

# The QuEChERS-dSPE Ionic-Liquid-Based Dispersive Liquid-Liquid Microextraction Coupled With High-Performance Liquid Chromatography-Tandem Mass Spectrometry for the Determination of Multiple Pesticide Residues in Red *Syzygium samarangense* Fruits

Abubakar Lawal<sup>1,2,\*</sup> and Khalid Haliru<sup>1</sup>

<sup>1</sup>Department of Chemistry, Umaru Musa Yar'adua University Katsina, Nigeria

<sup>2</sup>Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

\*Email: abubakarlawal360@yahoo.com

## ABSTRACT

*Syzygium samarangense* (Jambu) is a tropical fruit that is nutritionally and medicinally important and that has been consumed in Southeast Asian countries for decades. Unfortunately, the fruits accumulate pesticide residues due to their agricultural production. Consequently, this results in health issues such as congenital diseases and cancers. For this reason, the QuEChERS-dSPE ionic-liquid-based dispersive liquid-liquid microextraction method coupled with high-performance liquid chromatography-tandem mass spectrometry was used for the determination of multiple pesticide residues (propamocarb, carbaryl, Baycarb, thiobencarb, metalaxyl, thiamethoxam, diazinon, and chlorpyrifos) in a red *Syzygium samarangense* sample. The results show that accuracy (88%–106%) and precision (1%–14%) ranges were satisfactory because they were within recommended ranges: 70%–120% and  $\leq 20\%$ , respectively. The method limit of detection and limit of quantitation range results were satisfactory: 0.02–0.17  $\mu\text{g}/\text{kg}$  and 0.06–0.56  $\mu\text{g}/\text{kg}$ , respectively. The linearity range (5–400  $\mu\text{g}/\text{kg}$ ) results were linear with a coefficient of regression ( $R^2$ ) greater than 0.999. The matrix effect results were very weak, being  $\leq -86\%$ . The measurement of uncertainty range results (4%–19%) were satisfactory as recommended ( $\leq 50\%$ ). Therefore, the sample preparation technique proved reliable for routine determination of pesticide multiresidue in *Syzygium samarangense*. Also, the consumption of *Syzygium samarangense* from the sourced area is justified based on the obtained concentration levels of pesticide residues in the blank sample, which were lower than European Union maximum residue limits.

**Keywords:** *Syzygium samarangense* (Jambu) fruits, pesticide residue, QuEChERS-dSPE, ionic-liquid-based dispersive liquid-liquid microextraction (DLLME), high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS)

## INTRODUCTION

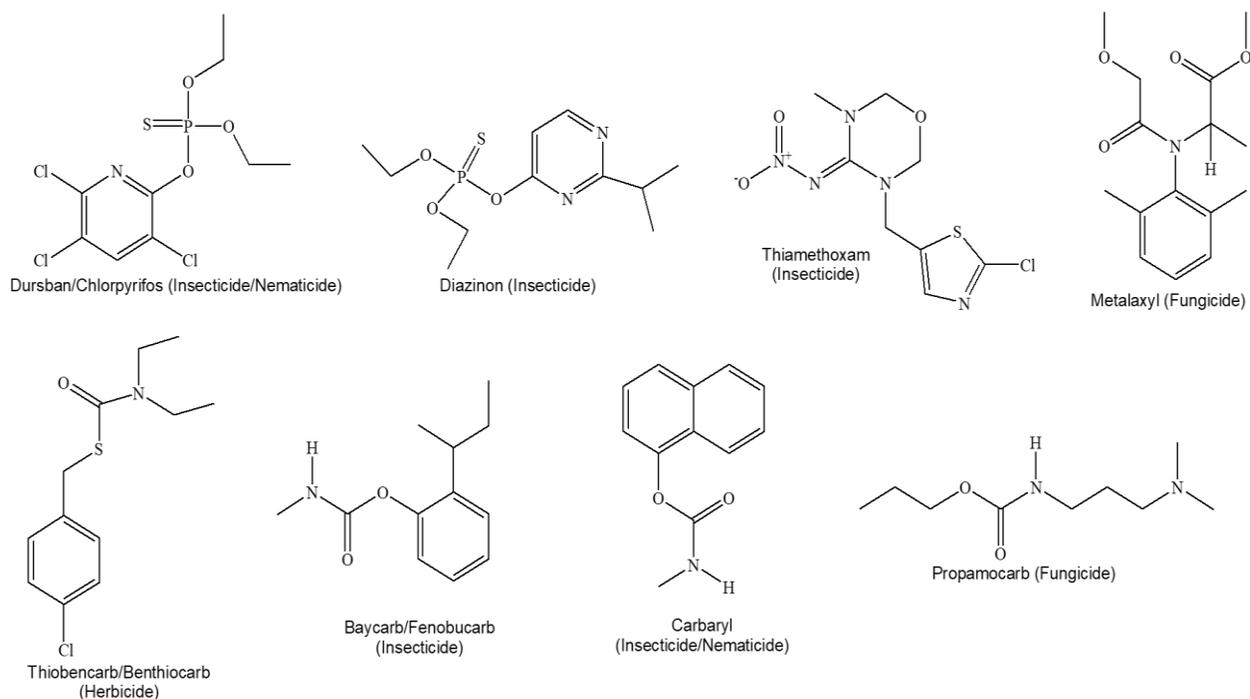
In fact, some Southeast Asian countries are blessed with lots of tropical flowering trees that provide edible fruits for their nutritional and medicinal needs (Shukla, 2013). Such fruits include the Jambu madu fruit (*Syzygium samarangense*), which is also called water apple, Java apple, rose apple, and wax apple. The fruit is a native of Indonesia, India, Pakistan, Afghanistan, Myanmar, Thailand, Taiwan, and Malaysia (Moneruzzaman et al., 2011; Shu et al., 2006). The fruit has a close resemblance to pears and appears in different colors such as green, red, and pink (Holidify, 2021). Importantly, the fruit is used as food and helps to remediate liver cirrhosis and bleeding of the pile (Ragasa et al., 2011; Shukla, 2013). It also serves as an antiviral, antidiarrheal, anti-inflammatory, antifertility, antipyretic, and neuropsychological agent due to the presence of sugar and other bioactive compounds (Sagrawat et al., 2006). The bioactive compounds in *Syzygium samarangense* include ethanol, anthocyanins, phenols, total flavonoids, volatile oils, gallic acid, tannin, ellagic acid, jamboline, etc. (Shukla, 2013).

Besides, *Syzygium samarangense* fruits have been produced in agricultural practice over the years for subsistence, commercial, and industrial consumption (Moneruzzaman et al., 2011). Unfortunately, the agricultural production of the fruits resulted in the continuous accumulation of hazardous pesticide residue in the plants because pesticides serve as pest controllers in the course of production and preservation of the farm products during transportation and storage (Lawal et al., 2018b). Unfortunately, the

longtime consumption of such fruits containing pesticide residue present in concentration levels higher than the recommended maximum residue limits could lead to detrimental health problems that include congenital disabilities and cardiovascular diseases as well as the risks of cancer in children and adults (Lawal et al., 2018a).

Therefore, the aim and objective of this study is to determine the concentration levels of the accumulated pesticide residue in a sample of *Syzygium samarangense* fruits for better environmental awareness and food safety (Adebisi et al., 2018; Lawal et al., 2016; Xu et al., 2012). This could be done by analysis of the targeted pesticide residues using the advance sample preparation method such as the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method with the dispersive solid phase extraction (dSPE) linked with 1-hexyl-3-methylimidazolium hexafluorophosphate ([C<sub>6</sub>MIM][PF<sub>6</sub>]) ionic-liquid-based (IL-based) dispersive liquid-liquid microextraction (DLLME), coupled with quantification by a high-performance liquid chromatography-tandem mass spectrometry (LC-MS/MS) instrument (Abdulra'uf et al., 2019; Lawal, 2018; Lawal & Abdulra'uf, 2020; Lawal & Koki, 2019; Lawal & Low, 2021; Lawal & Wong, 2021).

The targeted pesticide residues studied in this research (Figure 1) include propamocarb, carbaryl, Baycarb, thiobencarb, metalaxyl, thiamethoxam, diazinon, and chlorpyrifos in *Syzygium samarangense* samples sourced from Kuala Lumpur (Malaysia). And it is hoped that this research will serve as a reference guide for the future studies of pesticide residue in other fruits and food samples.



**Figure 1.** Structural illustration of the analyzed multiple pesticide residues.

## MATERIALS AND METHODS

### Sampling and Treatments

Ten samples of red *Syzygium samarangense* fruits were purchased from a commercial market in Kuala Lumpur, Malaysia. The fruits were homogenized and preserved in a refrigerator. The ProElut™ AOAC 2007.01 QuEChERS and d-SPE kits for general vegetables and fruits were obtained from Dikma Technologies Inc. (Lake Forest, USA). The molten salt (HPLC grade) of [C<sub>6</sub>MIM][PF<sub>6</sub>] ionic-liquid-based ( $p \geq 97.0\%$ ) was purchased from Sigma-Aldrich (Germany). The LC-MS grade organic solvents were used for this research work. The solvents include methanol and acetonitrile (ACN; Merck, Germany), ethanol, HOAc, acetone, and formic acid, which were obtained from Fisher Scientific. The Millipore-filtered (deionized) water was obtained using the Merck Millipore water purification system (Billerica, USA). The stock solutions for the analyzed pesticides

standard were procured from AccuStandard®, New Haven, USA. Then, the stock solutions were diluted individually from 100 mg/kg to 10 mg/kg. Subsequently, the 10 mg/kg (10,000 µg/kg) was diluted to 0.4 mg/kg (400 µg/kg), 0.3 mg/kg (300 µg/kg), 0.2 mg/kg (200 µg/kg), 0.1 mg/kg (100 µg/kg), and 0.005 mg/kg (5 µg/kg; working standard solutions) with the estimated volume of methanol, and the solutions were preserved in a refrigerator at 4 °C.

### Sample Preparation Method

The QuEChERS-dSPE coupled with IL-DLLME sample preparation method that was used by Lawal et al., (2018) was adopted for this research. The sample preparation method started by transferring 20 g of the homogenized sample of red *Syzygium samarangense* fruits into five 50-ml centrifuge tubes. Each tube's content was spiked serially with the estimated volumes of working standard solutions of 5,

100, 200, 300, and 400 µg/kg. Then, each tube was vortexed for 1 min after the addition of 15-ml acetonitrile. The sachet of ProElut™ AOAC 2007.01 QuEChERS extraction salt (6 g of MgSO<sub>4</sub> and 1.5 g of NaOAc) was added and shaken vigorously for 1 min before centrifugation (4,000 rpm) for 2 min, followed by the d-SPE methodology that was carried out by occupying the 2-ml centrifuge tube containing the cleanup salt (150 mg of MgSO<sub>4</sub> and 50 mg of PSA) with 1.5 ml of supernatant obtained from the QuEChERS extraction. The tube was later centrifuged at 4,000 rpm for 5 min.

Subsequently, the IL-DLLME cleanup procedure was performed by transferring 1 ml of supernatant extract from the d-SPE cleanup into a 15-ml centrifuge tube that was occupied with 10% NaCl (w/v) in 9 ml of distilled water. Then, the 130 µl of IL-based was added into the centrifuge tube before centrifugation at 7,000 rpm for 5 min. Then, the resulting 100 µl of the sedimental extract was collected with a microsyringe and transferred into a 2-ml HPLC autosampler vial. The vial was vortexed for 1 min after addition of 0.5 ml of methanol. Finally, the extracted solution was analyzed using the high-performance LC-MS/MS (Agilent G6490A LC-MS/MS) instrument. Notably, the method was repeated on all the tubes spiked at different concentrations levels as well as a blank (unspiked) portion of the sample, and all were analyzed in triplicates.

### Validation of Sample Preparation Method

The SANTE-11813 (2017) guidelines were used for the validation of the method. These include accuracies (relative recovery;

70%–120%), repeatability (precisions; ≤20%), and linearity range with the coefficient of regression ( $R^2$ ). The relative recovery and precision were estimated from the triple ( $n = 3$ ) extractions/cleanups spiked at three concentration levels (5, 100, and 300 µg/kg). 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. Furthermore, the limit of detection (LOD) and limit of quantitation (LOQ) were estimated (Equation 1) from the calibration curve based on the signal-to-noise (S/N) ratio corresponding to a factor of 3 and 10, respectively (Xiu-Ping et al., 2017).

$$\text{LOD or LOQ } (\mu\text{g/kg}) = \frac{F \times \text{STEYX}}{m} \quad (1)$$

where

- $F$ : LOD and LOQ, which have factors of 3 and 10, respectively
- STEYX: standard error estimated on Microsoft Excel 2013
- $m$ : slope of the linear regression

And the matrix effect (ME) for each sample was estimated as indicated in Equation 2 (Dias et al., 2016). Note that the ME indicates suppression (–20%) or enhancement (+20%) of analyte recoveries in comparison with 100% mean.

$$\text{ME } (\%) = \left[ \left( \frac{\text{Slope of a calibration curve for the analyte in a matrix}}{\text{Slope of a calibration curve for analyte standard solution in acetonitrile}} \right) - 1 \right] \times 100 \quad (2)$$

### LC-MS/MS Instrumentation

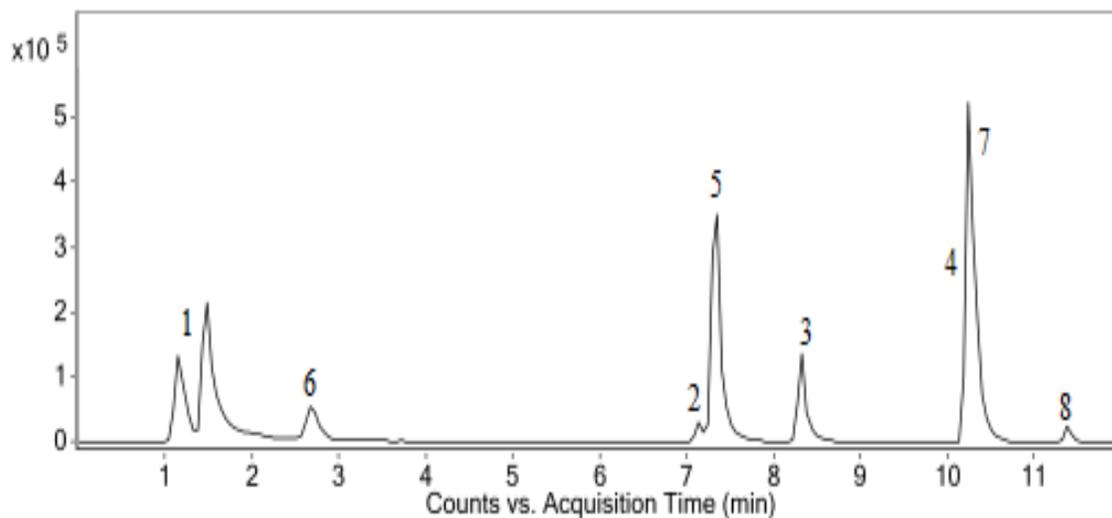
The instrumental analysis of multiple pesticide residues in the prepared sample solution of *Syzygium samarangense* fruit was carried out after auto-tuned optimization of the Mass-Hunter of the instrument using 1 mg/kg of the standard solution of pesticide mixture, yielding their precursor and product ions (m/z) and collision energies (eV) as tabulated (Table 1).

In addition, good acquisition setups were attained, such as nebulizer, stabilized gas flow, temperature, and capillary voltage. Nevertheless, the instrument was set up at 15% starting organic mobile phase B (acetonitrile + 0.1% formic acid) coupled

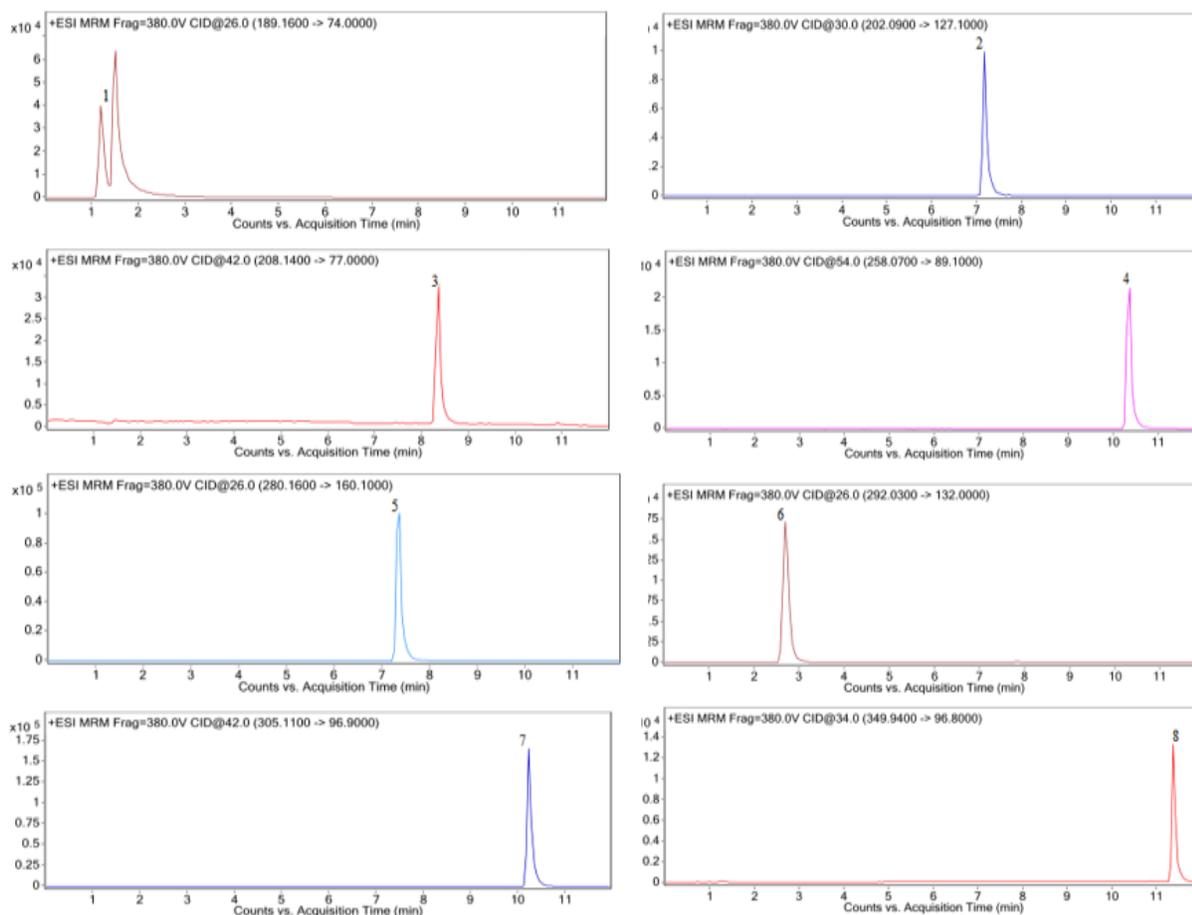
with mobile phase A (deionized water + 0.1% formic acid + 1% acetonitrile) flowed by the pump. The 5- $\mu$ l analyte solution was injected, passed, and ran through a Supelco HPLC column (Ascentis® Express C<sub>18</sub> [5 cm  $\times$  2.1 mm, 2.7  $\mu$ m]; Sigma-Aldrich, USA) at 30 °C and the flow rate of 0.1 ml/min. The gradient path was estimated as follows: 0–1.6 min, 15% B; 1.6–10.4 min, 15%–100% B; 10.4–12.0 min, 15% B. Note that the total chromatographic peak areas (TCPA) or total ion chromatography of the multiple reaction monitoring scans obtained from LC-MS/MS analysis (Figures 2 and 3) were used for the analysis of the multiple pesticides. It is because TCPA is an index that corresponds to the number of analytes present in analyzed samples (Lawal et al., 2018).

**Table 1. The Mass-Hunter and Auto-Tuned Optimization for the Setup of Liquid Chromatography–Tandem Mass Spectrometry**

No.	Pesticides	Molecular Formula	Pesticide Type	Ionization Mode	Precursor Ion (m/z)	Product Ions (m/z)	Collision Energies (eV)
8	Chlorpyrifos	C <sub>9</sub> H <sub>11</sub> C <sub>13</sub> NO <sub>3</sub> PS	Insecticide/Nematicide	[M+H] <sup>+</sup>	350	97;198	34;22
7	Diazinon	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS	Insecticide	[M+H] <sup>+</sup>	305	97;169	42;22
6	Thiamethoxam	C <sub>8</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>3</sub> S	Insecticide	[M+H] <sup>+</sup>	292	132;211	26;10
5	Metalaxyl	C <sub>15</sub> H <sub>21</sub> NO <sub>4</sub>	Fungicide	[M+H] <sup>+</sup>	280	160;220	26;10
4	Thiobencarb	C <sub>12</sub> H <sub>16</sub> ClNOS	Herbicide	[M+H] <sup>+</sup>	258	89;125	54;26
3	Baycarb	C <sub>12</sub> H <sub>17</sub> NO <sub>2</sub>	Insecticide	[M+H] <sup>+</sup>	208	77;95	42;10
2	Carbaryl	C <sub>12</sub> H <sub>11</sub> NO <sub>2</sub>	Insecticide/Nematicide	[M+H] <sup>+</sup>	202	127;145	30;6
1	Propamocarb	C <sub>9</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	Fungicide	[M+H] <sup>+</sup>	189	74;102	26;14



**Figure 2.** Total ion chromatograph for the multiple pesticide analytes.



**Figure 3.** The selected multiple reaction monitoring for the multipesticide analytes.

## RESULTS AND DISCUSSION

Table 2 highlights results of the accuracy and precision results for the analyzed multiple pesticide residue in red *Syzygium samarangense* fruits.

The accuracy (88%–106%) and precision (1%–14%) ranges at the three spiked concentration levels were found within the SANTE-11813 (2017) guidelines of 70%–120% and 0%–20%, respectively. Also, the precision results of the analyzed pesticide residue in *Syzygium*

*samarangense* were satisfactory ( $\leq 20\%$ ) as recommended by SANTE-11813 (2017) and found within the documented range. The accuracy results are in the same range reported by Uclés et al. (2015), Gao et al. (2015), Li et al. (2014), and Han et al. (2016) for the analysis of pesticide residue in the samples of pears, apples, and other fruits.

Moreover, Table 3 shows the results of the LOD and LOQ, regression coefficient, matrix effect, measurement uncertainty, and the detected pesticide residue in *Syzygium samarangense*.

**Table 2. The Obtained Results for Accuracy and Precision at Three Levels of Concentration in the Sample of Red *Syzygium samarangense* Fruits**

Pesticides	Spike ( $\mu\text{g}/\text{kg}$ )	RR (%)	RSD (%)
Durban	5	88	5
	100	97	3
	300	99	7
Diazinon	5	104	1
	100	100	2
	300	100	5
Thiamethoxam	5	95	3
	100	98	2
	300	98	3
Metalaxyl	5	97	10
	100	98	14
	300	101	5
Thiobencarb	5	99	1
	100	103	1
	300	99	4
Baycarb	5	102	2
	100	104	3
	300	101	5
Carbaryl	5	106	1
	100	98	2
	300	100	7
Propamocarb	5	102	5
	100	100	7
	300	100	4
Ranges	5–300	88–106	1–14

Note. RR = relative recoveries; RSD = relative standard deviation.

**Table 3. The Results for the Limit of Detection and Quantitation, as well as the Regression Coefficient, Matrix Effect, Measurement Uncertainty, Residue Detected, and European Union Maximum Residue Limits of Analytes in the Sample of Red *Syzygium samarangense* Fruits**

Pesticides	LOD ( $\mu\text{g}/\text{kg}$ )	LOQ ( $\mu\text{g}/\text{kg}$ )	$R^2$	ME (%)	MU (%)	DR ( $\mu\text{g}/\text{kg}$ ) $\pm$ RSD (%)	EU-MRL ( $\mu\text{g}/\text{kg}$ )
Chlorpyrifos	0.15	0.50	0.9992	-86	10	$5.78 \pm 4$	10
Diazinon	0.04	0.14	0.9998	-98	5	<LOQ	10
Thiamethoxam	0.17	0.56	0.9990	-100	5	<LOQ	300
Metalaxyl	0.08	0.26	0.9997	-100	19	<LOQ	50
Thiobencarb	0.10	0.34	0.9996	-96	4	<LOQ	10
Baycarb	0.14	0.47	0.9992	-88	7	<LOQ	10
Carbaryl	0.08	0.27	0.9997	-100	7	<LOQ	10
Propamocarb	0.02	0.06	0.9999	-100	11	<LOQ	10
Ranges	0.02– 0.17	0.06– 0.56	>0.999	$\leq$ -86	4–19		

*Note.* LOD = limit of detection; LOQ = limit of quantitation;  $R^2$  = regression coefficient; ME = matrix effect; MU = measurement of uncertainty; DR = detected residue; ND = not detected; EU-MRL = European Union maximum residue limits (European Union, 2016).

Fortunately, the European Union (2016) recommended maximum residue limits as well as the lowest calibration level ( $5 \mu\text{g}/\text{kg}$ ) are greater than the range of LOD ( $0.02\text{--}0.17 \mu\text{g}/\text{kg}$ ) and LOQ ( $0.06\text{--}0.56 \mu\text{g}/\text{kg}$ ) results. And comparatively, the results were lower and better than the ones documented by Li et al. (2014; LOD =  $0.03\text{--}2.17 \mu\text{g}/\text{kg}$  and LOQ =  $0.1\text{--}7.25 \mu\text{g}/\text{kg}$ ) and Han et al. (2016; LOD =  $0.3\text{--}3.3 \mu\text{g}/\text{kg}$  and LOQ =  $1\text{--}10 \mu\text{g}/\text{kg}$ ). The results of the linear regression coefficient ( $R^2$ ) for the linearity range are greater than 0.999, which agrees with the documented result of Lee et al. (2014) for the determination of pesticide residue in apples and other fruits. The matrix effect results appear to be very weak

( $\leq -86\%$ ), which may be due to the extra cleanup of matrix interferences performed by the sample preparation method. Thus, the matrix effect is less effective as indicated by the guidelines: suppression ( $-20\%$ ) or enhancement ( $+20\%$ ) of analyte recoveries. The estimated measurement of uncertainty result ( $4\text{--}19\%$ ) is acceptable within the recommended range ( $\leq 50\%$ ). Eventually, the quantified concentration level of chlorpyrifos ( $5.78 \pm 4 \mu\text{g}/\text{kg}$ ) in the unspiked samples of red *Syzygium samarangense* fruits were found to be lower than the EU-MRL, even though the EU-MRL of pears ( $10 \mu\text{g}/\text{kg}$ ) was used to express that of *Syzygium samarangense* fruits due to their close relationship. Meanwhile, the

concentration levels of the other analyzed pesticide residues were less than the LOQ, which could be a result of the good management and handlings of pesticides during agricultural production of red *Syzygium samarangense* fruits.

## CONCLUSION

The determination of multiple pesticide residues in the red *Syzygium samarangense* fruits sample with the QuEChERS-dSPE IL-based DLLME technique coupled with high-performance LC-MS/MS instrumentation was successfully carried out. Fortunately, the method provided the optimum condition for the analysis and maximum cleanup of matrix interferences with less organic solvents consumption, which consequently improve detectability, selectivity, and quantification of the targeted multipesticide residues. Therefore, the sample preparation technique proved to be suitable and reliable for the routine determination of multipesticide residues in red *Syzygium samarangense* fruits. Also, the consumption of red *Syzygium samarangense* fruits from the sourced area is justified based on the obtained concentration levels of pesticide residues in the blank sample of fruits, which were found below the EU-MRLs.

## CONFLICT OF INTEREST

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

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