 1200 mg MgSO<sub>4</sub>, 400 mg PSA, and 200 mg MWCNTs which is much higher than the usage reported in the current study.<sup>29</sup> Hiago de O. Gomes *et al.* analyzed three compounds, namely azoxystrobin, difenoconazole, and propiconazole, using a modified QuEChERS-dSPE-GC/MS method. Results obtained indicated LOD values of 0.018, 0.066, and 0.007, LOQ values of 0.054, 0.199, and 0.022, and  $r^2$  values of 0.9985, 0.9966, and 0.9997, respectively.<sup>30</sup> Sun-Il Choi *et al.* conducted an analysis of thiabendazole in banana and citrus fruits using HPLC-PDA and LC-MS/MS. The results reported LOD, LOQ, recovery, RSD, and  $r^2$  of 0.009 and 0.017  $\mu\text{g mL}^{-1}$ , 0.028 and 0.052  $\mu\text{g mL}^{-1}$ , 93.61 to 98.08%, 1.33% and 0.999 respectively.<sup>31</sup>

Salient features of similar studies carried out over the last few years have been tabulated in Table S4.† A sneak peek into these studies indicated that those which examined up to 294 analytes did not specify the validation parameters. This study which used gas chromatography tandem mass spectrometry, in contrast, has details about recovery, RSD, LOD, LOQ, and ME employed for validation, all of which fell within acceptable ranges for the compounds analyzed. Further, the usage of MWCNTs too conferred a significant advantage due to their

Table 5 Levels ( $\mu\text{g kg}^{-1}$ ) of pesticide residues in banana samples at the MRL<sup>a</sup>

Sample no.	Fluchloralin	Isazofos	Tri-allate	Allethrin-3,4	Ethion	Tebuconazole	Propargite	Bifenthrin	Phenothrin	Pyriproxyfen	Cypermethrin
<b>Compound</b>											
BA 1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	26	<LOQ	<LOQ	<LOQ
BA 2	11	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BA 3	<LOQ	<LOQ	16	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BA 4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	37	12	<LOQ
BA 5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	18	<LOQ	<LOQ
BA 6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	17	<LOQ	<LOQ	<LOQ
BA 8	<LOQ	11	<LOQ	17	<LOQ	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ
BA 10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	21	<LOQ	<LOQ	<LOQ	<LOQ
BA 12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	21	<LOQ	<LOQ	<LOQ	<LOQ
BA 13	<LOQ	<LOQ	<LOQ	<LOQ	27	<LOQ	<LOQ	<LOQ	24	25	<LOQ
BA 14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	54	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BA 15	<LOQ	<LOQ	16	<LOQ	<LOQ	<LOQ	<LOQ	40	<LOQ	<LOQ	<LOQ
BA 16	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	31	11	<LOQ	<LOQ
BA 17	<LOQ	<LOQ	<LOQ	15	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BA 18	<LOQ	<LOQ	<LOQ	22	<LOQ	<LOQ	<LOQ	25	<LOQ	<LOQ	<LOQ
BA 19	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	18
BA 20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	20
BA 22	<LOQ	<LOQ	<LOQ	11	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BA 23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	15
BA 24	<LOQ	<LOQ	<LOQ	15	<LOQ	252	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BA 25	11	<LOQ	16	<LOQ	<LOQ	121	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>MRL</b>											
EU	—	—	100	—	10	1500	10	100	20	700	50
CODEX	—	—	—	—	—	1500	—	100	—	—	—
FSSAI	—	—	—	—	2000	1500	—	—	—	—	—

<sup>a</sup> Concentration of analytes and MRL:  $\mu\text{g kg}^{-1}$ , <LOQ: less than limit of quantification, BA: banana, MRL: maximum residual level.

cost-effectiveness as well as superior recovery rates across all analytes. By employing a simplistic combination of MWCNTs and PSA, this study was able to achieve an MLOD range of 0.45–6.33  $\mu\text{g kg}^{-1}$  and an MLOQ range of 1.44–9.59  $\mu\text{g kg}^{-1}$ .

The matrix effect characterization provided valuable information about the impact of the sample matrix on the accuracy and reliability of the analysis for each specific pesticide residue thereby implying that the analytical method employed was well-suited for analysing pesticide residue levels in vegetable and fruit samples.

### Application to real samples

In order to ascertain the applicability of the method and ease of sample treatment procedure, a total of 25 bananas were analysed by the proposed method. The banana samples were collected from the local markets of Ahmedabad, Gujarat. The outcomes of the examined samples are tabulated in Table 5.

Of all the samples analyzed, 84% ( $n = 21$ ) of bananas reported the presence of pesticide residues at or below the MRLs established by different agencies (EU, Codex, FSSAI).<sup>32–34</sup> The remaining 16% ( $n = 4$ ) of the samples reported no known pesticide residues used in the study. A total of 16% ( $n = 4$ ) of samples reported pesticide residues above EU prescribed MRLs. Those commonly found were propargite (8%) and phenothrin (8%) followed by ethion (4%).

Similar findings were echoed in a study conducted by Carneiro *et al.* in Brazil, wherein 3 out of 10 samples were found to

be contaminated with boscalid, carbendazin and imidacloprid residues.<sup>3,13</sup> A similar study conducted in Spain<sup>3</sup> too showed the presence of chlorpyrifos, malathion, fenitrothion and buprofezine in banana samples.

## Conclusions

The enhanced and validated modified QuEChERS-d-SPE method employed a multivariate approach and demonstrated successful extraction of diverse pesticide residues from bananas. The samples were subjected to quantitative analysis using gas chromatography-tandem mass spectrometry. The incorporation of a P–B design and Central Composite Design (CCD) in the multivariate approach significantly enhanced the efficiency of the extraction process as this approach aided in screening and optimizing factors. This resulted in effective removal of pigments as co-extractives and minimized the matrix effect during the clean-up step. The developed method demonstrated simplicity and required minimal amounts of sorbents as compared to other methods. The approach also enhanced the suitability of monitoring multi-pesticide residues in banana *via* application of developed method to real samples. The optimized method was validated in terms of recovery, linearity, precision and sensitivity with favourable outcomes achieved for all validation parameters. To conclude, results showed that the proposed method is simple, efficient, selective, reproducible, cost-effective, and environmentally friendly.

## Author contributions

Tushar Rajaram Ahire – investigation, validation, writing – original draft; Rupal Rajesh Thasale – data curation, methodology, validation, visualization; Ankita Das – formal analysis; Nikhil P. Kulkarni – writing – review & editing; Dhyam M. Vyas – formal analysis; Sivaperumal Perumal – conceptualisation, funding acquisition, project administration, supervision.

## Conflicts of interest

The authors declare no conflict of interest.

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