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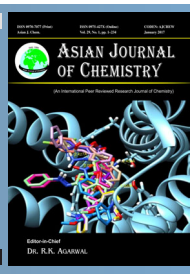

Development of Cypermethrin Pesticide Detection Method using Ultra Violet-Visible Spectrophotometry

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Cypermethrin is a pesticide that is widely used in agriculture of residue accumulation, which may remain in food causing concern of human health. The aim of this study was to develop a method of quantitative analysis for cypermethrin which generally used by gas chromatography technique. In this study, cypermethrin analysis was developed with ultra violet-visible spectrophotometry. The method is based on hydrolysis of cypermethrin in alkaline solution to cyanide ion and reacts with iron(III) ions to form coloured complex compounds and the concentration of cypermethrin can be measured quantitatively with a spectrophotometer. Ferricyanide complex ions are formed by adding iron(III) chloride, then it is measured the absorption to determine of cypermethrin concentration. In this experiments, maximum wavelength absorption was obtained at 420 nm and the method has a working range of concentration from 0.076 to 1.60 ppm with $r \geq 0.9998$. Limits of detection and limits of quantitation are 0.023 and 0.076 ppm, respectively. Based on accuracy and precision analysis, this methods can be used accurately and have good precision with value of recovery tested is 101.10 % and RSD is 0.25 %.

Keywords: Cypermethrin pesticide, Analysis, Ultra violet-visible spectrophotometry.

INTRODUCTION

Prior to about 1940, pesticides were primarily inorganic chemicals and a few natural agents derived from plant origin (*e.g.*, pyrethrum). After the discovery of the insecticidal activity of dichlorodiphenyl trichloroethane (DDT), the development of synthetic organic compounds increases in its use. Since 1940 to 1980, increasing in the production and use of synthetic pesticides was evident worldwide. Most of the pesticides used in the world is herbicide form but insecticide is widely applied in households [1].

Pyrethroid insecticides such a poison that can affect nerve fibers are often used in household. The compounds that included to pyrethroid group are metoflutrin, transflutrin, fenotrin, cyhalothrin, permethrin, cypermethrin, deltamethrin and etofenproks. Cypermethrin is an organic compound naturally produced by pyrethrum flowers (*Chrysanthemum cinerariaefolium* and *C. coccineum*). Cypermethrin or [cyano-(3-phenoxyphenyl)-methyl]3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate is a pesticide still used in agriculture in several countries including Indonesia [2-4]. Cypermethrin is one of the most active pyrethroids because its cyclopropane ring cypermethrin has two geometric isomers (*cis*- and *trans*-cypermethrin). Cypermethrin is stable to light in solid form but sensitive in solutions form [5].

The levels range of pesticide residues in vegetables was founded in sipermetrin onion samples of 98.8 to 245.6 ppb [6] and also founded in chili samples of 0.16 to 1.48 mg/kg [7,8]. Levels of pesticide residues that exceed the minimum residue limits (MRL) due to very excessive use of pesticides and it is very harmful to the environment, especially for human health. Analysis of pesticide residues can be done by various methods which the determination of gas chromatography is a technique that most often used for the analysis of pesticides. Measurement pesticide can also using high performance liquid chromatography (HPLC) [9-11], Fourier transform infrared (FTIR) [12] and biosensors [13]. These methods have some disadvantage such as the analyzed samples must go through a long process, takes a long time, complicated preparation in analyzing and its required significant costs. Therefore, need to be developed a new method that can be recommended.

Cypermethrin can be hydrolyzed using a base to form phenoxy benzene and release cyanide ions [14]. In subsequent studies, cypermethrin analyzed using spectrophotometric method with UV-visible by reaction of cyanide ion which released from the hydrolysis reaction of cypermethrin with potassium iodide and leuco malachite green and that is working at concentration range of 0.12 to 0.68 ppm [15]. To develop the analysis method of cypermethrin has a wider range of concentration with detection limits are small. This research

proposed a new method with complexing different by reaction of cyanide ion with ions of iron(III) which can form complex compounds ferricyanide coloured yellow. Stability of ions complex is very stable such as hexacyanoferrate(III) ion is not so easy to get back into iron(III) and cyanide ions [16]. Ferricyanide ions can be detected by measuring light absorption at a wavelength of 420 nm [17]. Therefore, the light absorption can be measured by UV-visible spectrophotometer to determine the levels of cypermethrin.

EXPERIMENTAL

Ethanol p.a, standard solution of cypermethrin (100 ppm), sodium hydroxide solution (20 %), iron(III) chloride solution (0.1 M), potassium chloride solution (0.1 M), pH 7 phosphate buffer, distilled water and chili samples from Konda, South Konawe, Southeast Sulawesi.

A UV-visible spectrophotometer (Jasco V-380) and equipped 1 cm path length quartz cell were used for UV-visible spectra and rotary vacuum evaporator (Butchi) with vacuum pump (V-700).

Sample preparation: Chili samples (50 g) and ethanol p.a. grade (96 %) (200 mL) were mixed for 2 min to homogeneous slurry form. The waste is filtered and rinsed with ethanol (50 mL) 2 times. Filtrate was collected and evaporated up to ± 20 mL then put in a 50 mL flask followed by adding ethanol.

Preparation of cypermethrin standard solution: Series cypermethrin concentration standard solution prepared by pipette cypermethrin 10 ppm as much as 0.1 to 15.0 mL, put into 50 mL volumetric flask. Afterwards, 1 mL of sodium hydroxide solution (20 %) was added, followed by 10 mL of phosphate buffer solution at pH 7; 1 mL of $FeCl_3$ solution (0.1 M); 5 mL of KCl solution (0.1 M) and distilled water.

Preparation of accuracy test solution: Pipette sample solution by 5 mL and put into each 50 mL to 4 different flask. Cypermethrin solution (10 ppm) was added of 4 mL in flask 1; 5 mL in flask 2; 6 mL in flask 3; and without the addition in the flask 4. After that, added 1 mL of sodium hydroxide solution (20 %) followed by adding 10 mL of phosphate buffer solution at pH 7; 1 mL of $FeCl_3$ solution (0.1 M); 5 mL of KCl solution (0.1 M) and distilled water.

RESULTS AND DISCUSSION

Maximum wavelength absorption: Fig. 1 shows the maximum absorption was obtained at a wavelength of 420 nm for 5 times measurement. Possibilities of absorption in the visible region was generated by electronic transitions of d orbitals in metal when the electrons of *d* orbitals in iron(III) ion interacting with a cyanide ion ligands to form a covalent bond coordination.

Linearity, limits of detection and limits of quantitation: Linearity of data was obtained by regression equation which plotting the absorbance of cypermethrin standard solution. Value of slope is 0.3079 ± 0.0026 and intercept value is 0.0245 ± 0.0021 in order to obtain the regression equation y = 0.3079 x ± 0.0245 with r ≥ 0.9998 (Fig. 2). Based on literature, linearity with correlation coefficient r > 0.995 is having a good linearity qualify.

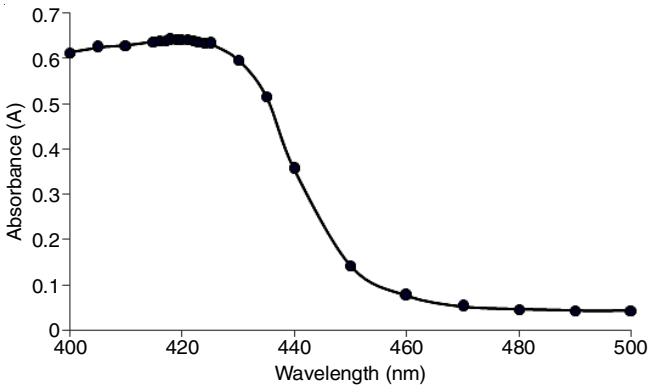

Fig. 1. Absorption spectra of compound formed by reaction hydrolysis of cypermethrin compound with iron(III) ion

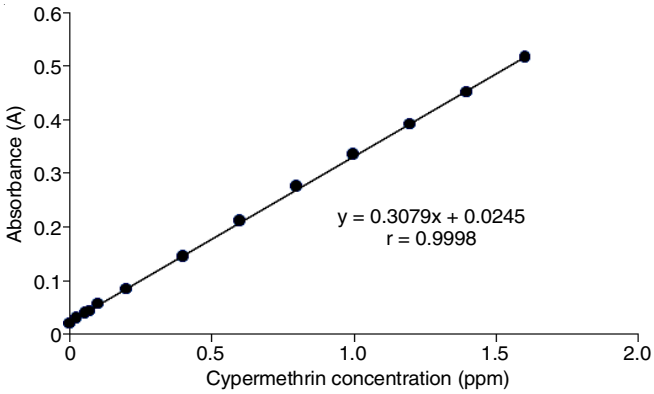

Fig. 2. Calibration curves of series cypermethrin standard solution

Limits of detection and limits of quantitation can be determined from the line of linearity test where these values are 0.023 and 0.076 ppm, respectively. It was obtained by regression data analysis. Limits of detection is the smallest concentration of analytes that can be detected by statistical measurements and its still can be reliable while limits of quantitation is the smallest concentration of analyte that can be measured [18,19]. Due to limit of quantitation is 0.076 ppm, the method of analysis in this study has a working concentration range of 0.076 ppm to 1.60 ppm. Under these values, the concentration of the sample can be concentrated while the value of concentrations above 1.6 ppm can be diluted with specific dilution factors, so its be able to included in working concentration range. Fig. 2 shows the curves obeys Beer's Law at concentration range of 0.076-1.6 ppm with r ≥ 0.9998.

Accuracy: Accuracy test is done by using the recovery of spiked sample or standard additions means. Sample to be analyzed was added a certain amount of analyte concentration. This method was carried out to determine of % recovery by percentage of analyte that was added previously to be found. The average percent recovery and standard deviation values were found to be 101.10 % and 1.28, respectively. Per cent recovery value was indicated may be acceptable due to the requisite accuracy was included range of 80-110 % while value of RSD < 2 %. Relative standard deviation (RSD) is one of the requirements of accuracy test where value of RSD in this experiment was found to be 1.27 %, hence the accuracy of test data can be received. Therefore, overall of the accuracy test requirements are acceptable due to fulfil the specified

requirements. Accuracy test data by recovery method can be seen in Table-1.

TABLE-1
ACCURACY TEST DATA

Sample concentration (ppm)	Analyte concentration added (ppm)	Total measured concentrations (ppm)	Recovery (%)
0.089	0.800	0.882	99.15
		0.882	99.15
		0.888	99.97
	1.000	1.106	101.74
		1.109	102.06
		1.109	102.06
	1.200	1.311	101.83
		1.314	102.10
		1.311	101.83
		Recovery	101.10 %
		SD	1.28
		RSD	1.27 %

Precision: Precision is defined as the degree of agreement between replicate measurements of the same quantity and can be expressed as the standard deviation, the coefficient of variation, the range of data or as a confidence interval about the mean value [20]. Precision repeatability can be determined at the time of the analysis carried out using equipment in the laboratory and be done in one day. For determination of precise repeatability, at least 6 independent analysis of three levels of concentration to do (80 %, 100 % and 120 % of the target concentration). RSD value acceptance criteria of precision test is < 2 % (repeatability, n ≥ 6). Precision data of repeatability test can be seen in Table-2. Average value of RSD in Table-2 is 0.19 % ($p < 0.05$) at concentration of 1.2 ppm and standard deviation is 0.0027 ($p < 0.05$). However, increasing of RSD values occurred when concentrations is smaller, which is 0.24 % at 1.0 ppm and 0.32 % at 0.8 ppm. It shows the smaller of concentration makes precision will decrease due to changes of signal absorbance form in small concentrations resulted in changes large enough concentrations when compared with the actual concentration. Based on the value of RSD of three levels of concentration solution with value of RSD < 2 %, overall of the precision test can be accepted due to fulfil the requirements set.

TABLE-2
PRECISION TEST DATA

Measurement	Concentration		
	0.80 ppm	1.00 ppm	1.20 ppm
1	0.8169	1.0053	1.1970
2	0.8137	1.0086	1.1937
3	0.8169	1.0053	1.1905
4	0.8137	1.0086	1.1937
5	0.8202	1.0021	1.1937
6	0.8169	1.0086	1.1937
7	0.8202	1.0053	1.1970
SD	0.0027	0.0025	0.0022
RSD	0.32 %	0.24 %	0.19 %
Mean of RSD = 0.25 %			

Conclusion

Analysis of cypermethrin detection method using UV-visible spectrophotometry has a working range of concentration from 0.076 to 1.60 ppm with the regression equation $y = 0.3079 x \pm 0.0245$ and $r \geq 0.9998$. Limits of detection and limits of quantitation are 0.023 ppm and 0.076 ppm, respectively. Based on accuracy, precision and selectivity data, this methods can be used accurately and have good precision with value of recovery tested is 101.10 % and RSD values is 0.25 %.

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