Chromatographia
https://doi.org/10.1007/s10337-018-3511-7

ORIGINAL

Multi-pesticide Residues Determination in Samples of Fruits and Vegetables Using Chemometrics Approach to QuEChERS-dSPE Coupled with Ionic Liquid-Based DLLME and LC–MS/MS

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Received: 19 October 2017 / Revised: 14 March 2018 / Accepted: 16 March 2018
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Abstract
Pesticides play vital roles in agricultural practices, but the nature and mishandling of the chemicals have led to their accumulation in moist soil, vegetables and fruits. Thus, development of efficient methods for pesticides determination is one of the most important ways to address such challenges. Multivariate response surface methodology optimisation using Placket–Burman and Box–Behnken designs were respectively used for screening and optimisation of significant factors of quick, easy, cheap, effective, rugged and safe (QuEChERS) with dispersive solid-phase extraction (SPE). Consequently, the optimised QuEChERS-dSPE technique coupled with modified ionic liquid-based (IL-based) dispersive liquid–liquid microextraction was used for sample preparation before LC–MS/MS. The developed method was validated (SANTE 11831-2017) for multi-pesticide residues determination in samples of bananas, cabbages, tomatoes, oranges and onions. The precision results were satisfactory in terms of relative standard deviation ($\leq 20\%$) as recommended. The results of accuracy for relative recoveries (82–137%) were satisfactory because 92.5% of results were within the recommended range (70–120%). The matrix effects in all the samples were very weak (less effective) ($\leq -80\%$). The linearity of the evaluated results was 5–400 μg kg^{-1} and regression coefficients (R^2) were > 0.99. The resulting limits of detection and quantitation were 0.02–0.32 and 0.07–1.06 μg kg^{-1}, respectively, and therefore satisfactory. Certifiably, the estimated measurement uncertainties range (1–16%) was acceptable ($\leq 50\%$). Thus, the developed method could be reliable and suitable for routine determination of multiple pesticide residues in various vegetable and fruit samples.

Keywords Chemometrics DOE and RSM · QuEChERS-dSPE and DLLME cleanups · Ionic liquid-based · Pesticide residues · Liquid chromatography–mass spectrometry · Fruits and vegetables

Introduction

The global increase in population and high demand for foods have been dominant factors contributing to the drastic application of pesticides during cultivation, transportation, and storage of farm produce [1]. Fruits and vegetables are needed daily for a balanced diet in addition to grains because of their nutritional contents [2]. Unfortunately, the nature and mishandling of pesticides in the environment leads to accumulation of their persistent residues in farm products, especially the fresh fruit and vegetables [3], causing disastrous health-related issues in humans and other animals such as cardiovascular diseases, congenital disabilities, and risk of cancers in both children and adults [4], etc. Thus, one of the most important ways of addressing these issues is by developing efficient techniques for routine determination of pesticide residues in fruit and vegetable samples [5].

The determination of pesticides has predominantly been carried out using conventional techniques such as solid-phase extraction (SPE), liquid–liquid extraction (LLE) and liquid-phase microextraction (LPME) [6]. Unfortunately, most of these methods possess poor selectivity of analytes

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Published online: 06 April 2018

in trace amounts and large consumption of toxic (organic) extraction solvents [7].

The use of non-toxic ionic liquid (IL)-based extraction solvents has gained remarkable interest as a green method for analysis of various contaminants in food samples [8]. Fortunately, employment of IL-based solvent as extractant/cleanup solvent in dispersive liquid–liquid microextraction (DLLME) provided good results for pesticides determination in fruits [9]. Therefore, 1-hexyl-3-methylimidazolium hexafluorophosphate [C_6MIM][PF_6] was selected for this research because of its low cost, excellent hydrophobic and chromatographic properties with high efficiency of analytes extraction when compared with other reported ILs, including [C_4MIM][PF_6] and [C_8MIM][PF_6] [10]. Hence, the use of C_6MIM][PF_6] in DLLME coupled with simple glassware techniques known as quick, easy, cheap, effective, rugged and safe with dispersive SPE (QuEChERS-dSPE) would greatly benefit sample preparation [11].

Moreover, the QuEChERS extraction method is renowned for its cleanup ability in sample preparation [12], while DLLME is also known for its excellent enrichment capacity and has gained lots of popularity since its inception [13]. Thus, coupling these two techniques will overcome the drawbacks of previous techniques used for extraction and cleanup of pesticide residues in a sample of vegetables and fruits before quantitative determination.

The application of chemometrics to research techniques in analytical studies has gained interest [14]. In fact, some factors of the Association of Official Analytical Chemists (AOAC 2007.01) QuEChERS-dSPE methodology require a chemometrics (multivariate)-based optimisation approach. The multivariate optimisation is based on the use of response surface methodology (RSM) for the design of experiment (DOE) before coupling it to a modified IL-based DLLME cleanup technique. The optimised factors are associated with the acid/base conditions of the extraction medium and the mechanical (extraction) setup. These include pH of the extraction solvent, centrifugation time and centrifugation speed in both the extraction and cleanup stages. These could play a significant role in achieving optimum conditions for the sample treatment and cleanup processes. The aforementioned RSM optimisation was also applied to sorbent materials used for the cleanup of the extracted residue of pesticides in fruits and vegetables. The sorbent materials include primary secondary amine (PSA), octadodecyl bonded silica (C_{18}), graphitized carbon black (GCB), and sodium acetate (NaOAc) salts [15–18]. Consequently, these studies enabled the optimisation of extraction of multi-pesticide residues in the homogenised samples. Thus, the potential of the developed method will contribute positively towards better extraction and quantification of pesticide residues in vegetables and fruit samples. Besides, it will serve as a reference guide for future studies and routine monitoring of pesticide residues in a diverse range of vegetables and fruits quantitatively using advanced analytical instruments.

Therefore, this study aimed to use a developed QuEChERS-dSPE IL-based DLLME technique for determination of multi-pesticide residues in a sample of bananas, cabbages, tomatoes, oranges and onions. The analyses were performed after the parameters of the AOAC 2007.01 QuEChERS-dSPE method were optimised using generated runs produced by Minitab-17 statistical software before coupling it to the modified IL-based DLLME technique for further extraction cleanup to provide better analyte accuracies and precisions.

Materials and Methods

Chemicals and Reagents

The stock standard solutions of pesticides (100 mg kg^{-1}) containing Dursban, Diazinon, Thiamethoxam, Metalaxyl, Thiobencarb, Baycarb, Carbaryl and Propamocarb were purchased from AccuStandard® (New Haven, USA). The stock solutions were singly diluted to 10 mg kg^{-1} standard working solution in methanol and stored in a refrigerator at 4 °C. The ProElut™ AOAC 2007.01 QuEChERS and d-SPE kits for the general sample of vegetables and fruits were purchased from Dikma Technologies Inc. (Lake Forest, USA). The LC–MS/HPLC grade organic solvents, which include methanol and acetonitrile, were purchased from Merck (Germany). Acetic acid (HOAc) and formic acid (FA) were purchased from Fisher Scientific. The [C_6MIM][PF_6] IL ($P \geq 97\%$) was purchased from Sigma-Aldrich (Germany). The Millipore-filtered (deionised) water was obtained using a Merck Millipore water purification system (Billerica, USA).

LC–MS/MS Conditioning

The prepared 1000 µg kg^{-1} working standard solution of the eight pesticide mixture was used for the Mass-Hunter and autotuning optimisation of the triple quadrupole LC/MS (G6490A) instrument (Agilent Technologies, Singapore). The instrument exploits electrospray ionisation (ESI±) MS/MS sensitivity and Jet Stream technology. The auto-optimisation generated a total ion chromatogram (TIC) (Fig. 1) and other parameters that supported the multiple reaction monitoring (MRM) scan (Fig. 2). These include analytes' precursor ions and product ions (qualifier and quantifier) with their respective collision energies (Table 1). Afterwards, the multi-residue analysis of the pesticides was carried out using the optimised instrument operated at 15% starting organic mobile phase B (ACN + 0.1% FA) coupled with mobile phase A (deionised H_2O + 0.1% FA + 1% ACN) pushed by a stream of nitrogen gas. A 5-µL aliquot of analyte solution

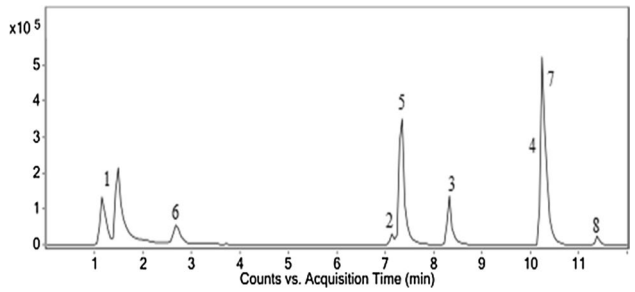


Fig. 1 Total ion chromatogram (TIC) of the multi-pesticide analytes

was injected and run through a Supelco HPLC column [Ascentis® Express C_{18} (5 cm × 2.1 mm, 2.7 µm)] (Sigma-Aldrich, USA) at 30 °C at a flow rate of 0.1 mL min^{-1}. The gradient path was 0–1.6 min, 15% B; 1.6–10.4 min, 15–100% B; 10.4–12.0 min, 15% B. All experimental runs took place after attainment of good instrumental conditions such as stabilised gas flow, nebulizer, temperature and capillary voltage.

RSM Optimisation

Minitab-17 software generated the two essential designs of RSM optimisation for the developed extraction method. The Placket–Burman (P–B) and Box–Behnken (B–B) designs were used respectively for the screening and optimisation of significant factors. Thus, the P–B and B–B design runs were initially carried out by the frequent use of distilled water (sample) to obtain proper optimisation results. This is because of its low matrix interferences and slow putrification property as compared to the use of a real sample of fruits and vegetables. Meanwhile, the total chromatographic peak areas (TCPA) resulting from several MRM scans for analyses of 100 µg kg^{-1} pesticides mixture of standard solutions were used for the method optimisation. This is because the TCPA obtained from LC–MS/MS analysis is an index

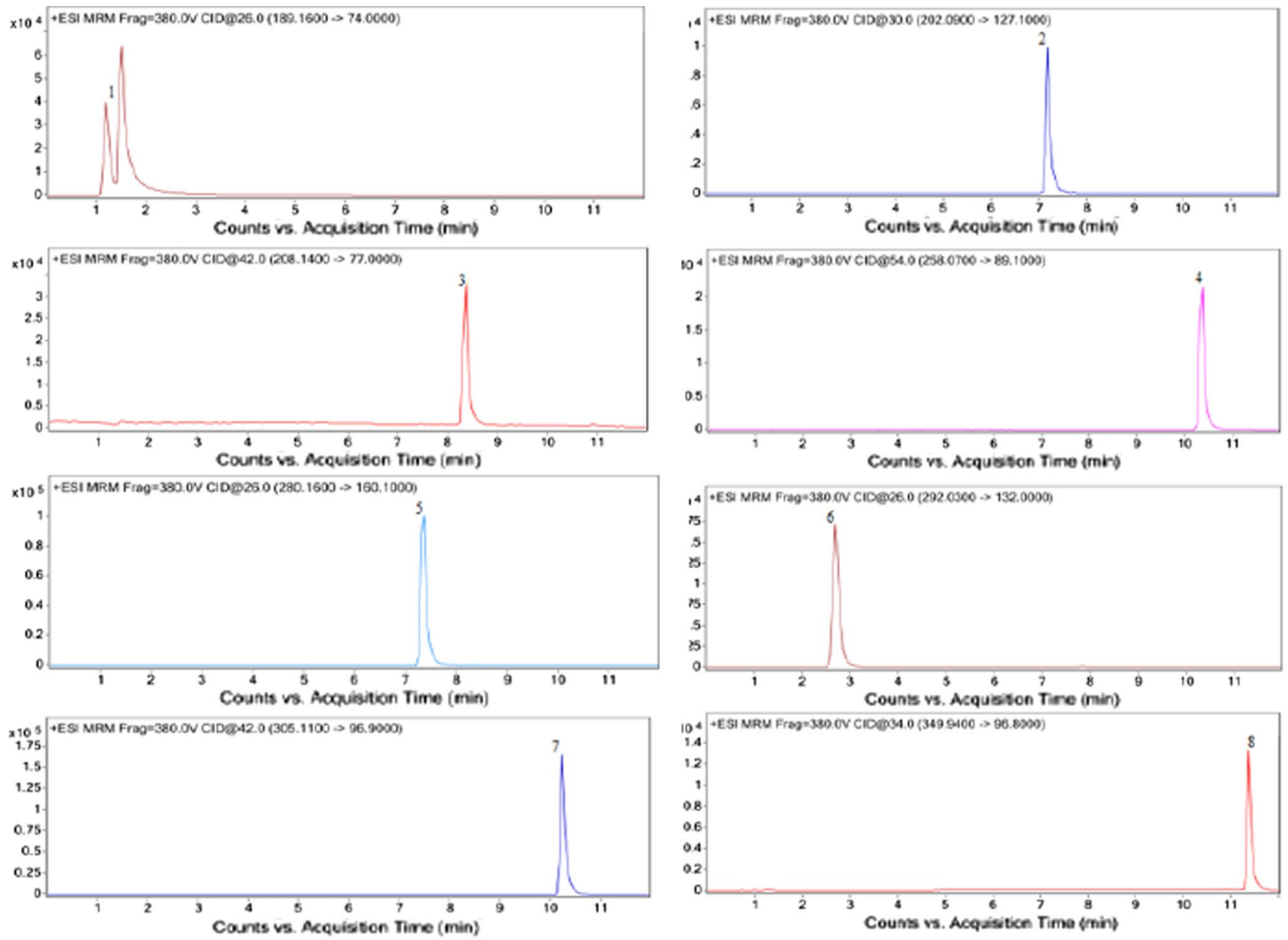


Fig. 2 Multiple reaction monitoring (MRM) data for the multi-pesticide analytes

Table 1 Mass-Hunter and autotuned optimisation for setup of the LC–MS/MS instrument

TIC	Pesticides	Molecular formula	Pesticide type	Ionization mode	Precursor ion (*m/z*)	Product ions (*m/z*)	Collision energies (eV)	RT_1; RT_2 (min)
8	Dursban	$C_9H_{11}C_{l3}NO_3PS$	Insecticide/nematicide	$[M+H]^+$	350	97; 198	34; 22	11.36; 11.36
7	Diazinon	$C_{12}H_{21}N_2O_3PS$	Insecticide	$[M+H]^+$	305	97; 169	42; 22	10.22; 10.22
6	Thiamethoxam	$C_8H_{10}ClN_5O_3S$	Insecticide	$[M+H]^+$	292	132; 211	26; 10	2.68; 2.68
5	Metalaxyl	$C_{15}H_{21}NO_4$	Fungicide	$[M+H]^+$	280	160; 220	26; 10	7.33; 7.33
4	Thiobencarb	$C_{12}H_{16}ClNOS$	Herbicide	$[M+H]^+$	258	89; 125	54; 26	10.34; 10.34
3	Baycarb	$C_{12}H_{17}NO_2$	Insecticide	$[M+H]^+$	208	77; 95	42; 10	8.34; 8.34
2	Carbaryl	$C_{12}H_{11}NO_2$	Insecticide/nematicide	$[M+H]^+$	202	127; 145	30; 6	7.16; 7.16
1	Propamocarb	$C_9H_{20}N_2O_2$	Fungicide	$[M+H]^+$	189	74; 102	26; 14	1.36; 1.36

TIC total ion chromatogram, *RT* retention time

that corresponds to the amount of analytes present in the analysed samples [19]. Notably, the MRM of the chromatographic peak areas for the obtained data were extracted and integrated using the Agilent Qualitative Analysis B.06.00 Mass Hunter Acquisition software.

Preparation of Sample

A 250-g portion of each of the homogenised analysed samples that were purchased from a local market (Petaling Jaya, Malaysia) was refrigerated (4 °C). Subsequently, some portions of each sample were analysed (blank) and other portions were spiked serially with the estimated volume of working standard solutions of known concentration of analytes mixture for the validation studies.

QuEChERS-dSPE Procedure

For the developed QuEChERS method, 20 g of homogenised (refrigerated) sample was transferred to a 50-mL centrifuge tube. Then 15 mL acetonitrile was added into the tube after spiking the content serially with the estimated volume of the known standard concentration of the analytes mixture. Then, the tube was covered and vortexed for 1 min before addition of a sachet of ProElut™ AOAC 2007.01 QuEChERS extraction salt (6 g $MgSO_4$ and 1.5 g NaOAc). The tube was covered, shaken vigorously (1 min) and centrifuged at 4000 rpm for 2 min. Subsequently, the d-SPE method began by transferring 1.5 mL supernatant from the QuEChERS extraction to a 2-mL centrifuge tube containing cleanup salt (150 mg $MgSO_4$ and 50 mg PSA). The tube was covered and vortexed for 30 s before it was centrifuged for 5 min at 4000 rpm.

IL-DLLME Procedure

The modified IL-DLLME method started by transferring 1 mL extract from the d-SPE cleanup stage to a 15-mL centrifuge tube containing 10% NaCl (w/v) in 9 mL of distilled water before addition of ≈ 130 µL of IL. The tube was centrifuged at 7000 rpm for 5 min and the 100 µL sedimental extract was transferred to a 2-mL HPLC autosampler vial containing 0.5 mL methanol. Finally, the mixture was vortexed for 1 min before quantitative analysis using an Agilent G6490A LCMS/MS instrument.

Method Validation

Validation shows the effectivity and desirability of the optimised sample preparation method for the extraction and cleanup of multi-pesticide residues in each analysis sample [20]. Moreover, it is a further step that demonstrates the certainty of the developed method for use in sample preparations before analytical determination [21]. The validated parameters include linearity range, repeatability (precisions) and accuracy (relative recovery). The linearity for each of the targeted analytes was evaluated from their respective calibration curves at five concentration levels ranging from 5 to 400 µg kg^{-1}. Also, the precision [relative standard deviation (RSD)] and accuracies were estimated by performing three repeatable ($n=3$) extractions/cleanups at three blank spiked concentration levels (5, 100 and 300 µg kg^{-1}) (Table 2). Moreover, the matrix effects (Eq. 1) in the samples were estimated [22]. The limits of detection (LOD) and quantitation (LOQ) were estimated (Eq. 2) from the calibration curve based on the signal-to-noise (*S*/*N*) ratio corresponding to a factor of 3 and 10, respectively [23]. Measurement uncertainty (MU) was estimated from the validated parameters using the coverage factor ($k=2$) based on the empirical model at 95% confidence level [24].

Table 2 Accuracy and precision at three concentration levels for the analysed samples

Pesticides	Spike (μg kg^{-1})	Banana		Cabbage		Tomato		Oranges		Onions	
		RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
Dursban	5	124	3	108	3	101	4	101	18	101	5
	100	98	4	99	3	98	3	96	8	99	4
	300	99	1	99	1	98	5	101	9	98	9
Diazinon	5	128	2	123	1	137	2	124	1	108	4
	100	100	0	99	1	100	1	100	0	98	6
	300	100	0	101	3	100	2	100	0	98	3
Thiamethoxam	5	93	6	135	4	110	2	118	3	112	6
	100	101	2	99	1	99	1	104	6	94	1
	300	99	1	99	2	100	3	100	1	98	7
Metalaxyl	5	82	6	115	3	106	8	82	4	99	2
	100	103	1	98	4	97	10	97	8	97	11
	300	99	10	99	19	101	14	100	4	100	10
Thiobencarb	5	95	20	90	8	112	1	98	2	100	6
	100	101	1	100	1	104	2	98	2	102	7
	300	100	3	101	2	99	1	100	3	98	0
Baycarb	5	95	1	134	1	115	0	109	1	120	1
	100	102	0	98	2	106	1	100	5	98	2
	300	98	0	100	2	101	2	100	1	97	1
Carbaryl	5	122	2	116	3	113	1	95	2	118	5
	100	97	7	99	3	101	0	97	3	104	3
	300	99	11	99	1	101	8	99	3	100	7
Propamocarb	5	137	9	113	3	88	3	92	3	112	4
	100	96	2	101	0	98	3	102	0	92	3
	300	101	3	100	0	101	1	98	0	98	1
Range	5–300	82–137	0–12	98–135	0–19	88–137	0–14	82–124	0–18	92–120	0–11

RR relative recovery, *RSD* relative standard deviation

$$\mathrm{ME}\ (\%) = \left[\left(\frac{\text{Slope of calibration curve for the analyte in the matrix}}{\text{Slope of calibration curve for analyte standard solution in ACN}}\right) - 1\right] \times 100 \quad (1)$$

$$\mathrm{LOD\ \ or\ LOQ\ (\mu g/kg)} = \frac{F \times \mathrm{STEYX}}{m}, \quad (2)$$

where F is LOD and LOQ having the factors of 3 and 10, respectively; STEYX is standard error estimated on Microsoft Excel 2013, and m is the slope of the linear regression.

Results and Discussion

Placket–Burman Design

The 12 experimental runs for P–B factorial design generated depend on the two levels of variables [low (−) and high (+)] as previously used for pesticide analysis [7]. Hence, the optimisation runs involved the use of 100 μg kg^{-1} working standard solution for the multi-pesticides mixture. The MRM of TCPAs was recorded accordingly after analysis by the Minitab-17 software. Thus, the analysed report for the 12 experimental runs of P–B design for six factors at two levels each was illustrated in a Pareto chart of standardised effects (Fig. 3a). It is an illustration of horizontal bars of the screened factors showing a red vertical line across the bars, which indicates the level of significant difference at 74% confidence interval (0.26 confidence limits). The six screened factors are sample quantity (A), 6.7 and 13.3 mL; HOAc in 15 mL of ACN (B), 0 and 2%; QuEChERS centrifugation speed (C), 1000 and 7000 rpm; QuEChERS centrifugation time (D), 2 and 8 min; d-SPE centrifugation speed (E), 1000 and 7000 rpm; d-SPE cleanup time (F), 2 and 8 min. Thus, the significant factors screened that required optimisation were B, D and A. Thus, these three

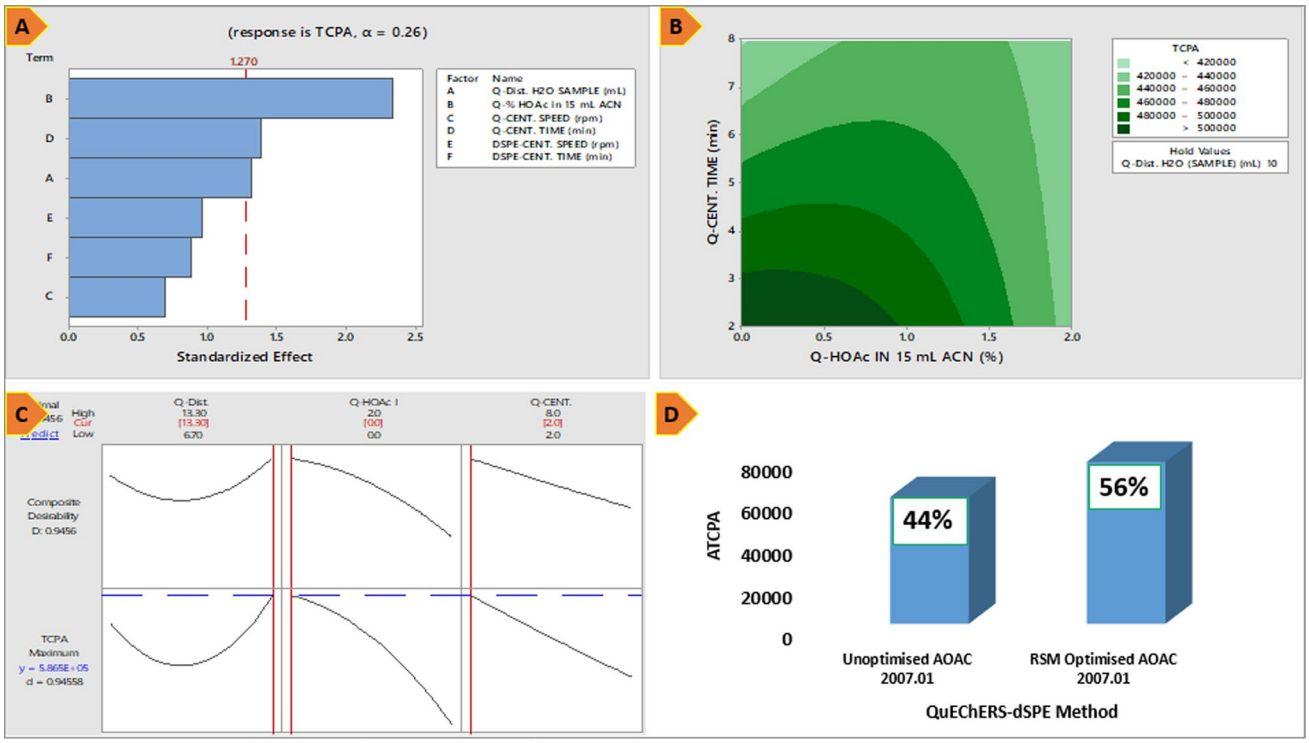


Fig. 3 Pareto chart (**a**) of the standardized effects and contour plot (**b**), as well as the composite desirability optimisation chart (**c**) and comparative chart (**d**) between unoptimised and RSM, optimised QuEChERS-dSPE method

factors increase the extraction and cleanup efficiencies of the QuEChERS-dSPE technique [25].

Box–Behnken Design

The three significant factors screened by P–B design were optimised using B–B design. However, the 15 optimisation runs were generated and carried out on the significant factors at three levels [low (−), medium (0) and high (+)] as employed by Dong et al. [26], while the other insignificant factors were operated at fixed (medium) level. The TCPA responses (Table 3) for the 15 runs of the multi-pesticides mixture (100 µg kg^{-1}) standard solution was used to generate the contour plot and desirability chart response optimisations.

The contour plot shows the response surface as a two-dimensional plane of two factors proportional to each other. Moreover, the contour lines were generated on the basis of the intercepted points of TCPA against the two factors. Thus, the most coloured contour (shaded) line of the plot (Fig. 3b) between the two significant factors (D against B) indicated the best-optimised point (value), which provided the highest TCPA (> 500,000). Moreover, the optimisation result indicated that the highest TCPA was possible when both factors of D and B approached zero (0). Meanwhile, the desirability chart shows the best-optimised values for the three significant parameters of the QuEChERS-dSPE extraction/cleanup method, which yielded maximum (optimum) desirable fit at the composite desirability of 0.9456 (Fig. 3c). Hence, the chart illustration predicted 13.3 mL (~ 20 g of fresh sample) for factor A as supported by Lee et al. [27]. In addition, the predictive values of 0% B (%HOAc in 15 mL of ACN) and 2 min D (QuEChERS centrifugation time) for the optimised factors are less than those of the AOAC official 2007.01 and European EN 15662 QuEChERS-dSPE methods for the sample preparation [28]. Subsequently, the comparative study was carried out between the optimised and unoptimised factors setup at a medium level. Fortunately, the comparative study (Fig. 3d) favoured the use of the RSM optimised setup (56%) over the unoptimised setup (44%) of the QuEChERS-dSPE method.

Subsequently, the RSM optimised QuEChERS-dSPE and QuEChERS-IL-DLLME methods were combined to form the QuEChERS-dSPE-IL-DLLME technique. Justifiably, comparative studies (Fig. 4a) of the developed RSM optimised QuEChERS-dSPE (1.73%), QuEChERS-DLLME (50.10%) and QuEChERS-dSPE-IL-DLLME (48.17%) techniques favoured the RSM optimised QuEChERS-IL-DLLME technique in the analysed (distilled water) samples. Unfortunately, the RSM optimised QuEChERS-IL-DLLME technique could not be used for the pesticide determination in the real sample of fruits and vegetables because of the

Table 3 Three-level significant factors in QuEChERS-dSPE method and responses of Box–Behnken design

Factors			Levels			
			Low (−)	Medium (0)		High (+)
Sample quantity (A)			6.7	10		13.3
HOAc in 15 mL of ACN (B)			0	1		2
QuEChERS centrifugation time (D)			2	5		8
Run order	Pt type	Blocks	A	B	D	TCPA
1	2	1	6.7	0	5	468,556
2	2	1	13.3	0	5	597,884
3	2	1	6.7	2	5	441,682
4	2	1	13.3	2	5	497,001
5	2	1	6.7	1	2	579,964
6	2	1	13.3	1	2	490,067
7	2	1	6.7	1	8	537,592
8	2	1	13.3	1	8	493,233
9	2	1	10	0	2	523,942
10	2	1	10	2	2	460,280
11	2	1	10	0	8	389,043
12	2	1	10	2	8	423,322
13	0	1	10	1	5	474,820
14	0	1	10	1	5	467,664
15	0	1	10	1	5	468,895

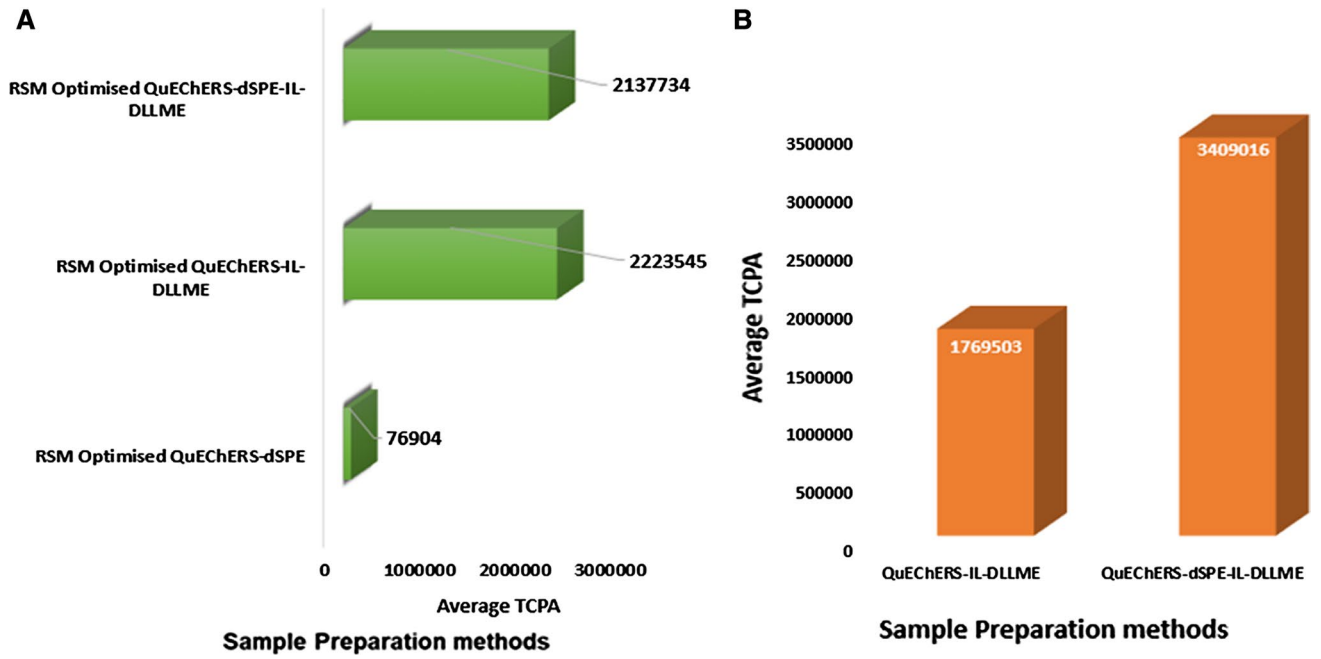


Fig. 4 Comparative analysis (**a**) of the RSM optimised QuEChERS extraction/cleanup methods and comparative illustration (**b**) between RSM optimised QuEChERS-IL-DLLME and QuEChERS-dSPE-IL-DLLME methods in the analysis of real samples

weak recoveries of analytes obtained, which was due to the absence of PSA. Consequently, the RSM optimised QuEChERS-dSPE-IL-DLLME technique (65.90%) was selected and used for the sample preparations after comparative studies with the QuEChERS-IL-DLLME technique (34.10%) in a real sample of fruits (Fig. 4b). Therefore, the combination

of the RSM optimised QuEChERS-dSPE extraction and IL-based DLLME cleanup methodologies provided more flexibility, sensitivity, selectivity and robustness of the developed QuEChERS-dSPE-IL-based DLLME technique. Then, the technique was validated by the determination of multi-pesticide residues in the real samples of fruits and vegetables.

Validation of Extraction/Cleanup Method

The parameters used for validation of the developed include linearity range, precisions, accuracies, matrix effect, LOD, LOQ and MU. Certainly, the linearity (Table 4) results were linear with a coefficient of regression (R^2) greater than 0.99 in accordance with Camino-Sánchez et al. [29]. Satisfactorily, the variation range of the precision (≤ 20%) (Table 2) was within the range reported by Nantia et al. [30]. Also, 92.5% of all obtained relative recovery results (82–137%, Table 2) were within the guideline recommendation of SANTE-11813 (70–120%) [31].

The estimated matrix effect measured the performance capability of the developed method by showing the effects of matrix interferences of the analyte recoveries [32]. Table 4 indicated that the matrix effects of all samples were very weak (less effective) (≤ − 80%) and not effective on the basis of the guideline indicating suppression (− 20%) or enhancement (20%) of analyte recoveries. This could be because of the excellent extraction/cleanup of matrix interferences to the lowest level performed by the developed method. In addition, the ranges of the LOD (0.02–0.32 µg kg^{-1}) and LOQ (0.07–1.06 µg kg^{-1}) were lower than the lowest calibration level (5 µg kg^{-1}) and the EU recommended maximum residue limits (MRLs) (Table 5) [33]. Table 4 shows the estimated MU (1–16%), and it is acceptably within the recommended range (≤ 50%). Furthermore, credibility and reliability of the developed method were certified further by analysis of three portions for each of the real (unspiked) samples. Thus, all the obtained results quantitatively showed (detected) the presence of the analytes in the respective samples analysed. However, most of the detected analytes were less than the LOQ and EU MRLs.

Conclusions

The RSM optimisation approach to some factors of AOAC 2007.01 QuEChERS-dSPE coupled with IL-based DLLME technique was successful. Consequently, the developed QuEChERS-dSPE-IL-based DLLME technique provided an optimum condition for multi-pesticides residue determination in a sample of bananas, cabbages, tomatoes, oranges and onions. The developed technique provided excellent results owing to its optimised cleanup of matrix interferences with less consumption of organic solvents. The advantages of

Table 4 Regression coefficient, matrix effects and measurement uncertainties of the analysed samples

Pesticides	Banana			Cabbage			Tomato			Oranges			Onions		
	R^2	ME (%)	MU (%)	R^2	ME (%)	MU (%)	R^2	ME (%)	MU (%)	R^2	ME (%)	MU (%)	R^2	ME (%)	MU (%)
Dursban	0.9995	− 80	6	0.9997	− 91	5	0.9992	− 86	8	0.9992	− 83	23	0.9995	− 98	12
Diazinon	0.9996	− 98	2	0.9995	− 97	3	0.9996	− 96	4	0.9997	− 95	1	0.9979	− 98	9
Thiamethoxam	0.9998	− 100	6	0.9995	− 100	4	0.9998	− 100	4	0.9985	− 100	7	0.9978	− 100	10
Metalaxyl	0.9997	− 100	11	0.9996	− 99	17	0.9994	− 100	22	0.9995	− 99	10	0.9997	− 99	15
Thiobencarb	0.9999	− 94	16	0.9998	− 96	7	0.9992	− 93	3	0.9998	− 93	5	0.9995	− 98	9
Baycarb	0.9995	− 99	1	0.9996	− 98	3	0.9983	− 88	2	0.9998	− 97	4	0.9982	− 96	2
Carbaryl	0.9994	− 100	13	0.9997	− 100	5	0.9997	− 100	6	0.9993	− 100	5	0.9989	− 100	10
Propamocarb	0.9995	− 100	9	0.9997	− 100	2	0.9997	− 100	5	0.9994	− 100	2	0.9966	− 100	5
Ranges	> 0.99	≤ − 80	≤ 16	> 0.99	≤ − 91	≤ 17	> 0.99	≤ − 86	≤ 22	> 0.99	≤ − 83	≤ 23	> 0.99	≤ − 96	≤ 15

R^2 regression coefficient, *ME* matrix effect, *MU* measurement uncertainty

Table 5 Pesticides detection and quantitation limit of the analysed samples

Pesticides	Banana			Cabbage			Tomato			Oranges			Onions		
	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	EU-MRL (μg kg^{-1})	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	EU-MRL (μg kg^{-1})	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	EU-MRL (μg kg^{-1})	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	EU-MRL (μg kg^{-1})	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	EU-MRL (μg kg^{-1})
Dursban	0.09	0.31	3000	0.06	0.20	10	0.14	0.48	300	0.14	0.48	300	0.11	0.36	50
Diazinon	0.07	0.25	10	0.10	0.33	50	0.07	0.22	10	0.06	0.20	10	0.25	0.82	50
Thiamethoxam	0.06	0.19	20	0.09	0.30	20	0.02	0.07	200	0.19	0.64	150	0.25	0.84	10
Metalaxyl	0.10	0.34	50	0.08	0.27	1000	0.12	0.41	200	0.12	0.39	500	0.09	0.29	500
Thiobencarb	0.03	0.11	10	0.06	0.19	100	0.14	0.47	10	0.07	0.22	10	0.11	0.36	10
Baycarb	0.11	0.38	10	0.05	0.16	10	0.22	0.73	10	0.03	0.09	10	0.22	0.75	10
Carbaryl	0.11	0.38	50	0.05	0.18	10	0.07	0.24	10	0.14	0.47	10	0.17	0.55	20
Propamocarb	0.08	0.28	10	0.06	0.19	700	0.08	0.28	4000	0.13	0.42	10	0.32	1.06	2000
Ranges	0.03–0.11	0.11–0.38		0.05–0.10	0.16–0.33		0.02–0.22	0.07–0.73		0.03–0.19	0.09–0.64		0.09–0.32	0.29–1.06	

LOD limit of detection, *LOQ* limit of quantitation, *EU MRL* European Union maximum residue limit

the developed method over the previously employed techniques for sample preparation include simplicity, rapidity, good selectivity and better detectability of targeted analytes. Therefore, the sample preparation technique could be reliable and suitable for routine determination of multi-pesticide residues in vegetable and fruit samples.

Acknowledgements The authors acknowledge the Postgraduate Research Project (IPPP) for supporting this research under the Grant no. PG 174-2014B, University of Malaya Kuala Lumpur, Malaysia.

Compliance with Ethical Standards

Conflict of interest The authors of this research agreed with no conflicts of interest.

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