Spectrophotometric determination of deltamethrine in pure and environmental samples

Ali Mahmood and Sumayya Muhammad
Baghdad university Ibn-AL-Haitham collage for pure and applied science

Email: sumayham@gmail.com

Abstract. An accurate and sensitive spectrophotometric method has been developed for the determination of deltamethrine (DLM) [(S)-Cyano-(3-phenoxyphenyl)-methyl] 3-(2, 2-dibromoethenyl)-2, 2-dimethyl-cyclopropane-1-carboxylate by reduction of 2, 3, 5-triphenyltetrazolium (TET) by cyanide ion yield from methanolic alkaline hydrolysis of DLM and subsequent react with p-nitrobenzyldehyde to form a good reduction agent for TET to yield the formazan has maximum absorption at 483 nm. Maximum colour absorption was attained in 15 min in the presence of 0.5 N NaOH. In addition to the considerably high values of the molar absorptivity of the chromogen formed, ideal adherence of the colour absorption to the Beer-Lambert law permitted a sensitive micro and nano determination of DLM in both pure and environmental samples. The Beer’s law was obeyed over the concentration range of (0.1-3) µg mL⁻¹. The analytical parameters were evaluated in the proposed method and have been successfully applied for the determination of DLM in its formulations and environmental samples. The aim of this study is it to develop rapid sensitive analytical method to evaluate the micrograms of DLM in various samples.

Key word: deltamethrine, spectrophotometric determination, tetrazolium, cyanide ion

1. Introduction

Pyrethroid pesticides are toxic to man and animals, carcinogenic to human and exert genotoxic, mutagenic and embryo toxic effects. The use of Pyrethroid insecticides is increasing for agriculture, commercial pest control [1]. The concern for human and animal food has become very important lately, especially after the huge population explosion, there is an urgent need to increase food resources and improve their quality. This is not successful with the presence of agricultural pests. The use of agricultural pesticides has spread to eliminate agricultural pests, the increase in these pesticides negatively affects the health of living organisms, especially human, and so there must be a balance between the abundant productivity and the process of consumption of pesticides. Several studies have shown that the residues of pesticides in the soil is a key factor for food contamination and biological chains [2]. DLM destroy insects on contact and through digestion. The Delta destroys insects by paralyzing its nervous system. It has a wide range in eliminating insect caterpillars that infect apples, pears, and for the control of bugs, crustaceans and white flies that infect vegetables in greenhouses and tomatoes as well as ornamental plants [3]. Several technique found to estimate various types of pesticide spatially with high performance liquid chromatography [4-7], Mass spectrophotometric [9],
GC-MASS technique[10-11] Spectrophotometric studied still the simpler, cheap and favourable technique to evaluate pesticide and There are many studies conducted using this technique[12-13]

Scheme1. The chemical structure of the deltamethrine

2. Experimental
2.1. Apparatus
Absorption measurements were made by spectrophotometer Shimadzu (UV-160A) in 1cm optical quartz

2.2. Chemicals
Chemical reagents used were of analytical grade. DLM (provided from Ministry of Agriculture \ Plant Protection Department \ National Centre for Pesticide Control) Solution (100ppm) was prepared by dissolving 0.05 g with methanol and diluted to 500 ml in calibrated flask then stored in amber coloured bottle and kept in refrigerator. The solution were diluted as needed. P- nitrobenzaldehyde (0.066M) was prepared by dissolving 1g with 100 ml methanol. Tetrazolium (1.97×10⁻⁴M) was attended by dissolving .0066g in 10 mL of methanol and diluted to the mark in a 100 volumetric flask with the same solvent. Sodium hydroxide (0.5M) was prepared by dissolving 2 g of sodium hydroxide in methanol and diluted to 100 ml in calibrated flask.

2.3. Recommended procedures
Different aliquots (0.05-1.6) mL equivalents to (0.1-3) ppm for DLM (100 µg mL⁻¹) was transferred into a series of calibrated flasks by means of a micro burette and the total volume was adjusted to 5.0 mL. To each flask, 0.3 mL of 0.5 M NaOH was treated to hydrolysed and release cyanide ion, the flasks were stoppered and the contents were mixed for 5 min then 1 mL of para nitrobenzaldehyde was added. Finally one mL tetrazolium was added and mixed well, the volume was diluted to the mark with methanol. The colour intensity of reduced tetrazolium was measured after 15.0 min against reagent blank solution treated similarly at their corresponding λmax 481nm.

2.4. Procedure for formulations
1- Solid formulation (raid)
Weight 0.5 g (0.05g\100 g) dissolved with 10 ml methanol and separate the insoluble mater by filter paper then complete the solution to the mark with same solvent to prepare 10µ g DLM and complete the procedure.

2- Solution formulation
A volume of 1 mL of deltamethrine formulation (2.5 g\100 mL), equivalent to 25mg of DLM placed in volumetric flask of 25ml with methanol to prepper stock solution of 1000 µg. The DLM was determined by the aforesaid procedures by taken a proper dilution from the stock solution.

2.5. Procedure for water sample
Applied the suggested procedure on determination of DLM in water sample done with 20 mL of tap water. To avoid the interferences from other ions in the sample, 1 mL of EDTA (0.1g\25 mL in methanol) was added to mask various metal ions. The sample spiked with 1 mL of 1000 ppm DLM then complete the volume to the mark with water. With 35 mL of ethyl acetate (7 time x 5 mL) extract DLM was done then evaporate the solvent on water bath at 50°C. , The residue was dissolved in 10 mL methanol then the volume of the extract was made up to the mark with methanol in 25mL calibrated flask. The solution was analysed as described above.
2.6. Procedure for soil sample
A known weight of 2.5 g well-powdered soil sample spiked with 1 mL of 1000ppm deltamethrine mixed and stirring well. The deltamethrine extract with 25 mL (5 time 5mL) methanol then filtered using Whitman filter paper and made up to 25mL with the same solvent.

3. Result and Discussion

3.1 Spectral characteristic
The method involved methanolic basic hydrolysis of DLM to release free cyanide. The cyanide anion react with p-nitrobenzyldehyed in alcoholic sodium hydroxide to form cyanohydrin which reduce the tetrazolium to yield pale orange colour formazan having $\lambda_{\text{max}}$ at 480 nm. The reagent blank has practically no absorbance at 480 nm as shown in Figure 1. The formation of coloured formazan with the reagents was shown in Scheme 2.

Figure (1) absorption spectra of reduced TETR with 2µ g of DLM

Scheme (2) reduction bath way of tetrazolium by cyanide ion
3.2. Optimization study
Hydrolysis of DLM to release free cyanide was studied at different alkalinity. It was showed that alkaline conditions must require for the complete hydrolysis. Maximum hydrolysis was observed with 0.3 mL sodium hydroxide at 5 min. However, the following optimum concentrations and volume ranges were needed for colour development. In the proposed methods, it was found that 1.0 mL of 1.0 % (w/v) p-nitrobenzyldelehyde was suitable for colour development to achieve the maximum intensity after 15 min (Figure 2) and what is worth to mention the study done at dark condition.

![Figure (2) effect of volume of NaOH (2%), volume of TET. (0.0066%) and volume of BENZ. (1%)](image)

3.3. Effect of foreign species
Study the interference effect from foreign ions commonly found with DLM were studied by adding known amounts of diverse ions to standard solution contained 2.0 μg DLM and 1 ml of (0.1 g in 25 ml) EDTA in 5 mL of final solution then analysed by the proposed method. The results shows that the excipients don't interfere in the determination of DLM in tolerance limit less than 10 ppm (Table 1).

| Cationic species | Relative error |
|-----------------|---------------|
| Na⁺1 | -1.500 |
| Ca²⁺ | 1.500 |
| Ba²⁺ | 0.000 |
| NO₃⁻ | -2.500 |
| SO₄²⁻ | -3.000 |
| Cl⁻ | 1.500 |
| CO₃⁻ | -1.500 |

3.4 Calibration curves and analytical data
Employing the best condition, the absorbance of formazan at 483nm versus different standard concentration of DLM was done. The linearity of the obtained plot of the DLM was in the concentration range (0.1-3) μg.mL⁻¹ as shown in Figure (3). The statistical treatment of the analytical data are summarized in Table (2).
Figure 3. Regression equation of proposed method

Table 2. Optical characteristics and statistical data

| Parameter                                | Value          |
|------------------------------------------|----------------|
| \( \lambda_{\text{max}} \) (nm)         | 482            |
| concentration (µg mL\(^{-1}\))           | 0.2-3          |
| Molar absorptivity L. mol\(^{-1}\) cm\(^{-1}\) | 26563          |
| Saddle sensitivity                       | 0.01903        |
| Regression equation                      | 0.0526x+0.0442 |
| slop                                     | 0.0526         |
| Correlation Coefficient (r)              | 0.9993         |
| Relative Standard Deviation (RSD %)       | 0.0016         |
| Detection limit µg mL\(^{-1}\) *         | 0.040          |
| Limit value µg mL\(^{-1}\) *             | 0.400          |
| colour                                   | Pale orang     |

*LOQ = 10s / b  
* LOD = 3.3s / b

3.5. Applications
The method apply to determination DLM in formulations (Table 3), soil, water samples and recovery of standard addition method (Table4)

Table 3. Determination of insecticide DLM in its formulations.

| Formulation                  | µg | Recovery% ±SD | Reference method(3) |
|------------------------------|----|----------------|---------------------|
| Raid (0.05g %) (Jorden)      | 0.8| 93.7 ±0.020    | 96.4 ±0.8           |
|                              | 1.6| 93.7 ±0.025    |                     |
| Delta baz25 Ec (2.5g%)(Jorden)| 1.2| 97.9 ±0.080    |                     |

Table 4. Recovery of deltamethrine from soil and water samples

| sample | Added amount µg | Found amount µg | Recovery ±SD       |
|--------|-----------------|-----------------|-------------------|
| Tap water | 0.4          | 0.39            | 97.50±0.0350      |
|         | 0.8          | 0.73            | 91.25±0.0040      |
|         | 1.2          | 1.15            | 95.00±0.0050      |
|         | 0.4          | 0.4             | 100.0±0.0045      |
| soil   | 0.8          | 0.8             | 100.0±0.0055      |
|         | 1.2          | 1.17            | 97.50±0.0074      |
3.5.1 Standard addition
Standard addition method was applied to evaluate DLM in presence of different spescious to increase the insurance, the proposed spectrophotometric method was applied (weight 1 g from each : glucose , starch , acacia , magnesium setrate and lactose) mixed well and weight 0.01 g from the mixture dissolved in methanol and complete the volume to the mark with distilled water to 5mL volumetric flask). Following the standard addition technique. Good recovery(R 107%±S.D) of the drug present in studied sample indicates that no interference from the matrix affect the determination of DLM. Figure (10) shows the standard additions plot and Table (10) shows the result of recovery for the method.

![Figure 4. Standard addition plot applied to determination of 0.4µg of DLM](image)

3.5.2 Accuracy and precision
The precision and accuracy of the proposed method was tested by analysing five replicate samples of DLM in three different levels (within Beer's law range). The result listed in Table (5) indicates an acceptable accuracy and precision to suggested work.

| Taken(µg/ml)* | Recovery % | Precision(RSD %) | Accuracy R.E% |
|---------------|------------|------------------|---------------|
| 1             | 98         | 2.3×10⁻²         | -3            |
| 2             | 98         | 3.5×10⁻²         | -1            |
| 3             | 96         | 3×10⁻²           | -4.3          |

*Five replicate

CONCLUSION
The proposed method was found to be very simple, rapid, low cost and fairly selective than other method. The proposed method was applied to the analysis of DLM in pure, and can be used for the routine analysis of commercial formulations. The release of free cyanide ion from DLM and reaction with P-nitro benzaldehyde makes it possible for reduction TET in alkaline media then formation of formazan to give a light orange colour. The accuracy and precision of the proposed method were tested by analysing five replicate of DLM for three different concentrations, the values of RSD% and relative error Erel. % indicated good accuracy and precision.

References
[1 ] Alaa S Amin, Sayed MN Moalla, Mohammed SS Salama, Amani Ali, Ayman A Gouda, Spectrophotometric determination of dimethoate and deltamethrin insecticides in their formulations, environmental and biological samples using cerric (IV) ammonium sulfate, International Journal of Research in Pharmacy and Pharmaceutical Sciences. Volume 2; Issue 3; May 2017; Page No. 47-56
[2] Bangeppagari Manjunatha1,2*, G. Venkata Subba Reddy3, Juan Ortiz Tirado1, Patricia Falconi Salas1 and Darwin Rueda Ortiz1, Determination of residues of deltamethrin in water and liver tissue of Zebrafish (Danio rerio) by HPLC, Der Pharma Chemica, 2015, 7(7):149-152

[3] Alaa S. Amin ,Sayed M.N. Moalla , Amani Ali Mohammed, S. SalamaAyman A. Gouda , Sensitive Spectrophotometric Determination of Deltamethrin Insecticide in its Formulation and Environmental Samples, International Journal of Advanced Research in Chemical Science (IJARCS) Volume 2, Issue 10, October 2015, PP 72-79 ISSN 2349-039X (Print) & ISSN 2349-0403 (Online)

[4] Jaabiri, I., Belhaj, D., Turki, N., Kallel, M., Ayadi, H., Ksantini, M., Bouzid, J. and Gargouri, R., 2013. Development and method validation for determination of Deltamethrin residue in olive oil using a reversed-phase high performance liquid chromatography. IOSR Journal of Applied Chemistry, 6, pp.01-08.

[5] Chen, Z.M. and Wang, Y.H., 1996. Chromatographic methods for the determination of pyrethrin and pyrethroid pesticide residues in crops, foods and environmental samples. Journal of Chromatography A, 754(1-2), pp.367-395.

[6] Amvrazi, E.G. and Albanis, T.A., 2006. Multiresidue method for determination of 35 pesticides in virgin olive oil by using liquid–liquid extraction techniques coupled with solid-phase extraction clean up and gas chromatography with nitrogen phosphorus detection and electron capture detection. Journal of agricultural and food chemistry, 54(26), pp.9642-9651.

[7] Boonchiangma, S., Ngeontae, W. and Srijaranai, S., 2012. Determination of six pyrethroid insecticides in fruit juice samples using dispersive liquid–liquid microextraction combined with high performance liquid chromatography. Talanta, 88, pp.209-215.

[8] Li, A.J. and Kannan, K., 2018. Urinary concentrations and profiles of organophosphate and pyrethroid pesticide metabolites and phenoxyacid herbicides in populations in eight countries. Environment International.

[9] Wong, J.W., Wang, J., Zhang, K., Hayward, D.G., Yang, P. and Wittenberg, J.B., 2018. Pesticides: An Update on Mass Spectrometry Approaches.

[10] Mekircha, F., Chebab, S., Gabbianelli, R. and Leghouchi, E., 2018. The possible ameliorative effect of Olea europaea L. oil against deltamethrin-induced oxidative stress and alterations of serum concentrations of thyroid and reproductive hormones in adult female rats. Ecotoxicology and environmental safety, 161, pp.374-382.

[11] Rutkowska, E., Lozowicka, B. and Kaczyński, P., 2018. Three approaches to minimize matrix effects in residue analysis of multiclass pesticides in dried complex matrices using gas chromatography tandem mass spectrometry. Food Chemistry.

[12] Kumar, K.S., Swaroop, B.L., Suvardhan, K., Rekha, D., Jayaraj, B. and Chiranjeevi, P., 2006. Facile and sensitive spectrophotometric determination of synthetic pyrithroids in their formulations, water and grain samples. Environmental monitoring and assessment, 122(1-3), pp.1-8.

[13] Priya, B.K., Subrahmanyam, P., Dakshayani, K., Jayaraj, B. and Chiranjeevi, P., 2007. WITHDRAWN: Spectrophotometric determination of deltamethrin in its formulations and environmental samples.

[14] Kumar KS, Swaroop BL, Suvardhan K, Rekha D, Jayaraj B, Chiranjeevi P. Facile and sensitive spectrophotometric determination of synthetic pyrithroids in their formulations, water and grain samples. Environmental monitoring and assessment. 2006 Nov 1; 122(1-3):1-8.