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RESEARCH ARTICLE

Studies on Physico-Chemical Properties of Commercially Available EC Formulations of Deltamethrin and Profenofos pesticides.

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Abstract

Agricultural chemical products can undergo chemical and physical changes on storage. Understanding the chemical and physical characteristics of a pesticide allows the applicator to make better decisions about which pesticide active ingredient and/or formulation to use for a particular situation. It also helps to understand how pesticides move in the environment. In the present studies the physico-chemical properties of various commercially available EC formulations of Deltamethrin and Profenofos insecticides, which are widely used for plant protection from insect pests were investigated. The physical and chemical properties of Deltamethrin and Profenofos were determined as per BIS specifications. The results of the present studies are further utilized for selection and also for agricultural application. The present study also focuses on quality of commercially available formulations of insecticides.

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INTRODUCTION

Pesticides constitute the key control tactics for management of pests and diseases and the productivity of crops depends on their effective control. Together with high-yielding crop varieties and fertilizers, pesticides have helped the Indian farmers in achieving a substantial increase in agricultural productivity [1] .These pesticides can be generally classified into four main chemical groups: organophosphate (OP), organochlorines (OC), carbamates, and synthetic pyrethroids. The introduction of synthetic insecticide organophosphate (OP) insecticides and pyrethroids has contributed greatly to pest control and agricultural output. About 5.2 billion Pounds of pesticides used worldwide [2]. Consumption of Pesticides in India is 55.54 Th Tonnes [3] out of which 70% of the pesticides belong to insecticide. In India context, farmers have been using pesticides frequently to have higher yields, but injudicious use of the pesticides gives rise to different problems like development of resistance in pests to pesticides, various diseases in crops, suppression in the population of beneficial flora and fauna and pesticide residues in food and the environment [4]. When used properly they constitute an important input in vegetable and fruit production in order to produce economically marketable products. The use of pesticide can be controlled by obeying regulation related to it. The right dose differentiates the poison and remedy.

Agricultural chemical products can undergo chemical and physical changes on storage. The rate at which these changes occur depends on the nature of the active constituent(s), the formulation type, the packaging and, notably, the storage conditions (temperature, light and humidity). The product remains fit for use as long as these changes have no adverse effects on application, biological performance, and the safety of operators, consumers and the environment. Understanding the chemical and physical characteristics of a pesticide allows the applicator to make better decisions about which pesticide active ingredient and/or formulation to use for a particular situation. It also helps to understand how pesticides move in the environment. The paper aims to study the Physico-chemical properties of the pesticides to ensure that the product can be safely and efficiently applied.

Several formulations of pesticides which are used as insecticides are commercially available as EC (emulsifiable concentrate), dust, wettable powder. However their quality and performance is the major constraint

faced by the users. With this background, commercially available and widely used formulations of Deltamethrin and Profenofos insecticides were tested and studied as per BIS specification. Deltamethrin is available as an emulsifiable Concentrate (EC), Suspension Concentrate (SC), Soluble Concentrate (SL), Wettable Powder (WP) whereas Profenofos is available as emulsifiable concentrate, dust,pellet, spray, granular and wettable powder in the market.

Deltamethrin is a broad-spectrum insecticide with a versatile active ingredient belonging to the family of pyrethroids discovered by M. Elliott et al. in 1974 and marketed by Roussel Uclaf in 1977 [5].It is registered for use on various crops including cotton, corn, cereals, soybeans, and vegetables for pests such as mites, ants, weevils, and beetles.[6,7]. It is effective against insects via ingestion and direct contact. Deltamethrin, have an α-cyano group that induces "long-lasting" inhibition of the sodium channel activation gate. This results in prolonged permeability of the nerve to sodium and produces a series of repetitive nerve signals in sensory organs, sensory nerves, and muscles.[8,9] Deltamethrin may also affect ion channels in the nervous system other than sodium channels, possibly due to their phosphorylation state.[10,11] Profenofos is an organo-thiophosphate insecticide that is mainly applied to control cotton bollworm and tobacco budworm. Profenofos is a broad spectrum organophosphate insecticide and acaricide. Its mode of action is by inhibiting acetlycholinesterase. [12] .

Commercially available and widely used EC formulations of Deltamethrin and Pofenofos were assessed for their physico-chemical properties as per BIS specification in order to know their standard. To assess these properties, different samples of commercial EC formulation of Deltamethrin and Profenofos were collected from local market and tested in the laboratory as among different formulations of these insecticides EC formulations are widely used.

II . MATERIAL METHOD

According to BIS specification the samples were tested for important physical tests and chemical tests like cold test, flashpoint, emulsion stability, acidity/alkalinity of deltamethrin[13] and profenofos [14] active ingredient deltamethrin [15] and profenofos [16] Thus various samples from different manufacturers were subjected to study to physico-chemical properties.

2.1 physical tests:

Following tests were carried out on the collected samples of Deltamethrin and Profenofos.

1. **Cold test:**

Procedure: 50ml sample was taken in clean, transparent container and closed with a cork / stopper fitted with thermometer. The sample was cooled to 10^0c by placing the container in ice cold water. The sample was stirred at short intervals for 1 hour maintaining the temperature of the sample at 10^0c. At the end of one hour, the material was examined for any turbidity or separated solid or oily matter or both.

Significance of cold test: Liquid formulations may be adversely affected by storage at low temperature. As storage at low temperature may result in crystallization of active constituent(s) or there can be significant changes in viscosity or phase separation of emulsions.

2. **Flash Point:**

Procedure: Using Abel's apparatus, samples were tested for their flash point. In this method sample under test was placed in the cup of the Abel's apparatus and heated at a prescribed rate. A small test flame was directed into the cup at regular intervals, and the flash point was noted as the lowest temperature at which application of the test flame causes the vapor above the sample to ignite with a distinct flash inside the cup. The flash point of the sample should be above 24.5^0c.

Significanceof Flash point: As the pesticides contain petroleum distillates as part of their inert ingredient it becomes necessary to know whether the product is combustible, flammable or extremely inflammable as this knowledge is helpful in providing safeguards against fire hazards during their storage,transportation,handling and use.

3. **Emulsion stability:**

Procedure: 2ml sample was taken in clean, transparent container. Standard hard water (dissolve 0.304g of calcium chloride anhydrous and 0.139g of magnesium chloride hexa hydrate in distilled water and make up to 1 litre) was poured at 30^0c to the sample at the rate of 15 to 20 ml/min. During addition, the contents of the beaker were stirred continuously with the glass rod and when the volume of diluted emulsion in the beaker reached 100ml then addition of standard hard water was stopped. The diluted emulsion was immediately transferred to clean and dry graduated cylinder. The cylinder was kept with the content for 1 hour at 30^0c. After 1 hr., the volume of the creamed matter at the top and sediment at the bottom, if any was noted.

Significance of Emulsion stability: If the volume of the creamed matter at the top and sediment at the bottom is within acceptable limits it shows that the product remains homogenous or uniform during application.

2.2 chemical tests:

1. **Acidity/Alkalinity test:**

Qualitative Test:

About 0.5ml sample was taken in a test tube and mixed with about one milliliter of water. The mixture was tested for acidity or alkalinity with litmus paper. (Determined as the case may be, acidity or alkalinity.)

All the collected samples were found to be acidic and therefore their acidity was determined.

Determination of Acidity:

Procedure:10g of the sample was weighed accurately into a dry conical flask and diluted with 100ml water. The contents of the flask were titrated immediately with the standard sodium hydroxide solution using methyl red or bromocresol purple as the indicator. A blank reading with 100ml. of water was also determined.

Calculations:

Acidity (as H_2SO_4) percent by mass = $\frac{4.9\,(V-v)N}{M}$

[Where, V= volume in ml of standard sodium hydroxide solution required for the test,
v= volume in ml of standard sodium hydroxide solution required for the blank determination.
N= normality of standard sodium hydroxide solution
M= mass in g of the material taken for the test.]

When samples were tested by the above prescribed method, acidity should be 0.05percent by mass maximum

Significance of testing Acidity/Alkalinity : A change in pH on storage can give an indication of instability of the active substance or product.

2. **Active ingredient test:**

For Deltamethrin, HPLC with UV spectrophotometer and for Profenofos insecticide, GLC with FID was used for the determination.

A. Active ingredient test: Deltamethrin

For Deltamethrin by HPLC method after dilution of the sample, deltamethrin content was determined by comparing the response of the sample to that of the deltamethrin standard of known purity by HPLC on the column packed with silica. A solution containing a known mass of sample solution and the internal standard solution was injected. The percentage of Deltamethrin was then calculated by standard relationship. In HPLC method the column used was stainless steel, 15-18 cm long, 4.6mm internal diameter packed with Lichrosorb silica 60-80 mesh detector used is UV spectrophotometer and the mobile phase is a mixture of dioxane and iso-octane.During sample testing the column temperature was Ambient flow rate was 1 to 1.7 ml/min detector was set at 254 nm and retention time was 8 min [14]

Procedure:

a) A standard solution was prepared by weighing 50 mg of deltamethrin standard (r_1g and r_2g) in a 50 ml volumetric flask then diluting with a mixture of dioxane and iso-octane in ratio 200ml/800ml (solutions R_I andR_2)
b) Similarly sample solution was prepared by weighing 0.1 mg samples containing nearly 50 mg of deltamethrin M_1g and M_2g in a 50 ml volumetric flask then diluting with a mixture of dioxane and iso-octane in ratio 200ml/800ml (solutions S_1 and S_2).
c) Then with the injector ,inject one of the standard solutions until peak height or area of two successive injections agree to within 2%.inject the standard and sample solutions in successions according to following sequences:R_1S_1,R_2S_1,$R_1S_2$and R_2S_2
d) From the print out, peak areas of deltamethrin and internal standard peaks were noted down for calculating the percentage.

Calculation:

Deltamethrin content, percentage by mass = $\frac{A_x \times r \times P}{A_r \times m}$

Where

A_x = deltamethrin peak area of the sample solution (S_1 or S_2)
r = mass in g,of the deltamethrin in the standard solution (R_1 or R_2)
P = purity of deltamethrin standard;
Ar = deltamethrin peak area of the standard solution (R_1 or R_2); and
m = mass,in g, of the sample in the sample solution (S_1 or S_2).

B. Active ingredient test: Profenofos

Profenofos was determined by Gas chromatography using the internal standard technique.

For Profenofos GLC unit with FID is column used is Glass/S.S,length = 1.8m,ID= 2mm,packed with 3 percent Silicon OV-225 on gas Chrome Q,80-100 mesh. Carrier gas (N_2) 30ml/min ,Hydrogen (H_2) 30ml/min and Air 300ml/min along with internal standard Isopropyl 4,4'dibromobenzilate. During sample testing temperatures were maintained as per BIS .The temperature of column oven 210^0C, detector 260^0C and of injection port 240^0C. [16]

Procedure:

a) Internal standard solution was prepared by weighing 1.9gm of into 250ml volumetric flask and make up to the volume with acetone.

b) Then for preparing standard solution 0.100 gm of profenofos reference standard was weighed into 25ml volumetric flask, to which 20ml of internal standard solution was added and then the volume was made up to mark with acetone.

c) Sample solution was prepared similar to standard solution only difference was instead of reference standard, sample was used in the preparation.

d) Initially the standard solution was injected repeatedly, until the area ratio of reference substance and internal standard of two successive injections did not deviate from each other by more than 2 percent. After which sample was injected. The sequence of injection to be followed was …..CS_1, CS_2, CS_3 …..(Where C = standard solution and S_1 = sample solution)

Calculation: From the chromatograms of standard solution and sample solution, peak area of profenofos and internal standard peak was measured from which percentage of profenofos was calculated.

Profenofos, percentage by mass = $\frac{M1 \times A3 \times A2 \times P1}{M2 \times A4 \times A1}$

Where,

M_1= mass in g of standard profenofos in standard solution,

M_2= mass in g of sample taken for test.

A_1 = peak area of profenofos in the chromatogram of standard solution

A_2= peak area of profenofos in the chromatogram of sample solution,

A_3= peak area of internal standard in the chromatogram of standard solution,

A_4= area of internal standard peak in the chromatogram of sample solution,and

P= percentage purity of profenofos standard.

Significance of testing Active ingredient: The biological efficacy of pesticides gradually decreases with time. The active ingredient may change chemically and break down into products that may no longer have pesticidal properties, thus decreasing the concentration of the original active ingredient. For this purpose the active ingredient is generally tested after a period of six months ,starting from manufacturing date till the expiry date of the sample.

III. RESULTS OF PHYSICO-CHEMICAL PROPERTIES:

3.1 A] Result of the various physical and chemical tests performed on different samples of Deltamethrin collected are as follows:

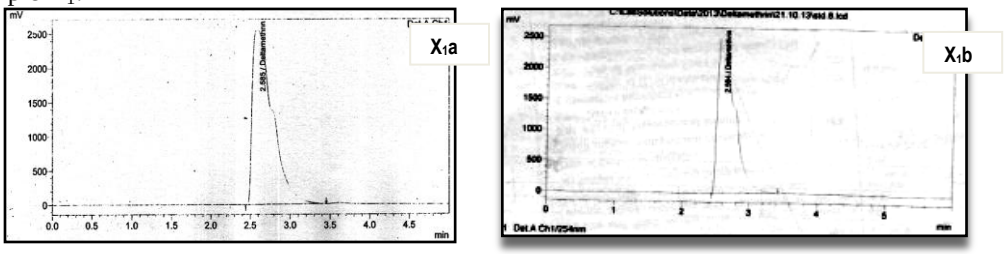
Samples of Deltamethrin (EC2.8)

No.	Sample	Test performed	Result	Standard Results
1	X_1	Cold test Emulsion stability Flash point Acidity Active ingredient (A. I.)	No turbidity No creaming 44^0 C 0.02 2.8	▪No turbidity or separation of solid ▪Any separation including creaming at the top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limit
2	X_2	Cold test Emulsion stability	No turbidity No creaming	▪No turbidity or separation of solid ▪Any separation including creaming at the

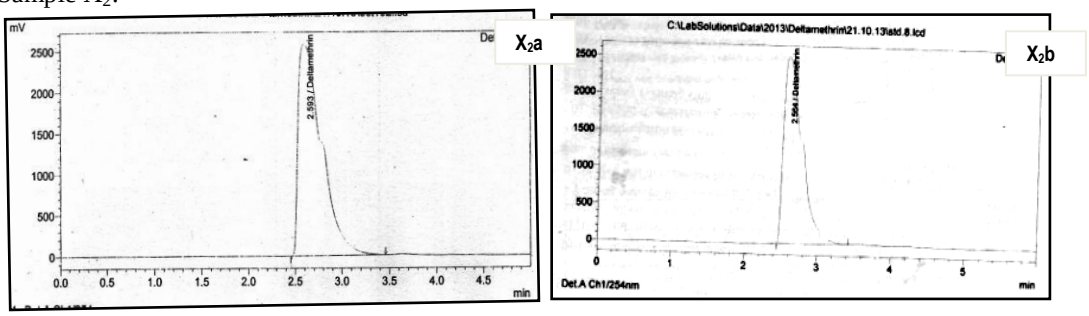
		Flash point Acidity Active ingredient (A. I.)	 51^0c 0.02 2.81	top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limit

Results of Active Ingredient (A.I.) for samples X_1, X_2,of Deltamethrin EC formulation are based on following chromatogram obtained using HPCL with UV spectrophotometer detector.

Sample X_1:



Sample X_2:



3.2 B] Result of the various physical and chemical tests performed on different samples of Profenofos EC formulations collected are as follows:

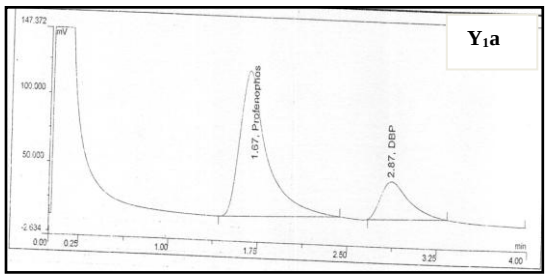
Samples of Profenofos (EC50)

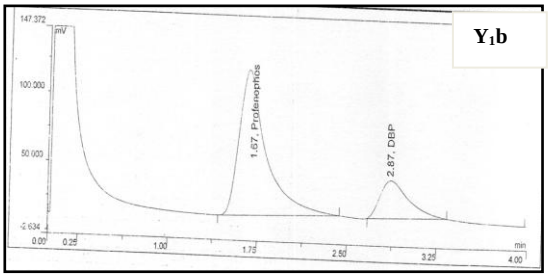
No.		Test performed	Result	Standard Result
1	Y_1	Cold test Emulsion stability Flash point Acidity Active ingredient (A.I.)	*No turbidity *No creaming *49^0c *0.02 *49.3857	▪No turbidity or separation of solid ▪Any separation including creaming at the top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limit
2	Y_2	Cold test Emulsion stability Flash point	*No turbidity *No creaming *43^0c	▪No turbidity or separation of solid ▪Any separation including creaming at the top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C

		Acidity Active ingredient (A.I.)	*0.02 *50.4834	▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limit
3	Y_3	Cold test Emulsion stability Flash point Acidity Active ingredient(A.I.)	*No turbidity *No creaming *47^{0}c *0.02 *48.74	▪No turbidity or separation of solid ▪Any separation including creaming at the top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^{0}C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limit

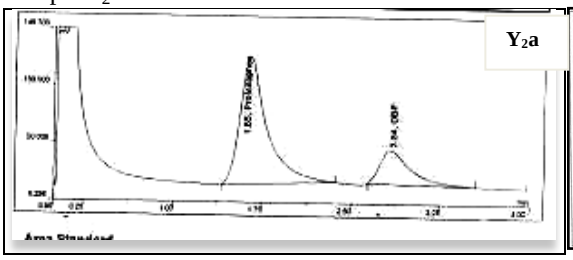
Results of Active Ingredient (A.I.) for samples Y_1, Y_2 and $Y_3$of Profenofos EC formulation are based on following chromatogram obtained using GLC-FID detector

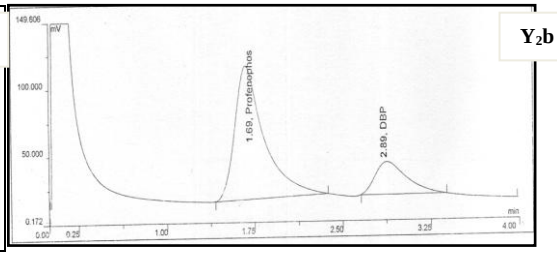
SampleY_1:



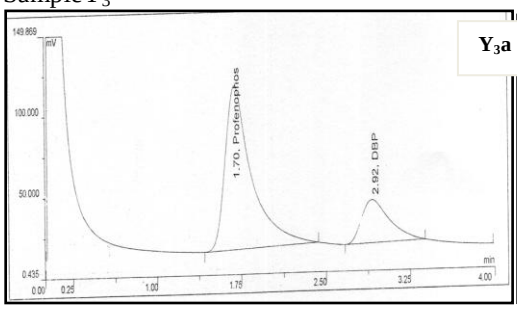


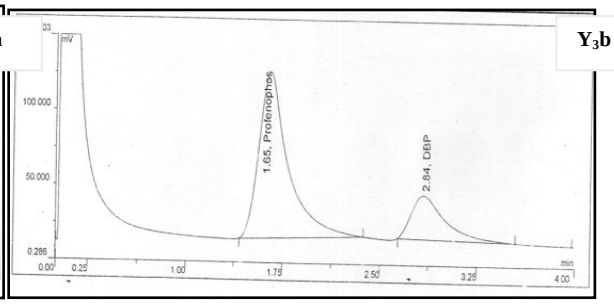
SampleY_2:





SampleY_3





IV. DISCUSSION:

Samples of EC (2.8) formulations of Deltamethrin collected from the market were tested as per guidelines given in the BIS specification of EC formulations . There were two samples (X_1 and X_2) out of which one was from an Indian manufacturing company and one was from the International manufacturing company. Both the samples were up to the mark in their results for cold test ,emulsion stability test and acidity/alkalinity test . Both the samples had a flash point above 24.5^0 C as per BIS specification. Even Active Ingredient in both samples was around 2.8
Samples of EC (50) formulations of Profenofos, collected from the market were tested as per guidelines given in the BIS specification of EC formulations. There were three samples (Y_1, Y_2 and Y_3) out of which two were from Indian manufacturing companies and one was from the International manufacturing company. All samples were up to the mark in their results for physical tests such as cold test, emulsion stability test and flash point (which should be above 24.5^0c). Acidity/alkalinity test for all samples were up to the mark. In all samples active Ingredient was around 50.0 i.e. up to the mark. . In India Under the Insecticides Act 1968, Every year, the insecticide samples are analysed by the insecticide inspectors. Last year, 1100 samples out of 50,000 failed[17].Thus present investigations have great importance as far as quality of pesticides is concerned .

V. CONCLUSION:

Physico-chemical properties of EC formulations of Deltamethrin and Profenofos which are commercially available are important in their selection to use against insect pests on crop. In the above studies as per BIS specification various national and international formulations available were tested for various physical and chemical tests and based on the results of these tests the formulation having better results for all tests performed on it was selected for the application.

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