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Method Validation for Pesticide Residues on Rice Grain in Aceh Besar District, Indonesia Using Gas Chromatography-Electron Capture Detector (GC-ECD)

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Abstract

Analysis of pesticide residues in rice in Aceh Besar District using the Gas Chromatography – Electron Capture Detector (GC-ECD) method has been carried out. This study aims to validate the analytical method and determine the pesticide residue levels of Dichlorvos, Dimethoate, Bifenthrin, and λ-Cyhalothrin in rice samples. Rice samples in branded rice were taken from the Districts of Want Jaya, Indrapuri, Darussalam, Suka Makmur, Simpang Tiga, Kuta Baro, and ground using a grinder. The powder sample was extracted by the QuEChERS method and analyzed by GC-ECD. The results of the linearity test have met the requirements with the coefficient of determination (R^2), which is an average of 0.98. The LOD values ranged from 0.013 to 0.017 mg/kg, while the LOQ ranged from 0.022 to 0.079 mg/kg. The results of precision and reproducibility (% RSD, n = 6) show the values of 0.56 - 1.26% and 1.14 - 2.19%, respectively, and the accuracy value (%Recovery) shows the results of 99.71 - 101.84%, with an RSD value of 2.42 - 3.59%, meet the requirement of 20%. The results of the analysis of the sample showed that sample A had a large %Recovery value in the Dichlorvos analyte, namely 139.10%, with the calculation that the Dichlorvos analyte contained 0.0206 mg/Kg. This value has not passed the MLR set by the European Food Safety Authority, which is 0.2 mg/Kg. In the other rice samples, no pesticide residue analytes were detected. The calculation of %Recovery of each analyte in the spiked sample ranged from 80-101%, which indicated that the pesticide residue analysis carried out had good accuracy, namely the requirement of 70-120%.

1. Introduction

Rice, one of the world's staple foods, is a critical food product. Rice plants have various types of rice, including white rice (Oryza sativa L.) and brown rice (Oryza nivara). White rice is a staple food for most Indonesians [1]. Aceh

Province is one of the central provinces of rice production in Indonesia, which is targeted to become self-sufficient in rice and become a national food barn. [2]. Aceh Province, consisting of 23 regencies/cities, all produce rice except for the City of Sabang [3]. Aceh Besar Regency is the fourth largest rice producer with a total production of around 159,929 tons per year, rice production in Aceh Province in 2021 has decreased by 9.72 thousand tons or 1.21 percent compared to 2020 [4]. Decreased productivity can be caused by various factors, including climate disturbances, pests, and diseases, fertilization that does not comply with site-specific recommendations, and improper harvesting methods [5].

Therefore, efforts to increase the need for food require intensification of agriculture. One form of agricultural intensification is the use of pesticides. In modern agriculture, agricultural chemicals or pesticides are used globally in the agrarian sector to control pest populations [6].

Pesticides that farmers widely use are pyrethroid. The active ingredients are alphamethrin, bifenthrin, deltamethrin, fenvalerate, λ-cyhalothrin, permethrin, and cypermethrin. Farmers often use pyrethroid pesticides because they are affordable and effective for controlling pests and have stable properties when exposed to sunlight [7]. Therefore, it is necessary to analyze the pesticide residues contained in rice, especially rice in the Aceh Besar area.

The analytical method that is often used is the gas chromatography method. Gas chromatography is the most widely used technique in simultaneous pesticide analysis due to its high-resolution capacity and availability of selective detectors [8–10]. Several gas chromatography methods with particular detectors, such as Electron Capture Detector (ECD), Flame Photometric Detector (FPD), Nitrogen Phosphorus Detector (NPD), and mass spectrometer (MS) detectors [11, 12], have been widely used for the determination of pesticide residues in plants [13, 14].

In this study, the analysis of the pesticide residue content in rice was carried out using the QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction method based on the Association of Analytical Communities (AOAC) Official Method 2007.01 [15, 16]. The QuEChERS extraction technique for pesticide residue analysis is frequently used today and has been extensively modified to suit the specific characteristics of the sample [17–20]. The instrument used is a gas chromatograph equipped with an ECD detector which has a sensitivity to organophosphate groups (Dichlorvos and Dimethoate) and pyrethroids (Bifenthrin, λ-cyhalothrin).

Table 1. Gas chromatographic conditions.

Parameter	Detail
Capillary column	RTX-5 (*crossbond*, 95% *dimethyl polysiloxane* - 5% *diphenyl*)
Detector	ECD (*Electron Capture Detector*)
Column size	30 m × 0.25 mmID × 0.25 µmDF
Mobile phase	Helium (UHP 99,9995%)
Mobile phase velocity	1.2 mL/min
Make-up Gas	30 mL/min
Detector temperature	280 °C
Injector temperature	230 °C
Injection mode	Splitless
Oven temperature	100 – 280 C (temperature up 15 C/min, hold 5 min)

2. Materials and Methods

2.1. Tools and Materials

The instruments used are Gas Chromatography-Electron Capture Detector (GC-ECD) (Shimadzu, GC-2010 Plus), Capillary Column (Restek) Rtx-5 (30 m × 30 mmID × 30 mdf), auto sampler (Shimadzu, AOC -5000 Plus), 10 L syringe (Shimadzu), vortex-homogenizer (IKA), Grinder (IKA), Centrifuge (Thermo Scientific), 10 mL volume micropipette (BrandTech), 10-1000 µL adjustable micropipette (Eppendorf), vial vial 2 mL, 10 mL volumetric flask, 50 mL and 15 mL poly-ethylene (PE) tubes.

The materials used were rice samples, organic rice samples (for validation methods), acetonitrile Chromatography Grade (Merck), glacial acetic acid (Merck), QuEChERS kit powder (containing 6 g $MgSO_4$ and 1.5 g Na-Acetate) and powder kit clean– up (containing 1.2 g $MgSO_4$, 400 mg Primary Secondary Amine (PSA) and 400 mg C_{18}) obtained from Agilent Technologies, pesticide standard (dichlorvos, dimethoate, bifenthrin and λ-Cyhalothrin) with purity >98% obtained from Sigma-Aldrich and ceramic homogenizers.

2.2. Chromatography Conditions

Table 1 presents the gas chromatography parameters employed for this research.

2.3. Sampling technique

Samples were taken from rice production in the Aceh Besar District, Aceh Province with different areas. The rice

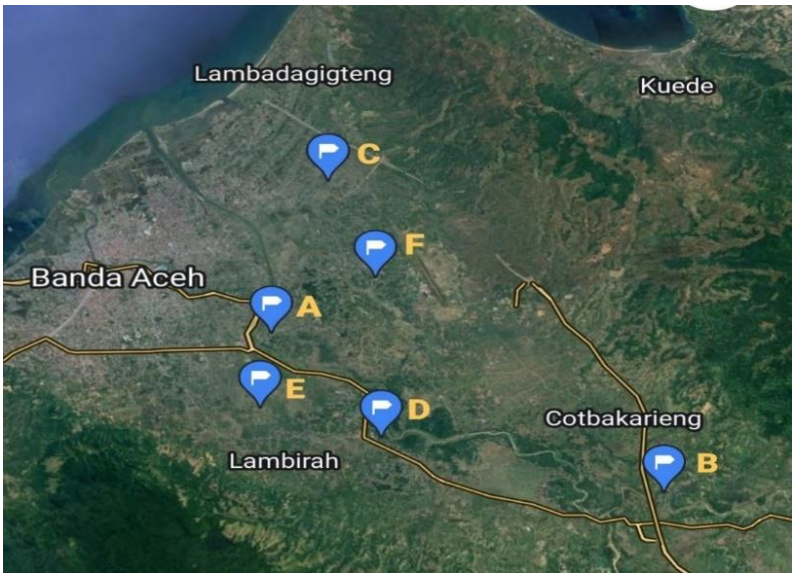

Figure 1. Google Earth satellite image of the rice sampling point.

samples used were 6 samples in the form of branded rice products. The branded rice used in this study were rice A from Siron Village, Ingin Jaya District, rice B from Blang Jaroe Village, Indrapuri District, C rice from Lamreh Village, Darussalam District, rice D from Sibreh Village, Suka Makmur District, E rice from Ateuk Mon Panah Village. Simpang Tiga District, and F rice from Lam Neuheun Village, Kuta Baro District. Meanwhile, organic rice samples were used, namely rice without chemical pesticides, as blanks for the validation method as supporting data in this study. The sampling point is shown in Figure 1.

2.4. Method Validation

The method validation for the analysis of pesticide residues in food and feed was performed following the guidelines outlined in the Guidance document on analytical quality control and method validation procedures [16, 21]. The validation parameters performed are linearity, precision, accuracy (% Recovery), detection limit (LoD), and quantification limit (LoQ). At least five concentration levels are made to determine the calibration curve (linearity). Based on linearity, the values of LoD and LoQ are determined. Recovery (%), which is the lowest spike concentration validated to fulfill the requirements of an average in the range of 70-120% and RSD 20%, was used to calculate precision and accuracy values [21].

2.5. Extraction Method (Sample Pretreatment)

Rice samples were ground using a grinder and weighed 5 ± 0.2 grams using a calibrated analytical balance in a 50 mL polyethylene tube. Added (spike) 75 µL of mixed standard solution (dichlorvos, dimethoate, bifenthrin and -cyhalothrin) from a concentration of 10 g/mL and let stand for 30 minutes. Add Kit-QuEChERS powder containing (6 g $MgSO_4$ and 1.5 g Sodium Acetate) and enter the ceramic homogenizer. Add 15 mL of solvent (1% acetic acid in acetonitrile) and vortex until homogeneous for ± 2 minutes. Centrifugation was carried out for 5 minutes at 4000 rpm and produced a layer of the organic phase and a layer of waste [16].

8 mL of the organic phase was taken and put into a 15 mL polyethylene tube containing absorbent (1.2 g $MgSO_4$, 400 mg PSA, and 400 mg C_{18}), then vortexed for 30 seconds until homogeneous. Centrifugation was carried out for 2 minutes at 4000 rpm. Take 1000 L of the organic phase and put it in a vial. Place the vial in the autosampler and inject 1 µL in the gas chromatograph (AOAC, 2007). The preparation process for the blanks was carried out the same, but without adding mixed standards.

3. Results and Discussions

3.1. Method Validation

The analytical technique was validated using samples of proven organic rice that were devoid of the target analyte. The linearity test, LOD, LOQ, precision test (%RSD), accuracy (%Recovery), and selectivity were used to validate the analytical method [22–25].

3.1.1. Linearity and Analysis Performance Characteristics

Calibration curves were made using calibration standards at five concentration levels in the range of 0.01-0.30 mg/kg. Based on Table 2, the calibration curve data provides good linearity in various ranges, with a coefficient of determination of an average of 0.98, indicating that the linearity of the calibration curve meets

Table 2. Data on the characteristics of the analysis performance of the validated method.

Analytes	Calibration curve	Range Concentrations of Calibration (mg/kg)	R^2	LOD (mg/kg)	LOQ (mg/kg)	MLR (mg/Kg)
Dichlorvos	Y = 376.89x + 5.9583	0.01-0.30	0.9941	0.016	0.079	0.01
Dimethoate	Y = 428.1x + 3.2645	0.01-0.30	0.9980	0.015	0.044	0.01
Bifenthrin	Y = 544.96x + 5.4177	0.01-0.30	0.9984	0.013	0.040	0.01
λ-Cyhalothrin	Y = 583.23x + 2.8177	0.01-0.30	0.9995	0.017	0.022	0.2

Table 3. Values of precision (intraday) and reproducibility (interday) for spike rice samples.

Rice sample	Bifenthrin	Dichlorvos	Dimethoate	λ-Cyhalothrin
Intraday (%RSD) 0,01 mg/kg	0.62	1.26	1.01	0.56
Interday (%RSD) 0,01 mg/kg	1.14	2.19	1.94	2.05

Tabel 4. The %Recovery value of analyte in rice samples.

Analyte	Average %Recovery	%RSD (n=6)
Bifenthrin	99.94	3.59
Dichlorvos	100.08	3.45
Dimethoate	101.84	2.42
λ-Cyhalothrin	99.71	2.99

the requirements and is acceptable [22]. Determination of LOD and LOQ values were calculated based on the standard deviation of the rice sample extract with each minimum concentration of pesticide residue analyte [23]. The LOD values ranged from 0.013 to 0.017 mg/kg, while the LOQ ranged from 0.022 to 0.079 mg/kg. Maximum Residue Limit (MRL) value of rice samples based on the European Food Safety Authority [26].

3.1.2. Precision Determination

Precision is the analysis of repeatability and reproducibility of a method developed by spiking blank rice samples at a concentration level of 0.01 mg/kg with six measurement repetitions. Repetition is carried out on the same day and under the same conditions (intraday), while reproducibility is repeated between days with time differences (interday). The relative standard deviation values (% RSD, n = 6) precision and reproducibility were 0.56 - 1.26 % and 1.14 - 2.19 %, respectively (Table 3). The value of precision and reproducibility is stated to be good because it meets the requirements of 20% [21]. Thus, %RSD indicates that the method developed is correct.

3.1.3. Determination of Accuracy

Determination of the accuracy value in the form of %Recovery, which is a method used to observe the efficiency of an extraction method used. Rice blank samples were spiked with a concentration of 0.01 mg/kg to ensure the correctness of the method used. Each measurement was carried out in six repetitions. The results in Table 4 explain that the %Recovery of the analyte is in the range of 99.71 - 101.84%, with an RSD value of 2.42 - 3.59%. Based on the observations for each spike analyte and all %Recovery values of target analytes from rice samples in an acceptable range, i.e. from 70 to 120% [21, 27].

3.2. Sample Analysis Based on Validation Method

After validation of the optimal method effectiveness, an analysis was carried out for six local rice products that are often consumed by the community, especially the Aceh Province. Spiking the target pesticide residue analyte in the sample with a 0.01 mg/kg concentration. Subsequently, all samples were extracted and analyzed at the previously validated optimum conditions.

Figure 2 shows the chromatogram results for identifying each pesticide residue analyte spiked in one of the extracted rice samples. Based on observations on the chromatogram, it is known that the retention time (tR) of the analyte for Dichlorvos; Dimethoate; Bifenthrin; λ-Cyhalothrin (IS, Cis R); and λ-Cyhalothrin (IS, Cis S) which were 4,927 min, 9,308 min, 17,860 min, 18,826 min, and 19,098 min, respectively. In analyte, λ-Cyhalothrin has

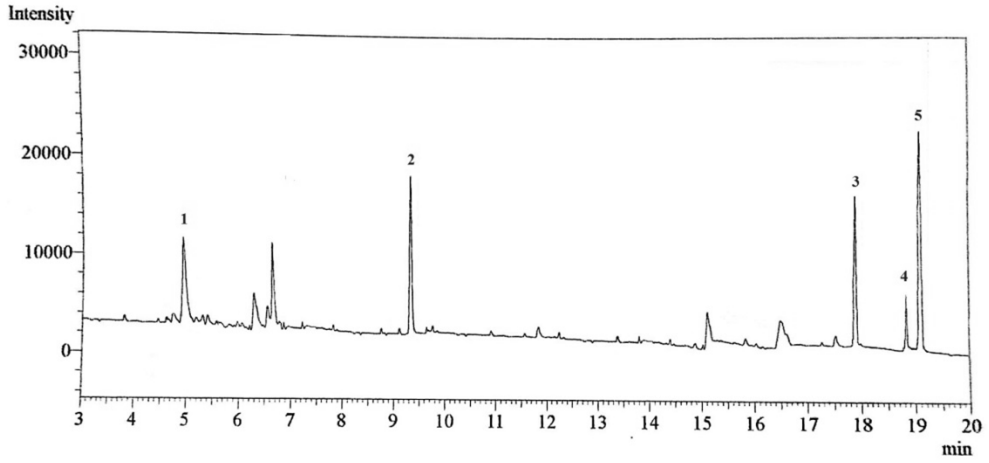

Figure 2. Chromatogram results for identification of each spiked pesticide residue analyte in one rice sample. Peak identification: (1) Dichlorvos; (2) Dimethoate; (3) Bifenthrin; (4) λ-Cyhalothrin (IS, Cis R); and (5) λ-Cyhalothrin (IS, Cis S).

Table 5. Results of rice sample analysis based on validated methods

Samples	% Recovery			
	Dichlorvos	**Bifenthrin**	**Dimethoate**	**λ-Cyhalothrin**
A	139.10	100.77	93.19	94.63
B	90.43	95.83	101.65	95.73
C	91.73	97.49	91.10	96.45
D	88.35	92.61	86.89	93.72
E	87.12	95.98	85.59	99.41
F	98.69	80.13	90.84	88.96

two chromatogram peaks in the form of diastereoisomers [28]. Table 5 describes the results of the spike analysis on the extracted rice samples. Sample A has a large recovery value for the Dichlorvos analyte, 139.10%. This indicates that there is Dichlorvos analyte in rice sample A. The calculation results show that the Dichlorvos analyte contained is 0.0206 mg/Kg. This value has not passed the MLR that the European Food Safety Authority [26] ie 0.2 mg/Kg. In other rice samples, no pesticide residue analytes were detected, and the results of the calculation of the %Recovery of each analyte in the spiked sample ranged from 80-101%, which indicated that the pesticide residue analysis carried out had good accuracy (70-120%) in indicating the level of suitability of a product. Measurement with the true value. Rice samples from Aceh Province were also studied by Fahmi (2021) showed that the pesticide analyte of Bifenthrin type was detected at 0.0442 mg/Kg in rice samples from the Tangse area, Kab. Pidie uses the GC-ECD method [29]. Dichlorvos analyte was detected at a concentration of 0.04 – 0.37 mg/kg for all rice samples in the Ondo State area of Nigeria GC-MS method [30]. There are several methods to reduce post-harvest pesticide residues, namely by washing or soaking with hot water on agricultural products [31, 32]. Research by Amirahmadi (2017) reported that the content of pesticide residues in rice can be reduced after cooking with the percentage reduction values of Dichlorvos 99.8% analyte, 55-60% Dimethoate, and 50-55% λ-Cyhalothrin [13].

4. Conclusions

The results of the validation method on analytes of pesticide residues of Dichlorvos, Dimethoate, Bifenthrin, and λ-Cyhalothrin showed good results, namely providing good linearity in various ranges, with a coefficient of determination that was on average 0.98. The LOD values ranged from 0.013 to 0.017 mg/kg, while the LOQ ranged from 0.022 to 0.079 mg/kg. The results of precision and reproducibility (% RSD, n = 6) show the values of 0.56 - 1.26 % and 1.14 - 2.19 %, respectively, and the accuracy value (%Recovery) shows the results of 99.71 - 101.84%, with an RSD value of 2.42 - 3.59%, meet the requirement of 20%. The analysis of the sample showed that sample A had a large %Recovery value in the Dichlorvos analyte, namely 139.10%, with the calculation that the Dichlorvos analyte contained 0.0268 mg/Kg. This value has not passed the MLR that has been set by the European Food Safety Authority, which is 0.2 mg/Kg. In the other rice samples, no pesticide residue analytes were detected, the calculated %Recovery of each analyte in the spiked sample ranged from 80-101%, indicating that the pesticide residue analysis performed had good accuracy (70-120%).

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