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Flotation-Dissolution Based Spectrophotometric Determination of Ethion

VINDHIYA PATEL[1], RAISA KHATOON[1], MAMTA NIRMAL[1], KALPANA WANI[1], MANISH KUMAR RAI[1,*] and JOYCE RAI[2]

[1]School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur-492 010, India
[2]Chhattisgarh Council of Science and Technology, MIG 25, Indravati Colony, Raipur-492 007, India

*Corresponding author: E-mail: mkjk.chem@gmail.com

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A simple and sensitive extractive spectrophotometric determination of organophosphorus insecticide ethion at trace levels based on flotation-dissolution method is presented. A molydophospho complex is formed when ethion is treated with ammonium molybdate in acidic medium. As an ion associate complex with methylene blue, the complex is present in between water and organic layers which is extracted and then dissolved with acetone. The greenish blue complex produced showed an absorption maximum at 660 nm. Beer's law is found to be in the range of 0.5 to 0.16 µg/10 mL for ethion. The molar absorptivity is 6.0×10^5 mol L^{-1} cm^{-1} and Sandel's sensitivity is 0.014 µg cm^{-2}. The standard deviation and relative standard deviation were calculated and found to be 0.022 µg mL^{-1} and 3.5 %, respectively. The method has been applied sucessfully for the determination of ethion in water, soil, vegetables and grains.

Keywords: Ethion, Spectrophotometry, Flotation-dissolution method, Organophosphate insecticide.

INTRODUCTION

Ethion [O,O,O,O-tetraethyl-S,S-methylene *bis*(phosphorodithioate)] belongs to the organophosphate insecticide class and from 1965 was registered for use in United States [1]. The first evolved insecticide, non-systemic insecticide as well as acaricide used on fruit trees, specially nut trees, grapes and citrus fruits [2]. This insecticide was developed for use on cotton and seed and forage crops as well as a broad range of fruits and vegetables against non-systemic insecticides. Bugs, aphids, mites, thrips, grasshoppers, maggots, larvae, suckers and soil-dweller insects on a broad scale of food, fiberous and decorative crops, fruits, vegetables and nuts can be eliminated [3]. Ethion is extensively to moderately poisionous by the oral path, which could result in influenza-like condition alongwith headache, malaise, weakness, loss of appetite and nausea [4]. Exposure to excessive levels of ethion can result nausea, sweating, loss of bladder, diarrhea and nervous system disorders [5]. On root cells of plants ethion can also result in a mitodepressive effect causing chromosomal abnormality toxicity, can also reduce their fertility, pathogenic resistivity, *etc*. [6].

There are several methods reported using some advance and sophisticated equipments such as infrared spectrophotometric method [7], gas chromatography method [4] and high performance liquid chromatography [8]. But all these equipments are expensive and also require regular maintenance, so an alternative method is required and here is a flotation-dissolution method for the determination of ethion is reported.

EXPERIMENTAL

For all spectral analysis, Systronics UV-visible spectrophotometric model 104 with matched silica cells was used. pH meter model Thermofisher Orion star A211 was used for pH determination. For centrifugation Remi C-854/4 clinical centrifuge force of 1850 rpm with fixed swing out rotors was used.

Chemicals used were of Analytical Reagent grade. Demineralized water was used all over the experiment. Ethion (Swal Corporation Ltd., Mumbai) 1 mg mL^{-1} was prepared as stock solution. Ammonium molybdate A 0.05 mol L^{-1} was prepared in dilute (1.5 mol L^{-1}) sulfuric acid. Methylene blue 4×10^{-5} mol L^{-1} solution was prepared by dissolving 0.013 g of methylene blue in 100 mL of water. Solution of 0.10 mol L^{-1} oxalic acid was used.

Preparation of calibration graph: In 250 mL Erlenmeyer flask, 10 mL of aqueous solution consisting 0.5-16 µg of ethion was taken and 1 mL of 1.5 mol L^{-1} sulfuric acid was added in each concentration of solution and then ammonium molybdate solution 0.6 mL of 0.05 mol L^{-1} were added. Left for 20 min and then the solution was brought to room temperature. In order to eliminate excess of molybdate the mixture is treated with 0.5 mL volume of oxalic acid and the solution was placed into a 250 mL separating funnel. Add methylene blue solution

0.2 mL in volume and then extraction was carried out with 5 mL of butanol. The lower water soluble layer was discarded and the floating ion containing layer with 1 mL of organic phase was transposed to a graduated tube and to which 5 mL of acetone was added and dissolved and then the absorbance was measured at 660 nm against a reagent blank [9].

Determination of ethion in polluted water: The sample water was filtered through Whatman No. 40 filter paper and the filtrate was then makeup to 25 mL, then treated with 1 mL of 1.5 mol L^{-1} sulfuric acid in addition to 1 mL of 0.6 mL ammonium molybdate solution. Then wait for 20 min to complete the reaction. To eliminate excess of molybdate treated with 0.5 mL volume of oxalic acid. The solution was transposed to 250 mL separating funnel. After this to the solution 0.2 mL of methylene blue solution was added. Then, the extraction was carried out alongwith 5 mL of butanol. The water soluble base layer was thrown out and upper layer consisting of suspended ion adjoining 1 mL of acetone and then the absorbance was analyzed at 660 nm against a blank solution.

Determination of ethion in soil: Soil sample (5 g) was taken in Erlenmeyer flask of 250 mL. 20 mL of 0.3 % sulfuric acid was added to this flask along with 10 mL of 6 % m/v hydrogen peroxide and glycerin 0.5 mL. The resulting mixture is boiled at 160-180 °C for 20 min on a sand-bath, then again add 2 mL of hydrogen peroxide and further boil it for 10 min. The mixture is cooled down to room temperature and add 50 mL of deionized water. Now strain the mixture, get the filtrate in order to eliminate excess of hydrogen peroxide 0.1 mL of 0.01 mol L^{-1} potassium permanganate solution were mixed. Then makeup with to 25 mL of water and add 1 mL of 1.5 mol L^{-1} sulfuric acid along with 0.6 mL ammonium molybdate solution. Then the absorbance was recorded at 660 nm after 20 min.

Determination of ethion in different fruits: Some samples of vegetables and fruits were gathered from crop field where an insecticide ethion was used. The samples were weighed, mashed alongwith acetone-deionized water (1:1) and then strained and passed from thin cotton cloth. The strained solution is then proceed with centrifugation at 1850 g for 10 min. A mixture was taken disolved to 10 mL sulfuric acid and 1 mL of 1.5 mol L^{-1}. 0.05 mol L^{-1} ammonium molybdate solution were added and analyzed for absorbance as described above.

RESULTS AND DISCUSSION

Maximum absorption by the colour system at 660 nm is shown in Fig. 1. All the spectral determination was carried out against deionized water as the blank showed negligible absorbance at this wavelength. Beer's law followed at the range of 0.5-16 µg for colour system of ethion per 10 mL of final solution at 660 nm (Fig. 2). In terms of ethion the molar absorptivity is found to be 6.0×10^5 mol L^{-1} cm^{-1} and Sandel sensitivity is 0.014 µg cm^{-2}.

Effect of reagent concentration: For full colour development it was observed that 0.6 mL of 0.05 mol L^{-1} ammonium molybdate solution was sufficient. The absorbance of the sample solution was found to be increased as the amount of ammonium molybdate was raised.

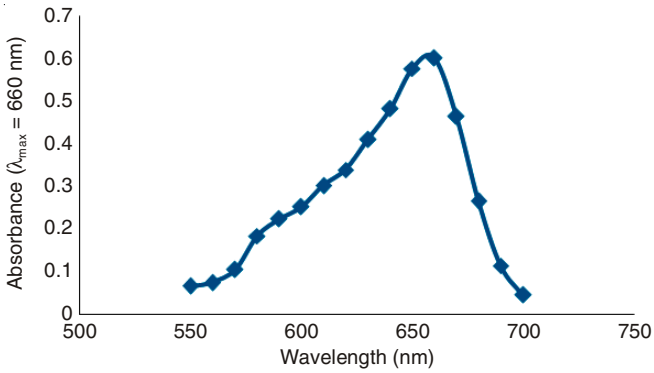

Fig. 1

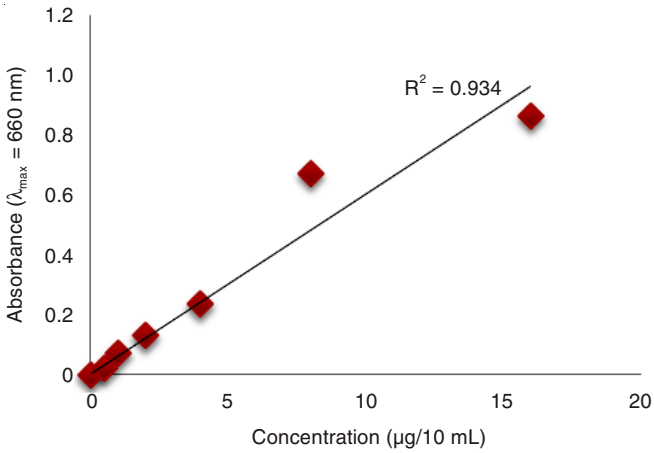

Fig. 2

Also, 0.2 mL volume of 4×10^{-5} mol L^{-1} methylene blue solution was found to be sufficient for complete interaction so that colour complex could be formed. If more than 0.2 mL was used, it was seen that the blank also produce colour. In order to mask excess of molybdate 0.5 mL volume of oxalic acid solution is sufficient (Fig. 3).

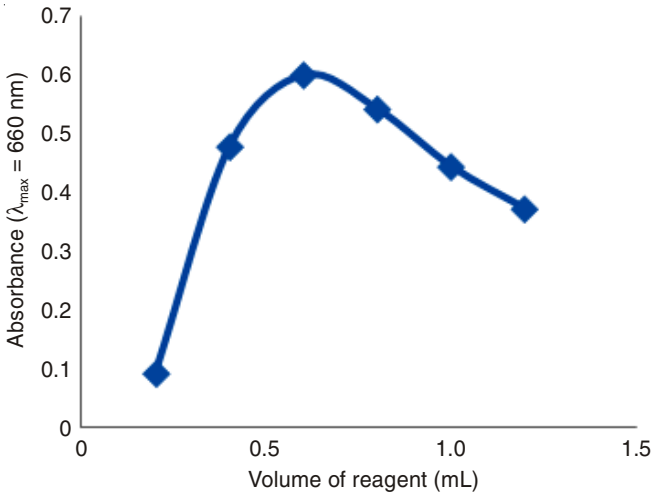

Fig. 3

Effects of foreign ions and species: For the determination of ethion, the effects of common foreign species and other insecticides were studied to check the validity of the method. Known amount of insecticides and foreign species were added to a standard solution containing 4 µg of ethion per 10 mL

TABLE-2
DETERMINATION OF ETHION IN VARIOUS ENVIRONMENTAL AND AGRICULTURAL SAMPLES

Sample	Ethion originally found* by proposed method (µg)	Ethion added (µg/L)	Total ethion found by present method*	Recovery (%)
Polluted water**	1.027	4	4.247	80.00
Soil***	1.350	4	5.217	96.68
Capsicum***	2.71	4	5.990	82.00
Radish***	2.992	4	6.739	93.68
Ladies finger***	1.710	4	5.083	84.32
Rice***	2.16	4	5.920	94.01
Apple***	1.97	4	5.860	97.34
Grapes***	1.141	4	4.690	88.75
Orange***	1.179	4	4.830	91.20
Orange peel ***	1.616	4	5.585	99.21

*Mean of three replicate analysis.
**Water sample 10 mL after treatment 10 mL aliquot was analyzed.
***Sample 5 g (taken from agricultural field, 10 mL aliquot of sample was analyzed after treatment).
****Sample 5 mg (taken from local market, 10 mL aliquot of sample was analyzed after treatment).

before the determination and the solution was carried out by the described method.

It was found that the foreign species are not interfering in the present method, as they degrade and release phosphorous at very higher concentration. Table-1 shows the limit acceptable for various other pesticides and ions.

TABLE-1
EFFECT OF FOREIGN ION AND SPECIES *i.e.* METAL ION AND INSECTICIDE (CONCENTRATION OF ETHION = 4 µg in 10 mL)

Foreign species	Tolerance limit* (µg/10 mL)	Foreign ions	Tolerance limit* (µg/10 mL)
Acetamiprid	700	Fe^{2+}, SO_4^{2-}	500
Triazophos	500	Al^{3+}	500
Isoprothiolane	250	Cu^{2+}, SO_4^{2-}	1000
Deltamethrin	1000	Ba^{2+}, Cl^{-}	250
Propenophos	500	Zn^{2+}, SO_4^{2-}	100
Cypermethrin	100	Ni^{2+}, SO_4^{2-}	250
Fenvalarate	1000	Ca^{2+}, SO_4^{2-}	250

*Amount causing an error of ± 2 % in absorbance value

Comparison with other spectrophotometric method: Only one method for determination of ethion spectrophotometrically was found using phloroglucinol for 0.1 to 0.8 ppm at 460 nm was reported and is less sensitive [10]. The proposed method using ammonium molybdate and methlylene blue, follows the Beer's law at the range of 0.5-16 µg and is more sensitive and selective than the previous one.

Precision and accuracy: By determining 10 µg of ethion in 10 mL final solution over a period of 7 days the accuracy and precision of the method was analyzed. The standard deviation and relative standard deviation of absorbance values were computed to be 0.022 µg mL^{-1} and 3.5 %, respectively.

Application: For the determination of ethion in different samples of soil, agricultural products and polluted water gathered from a crop field where ethion was used as an insecticide the proposed method was applied most efficiently. The outcome observed were far more better than those of the previously determined spectrophotometric method.

Known amounts of ethion were mixed with different samples of soil, agricultural products, *etc*. and then analyzed by the present method for the determination of ethion. Table-2 shows the recovery percentage of the samples analyzed.

Conclusion

This method is rapid, free from larger amount of foreign species. Reagents require for this method are easily available and low cost. It can successfully apply for the determination of ethion in water, soil, vegetables and cereals sample. The present method is selective and sensitive than other methods for the determination of ethion.

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REFERENCES

1. L.O. Brun, J.T. Wilson and P. Daynes, *Trop. Pest Manage.*, **29**, 16 (1983).
2. G. Singh, B. Singh, R.S. Battu, G. Jyot, B. Singh and B.S. Joia, *Bull. Environ. Contam. Toxicol.*, **79**, 437 (2007).
3. H. Abdel-Gawad, R.M. Abdelhameed, A.M. Elmesalamy and B. Hegazi, *Phosphorus, sulphur, silicon*, **186**, 2122 (2011).
4. S.W. Husain, V. Kiarostami, M. Morrovati and M.R. Tagebakhsh, *Acta Chromatogr.*, **13**, 208 (2003).
5. U. Tamrakar, V.K. Gupta and A.K. Pillai, *J. Anal. Chem.*, **67**, 437 (2012).
6. K. Lamsal and B. Ghimire, *Afr. J. Biotechnol.*, **9**, 4204 (2010).
7. F.A. Gunther, R.C. Blinn and G.E. Carman, *J. Agric. Food Chem.*, **10**, 224 (1961).
8. R. Kumar, *Biomed. Chromatogr.*, **3**, 272 (1989).
9. J.V. Das, K.N. Ramachandran and V.K. Gupta, *Analyst*, **119**, 1387 (1994).
10. J.V. Das and V.K. Gupta, *Fresenius J. Anal. Chem.*, **352**, 395 (1995).