Advanced Science Letters
Vol. 23, 12016–12019, 2017

Analysis of Cypermethrin Using an Electrode Solid Copper Amalgams Developed as a Working Electrode in Differential Pulse Voltammetry Compared with Gas Chromatography Methods

Pirim Setiarso* and I. Gusti Made Sanjaya

Department of Chemistry, Faculty of Mathematical and Natural Science, State University of Surabaya, Surabaya 60231, Indonesia

Cypermethrin determination has been conducted for agricultural soil samples of some districts in Nganjuk, East Java, using an electrode solid copper amalgams (CuSAE) in differential pulse voltammetry (DPV) compared with gas chromatographic (GC) methods. 100 g sample of agricultural soil which is smoothed with a size of 100 mesh, were extracted using 100 ml of acetone. Extraction is performed using extractor soxhlet with 10 times circulations. Most of the extraction is added with SDS surfactant for voltammetric analysis using CuSAE as the working electrode, Pt as the auxiliary electrode, and Ag/AgCl as the reference electrode. Partly the result of extraction were analyzed using GC. Voltammetry analysis carried out at pH 8 with supporting electrolyte $CaCl_2$ using a standard addition, while the chromatographic analysis using a standard graph. Based on voltammogram and chromatogram data which have been processed with origin 7.0 program generates a recovery of the average of cypermethrin determination with DPV is $(96.04 \pm 2.4336)\%$ and GC is $(100.77 \pm 4.5076)\%$. Comparison of DPV and GC methods performed by t-test result (t calculated $= 0.6529 < t$ table $= 2.31$). There is no difference between the two methods for the analysis of cypermethrin.

Keywords: DPV, Voltammetry, GC, Chromatography, Cypermethrin.

1. INTRODUCTION

Pesticide analysis of various samples like in water or living organism generally performed using chromatographic techniques, such as gas chromatography, high performance liquid chromatography, and gas chromatography coupled with mass spectroscopy.[1] Another technique of pesticide analysis is using biosensor based on enzyme linked immunosorbent assay, ELISA, used to monitor pesticides in the environment.[4] Gankin (1995) has conducted an analysis of pesticide using a column chromatographic containing an XAD-2resin, followed by GC-MS techniques to determine pesticide compounds in water and aquatic animal of Catfish.

Analysis of pesticides is necessary to monitor its presence in the environment, which can be toxic to living things if the threshold exceeds the allowable limit.[6] Threshold of allowable pesticides on the environment, is different in various countries. For example, Brazilian National Council for the Environment have a threshold 50 $\mu g \cdot L^{(-1)}$ on the waste water, while the Environmental Protection Agency of the United States certified 10 $\mu g \cdot L^{(-1)}$ in natural water.[10] Indonesia provides 2 $mg \cdot L^{(-1)}$ for pesticides threshold.

Pesticides analysis by HPLC and GC is used relatively frequently compared to spectrometry and electrometry techniques.[12] Pesticides analysis using GC is considered fast and requires only a sample of size in μL dimension, especially when used GC-MS equipped with a catalog of compounds, the type and molecular structures of pesticides can be determined in a one-time execution.

In chromatographic analysis, samples are treated physically and chemically in order for the samples can be read by chromatography. Physical treatment is not complicated but the chemical treatment may be very complicated because through several steps such as extraction, distillation, complexation, or created derivatives that can be read by the detectors used in chromatography equipment. Each step is certainly has errors, thus resulting in accumulation of errors in the overall analysis process. It was not expected to occur in the analysis by voltammetry method because it has a job step that is not as complicated as the steps above. Measurements can be done directly so it does not required a lot of chemical reagents, cheaper, and with a detection limit of the same or even better.

On this occasion, is conducted research on pesticides analysis by voltammetry using copper solid amalgam electrode (CuSAE)

---

*Author to whom correspondence should be addressed.

1936-6612/2017/23/12016/004 doi:10.1166/asl.2017.10564

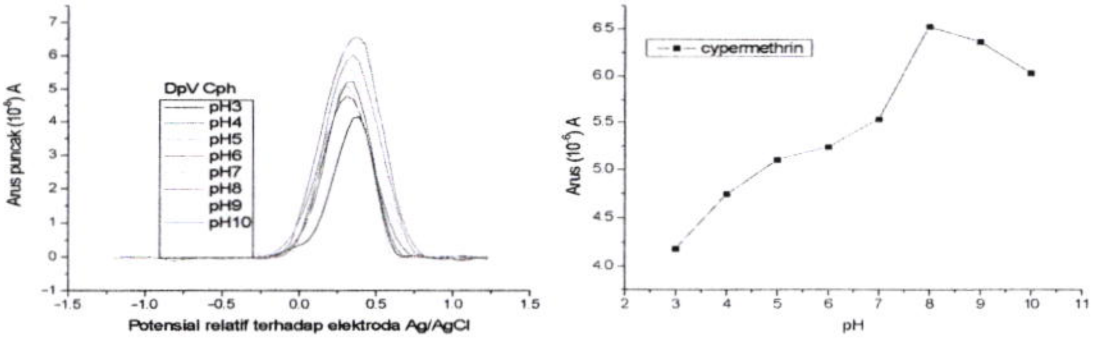

Fig. 1. Voltammogram of DPV of 10^{-5} M cypermethrin to the pH (3–10).

is made simpler than the previous CuSAE. Electrodes that had been used earlier were made by mixing powders of copper and mercury. Copper and mercury mixture is heated at a temperature 80 °C in an atmosphere of sulfuric acid to form amalgams.

Based on preliminary research, is revealed that the formation of amalgam of the above mixture is not perfect. It is evident that there was still some copper metal which does not form amalgam. In addition, color of the mixture remains black which estimated from the oxide of mercury and copper. Physically, the amalgam resulting does not adhere well to the electrode. This will affect the electrode response to the analyte.[5] The amalgam electrode CuHg in this research was made of copper wire that has undergone the process of electro-deposition using a solution of 0.1 M $CuSO_4$ with time variation. Conductor of copper wires that have been deposited with Cu, then formed amalgam using a saturated solution of $Hg(NO_3)_2$. This method is expected to be simpler and faster.

CuSAE product is chemically characterized to analyze the pesticide cypermthrin of the pyrethroid group with voltammetry. Cypermethrin pesticide was chosen as a sample on the grounds that pesticides are used widely in agricultural pest control in Indonesia. Therefore, the use of pesticides need supervision, so that the residue does not pollute the environment and agriculture. In the final stage, the working electrode of the best CuSAE will be tested for pesticide residue analysis at real samples in the area of agriculture.

2. METHODS

2.1. Materials

Materials used in this research are: acetone, cypermethrin, SDS 98%, $CaCl_2$, $Hg(NO_3)_2$, $CuSO_4$ 0.1 M, conductor wire with a length of 4.0 cm and a diameter of 1.2 mm, buffer Briton Robinson, agricultural soil samples, and distilled water.

2.2. Instrumentation

Instruments used in this research are epsilon potentiostat, Gas Chromatography, soxhlet extractor, Buchi evaporator, Ag/AgCl reference electrode, Pt electrode, CuSAE working electrode.

2.3. Procedure

CuSAE made of conductive wire with a length of 4 cm and diameter of 1.2 mm which is electro-deposited with Cu using a solution of $CuSO_4$ 0.1 M for 25 seconds by control potential electrolysis at a potential of 400 mV and the current 100 μA. This was made amalgam by dipping into a saturated solution of $Hg(NO_3)_2$ for 1 minute.

Optimization of CuSAE with cypermethrin was performed by differential pulse voltammetry. Sample of pesticide is taken from the extraction of 100 g of agricultural soil with size of 100 meshes which was added 20 ml cypermethrin 10^{-3} M in acetone.

Cypermethrin analysis of agricultural soil extraction is done by DPV using standard addition method.[8] In the analysis are used

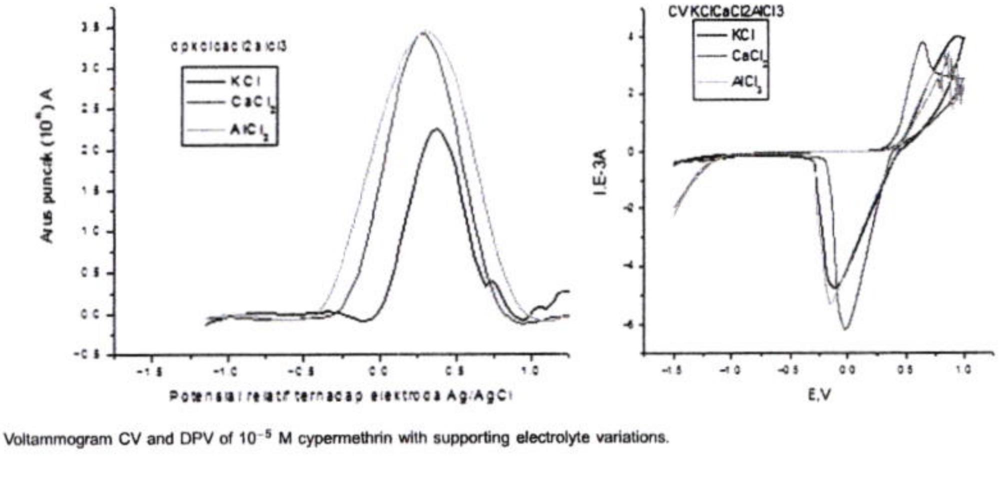

Fig. 2. Voltammogram CV and DPV of 10^{-5} M cypermethrin with supporting electrolyte variations.

Table I. Regression equation of cypermethrin on the variation of concentration and pH.

pH	Regression equation	*R*
3	$Y = 4.462667 + 1.449333X$	0.989189
4	$Y = 0.33 + 2.301636X$	0.995727
5	$Y = 3.022 + 2.226182X$	0.986618
6	$Y = 1.801333 + 1.481212X$	0.980681
7	$Y = 0.852 + 2.121636X$	0.991685
8	$Y = -4.402667 + 4.128848X$	0.997103
9	$Y = -1.597333 + 3.834242X$	0.990784
10	$Y = 1.050667 + 2.243152X$	0.989728

Table II. The peaks current of DPV of 10^{-5} M cypermethrin on the supporting electrolyte variations.

Electrolyte	Current 10^{-6} (A)
KCl	2.25
$CaCl_2$	3.40
$AlCl_3$	3.46

Table III. The regression equation of standard addition of cypermethrin from Nganjuk agricultural soil samples.

Location	Regression equation	Concentration (10^{-5}) M	Recovery (%)
Kuncir	$Y = 2.253625 + 6.568695X$	3.354	95.8
Loceret	$Y = 0.143653 + 0.878998X$	3.268	93.4
Pace	$Y = 0.789447 + 0.723448X$	3.274	93.5
Rejoso	$Y = 1.008361 + 0.869223X$	3.488	99.6
WaruJayeng	$Y = 0.135547 + 1.186282X$	3.428	97.9

Briton Robinson buffer pH 8, the supporting electrolyte 10^{-3} M $CaCl_2$, and SDS 10^{-2} M. The conditions of ephsilon potentiostat instrument on analysis of cypermethrin are the potential range (−400–400) mV, potential step 4 mV/s, amplitude 50, the current 100 μA, CuSAE as working electrode, Ag/AgCl as reference electrode, and Pt as auxiliary electrode.

Validation of cypermethrin analysis of the extraction of agricultural soil that is done by DPV is compared with the result of GC. The condition of GC in the analysis of cypermethrin are Ar-air carrier gas, Flow rate 1 ml/minute, injection volume of 20 μl, RP 18 column type, length 20 cm, diameter 0.4 mm, the injection temperature of 275 °C, column temperature of 250 °C, and FID detector.

3. RESULTS AND DISCUSSION

Optimization of CuSAE on cypermetrin for a variety of pH is done by making solutions of cypermethrin 10^{-5} M with pH (3–10). Here is the resulting voltammogram.

Based on the voltammogram, pH 8 gave the highest current that was chosen as the working pH. To support that statement, consider the table of the following regression equation.

Data in Table I supports the pH 8 as working pH for cypermethrin because it gives the highest peak of correlation coefficient.

Supporting electrolyte which selected to be used in measurements of cypermethrin are KCl, $CaCl_2$, and $AlCl_3$. The following figures show the voltammogram of CV and DPV respectively.

The resulting of peaks current of DPV on the supporting electrolyte variations can be seen in the following Table II.

The peak current of DPV of the supporting electrolyte $CaCl_2$ was chosen because it gives the best voltammogram for DPV and CV.

Validation of cypermethrin analysis was performed with voltammetry and then compared to the chromatography. Validation is performed as is done within cypermethrin by using standard addition.[7,9]

Agricultural soil samples were taken from five districts in Nganjuk Regency, East Java. 100 g mashed agricultural soil plus 20 ml cypermethrin 10^{-3} M extracted in soxlet using 100 ml acetone at temperatures of 80 °C. Extraction is performed 10 times. The result of extraction is evaporated and added 5 ml Brinton Robinson buffer solution, 2 ml of SDS surfactant 10^{-1} M. The result is further deluted to 20 ml and used to determine the concentration of cypermethrin with DPV. In Figure 3 is shown one of voltammograms from the standart addition curve of cypermethrin.

The concentration of cypermethrin which determined is 3.5×10^{-5} M. In Table III, indicated cypermethrin recovery from the extraction of the samples of agricultural soil from Nganjuk, East Java.

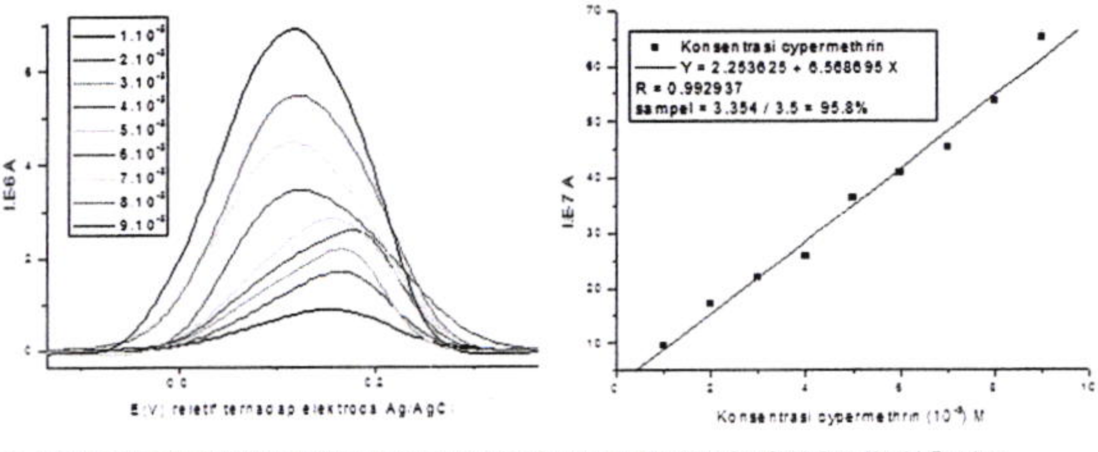

Fig. 3. DPV voltammograms and standard addition curve of cypermethrin of agricultural soil samples from Distric Pace, Nganjuk East Java.

Fig. 4. Cypermethrin chromatograms standard.

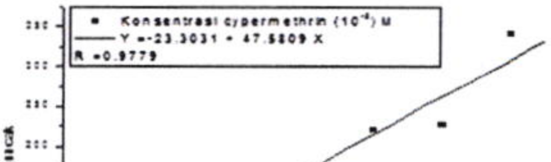

Fig. 5. Standard curve of cypermethrin.

The result of cypermethrin analysis with DPV are compared with the results of the analysis by GC. Standard chromatograms of cypermethrinis shown in Figure 4. From the chromatograms in Figure 4 can be made the following standard curve. Standard curve in Figure 5 is used to determine the concentrations of cypermethrin which extracted of agricultural soil samples from several districts of Nganjuk, East Java. The result of the determination of cypermethrin concentrations can be seen in Table IV.

Table IV. Concentration of cypermethrin which extracted of agricultural soil samples from Nganjuk, East Java.

Location	Concentration (10^{-5}) M	Recovery (%)
Kuncir	2.389	95.58
Loceret	2.586	103.46
Pace	2.380	95.20
Rejoso	2.586	103.46
WaruJayeng	2.654	106.17

Results of the determination cypermethrin concentrations on Tables III and IV were evaluated statisticaly with t-test to find out that both results significantly different. Based on the result of t-count 0.6529 which smaller than t-table 2.31 for the number of degrees of freedom 8 and $P = 0.05$, then it can be said determination of cypermethrin concentrations which extracted from the agricultural soil samples from several district in Nganjuk determined using voltammetry method DPV and GC method, is not statistically different.

4. CONCLUSIONS

The working pH and supporting electrolyte for cypermethrin analysis is pH 8 and $CaCl_2$. There is no significant difference between cypermethrin determination using DPV method and GC method, which is shown by using the t-test (t-count $= 0.6529 <$ t-table $= 2.31$).

References and Notes

1. H. R. Buser and M. D. Muller, *Anal. Chem.* 67, 2691 **(1995)**.
2. B. O. Dos Santos Luciana, G. Abate, and J. C. Masini, *J. Braz. Chem. Soc.* 17, 36 **(2006)**.
3. Y. V. Gankin, A. E. Gorshteyn, and A. Robbat, *Anal. Chem.* 67, 2548 **(1995)**.
4. J. L. Marty, B. Leca, and T. Noguer, *Analusis Magazine* 26, 144 **(1998)**.
5. Ø. Mikkelsen and K. H. Schrøder, *Electroanalysis* 15, 679 **(2003)**.
6. A. Mulchandani, P. Mulchandani, I. Kaneva, and W. Chen, *Biosens. Bioelectron.* 14, 77 **(1999)**.
7. H. C. Oudu, R. M. Alonso, and H. C. Bruun Hansen, *AnalyticaChemicaActa* 523, 69 **(2004)**.
8. C. G. Pinto, J. L. P. Pavon, and B. M. Cordero, *Anal. Chem.* 67, 2606 **(1995)**.
9. I. P. Rivas, M. E. Gil-Aegne, and A. I. Torres-Suarez, *AnalytcaChemicaActa* 557, 245 **(2006)**.
10. D. D. Souza, S. A. Machado, and R. C. Pires, *Talanta* 69, 1200 **(2006)**.
11. D. D. Souza, R. A. de Toledo, and A. L. Galli, *Anal. BioanalChem.* 387, 2245 **(2007)**.
12. R. F. Teofilo, E. L. Reis, C. Reis, G. A. da Silva, and L. T. Kubota, *J. Braz. Chem. Soc.* 15, 865 **(2004)**.

Received: 10 August 2016. Accepted: 15 May 2017.