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# Studies on physico-chemical properties of synthetic Pyrethroids Fenvalerate and Alphamethrin

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**ABSTRACT**

*The increasing pressure to increase food production to meet current demand requires protection of crops from pests. The use of pesticides is therefore inevitable and constitutes an integral part of modern crop management practice. Manufacturers design pesticide formulations with several active substances of different chemical classes with different mechanisms of action and direction. Pesticide formulations are broken down into active ingredients and inert ingredients. Uncontrolled technical impurities accompanying any active substance or base material used for the formulation could worsen the toxicological properties of final products and thereby cause additional adverse health and environmental effects. By the same token, inappropriately defined concentrations can lead to overuse and misuse of pesticides by the user. Regular quality control of pesticide is essential to facilitate their safe and efficient use and for increasing agricultural productivity while at the same time protects the farmers, consumers and the environment. The biological activity of a pesticide to the target pest species is greatly influenced by its physical and chemical properties. In the present studies the physico-chemical properties of various commercially available EC formulations of synthetic pyrethroids like Alphamethrin and Fenvalerate insecticides, which are widely used for plant protection, are determined as per BIS specifications. The results of the present studies will be further utilized for selection and also for it's application.*

**Key words:** Alphamethrin, Fenvalerate, physico-chemical properties, BIS specifications.

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## INTRODUCTION

Pesticides are a group of artificially synthesized substances used to fight pests and improve agricultural production [1] In the last 50 years, the use of pesticides have greatly increased the quantity and improved the quality of food for the growing world population [2]. However, with increasing amounts used, concern about their adverse effects on non target organisms, including human beings, has also grown[2] Pesticide use must ensure public safety and environmental protection with regards to both the chemical itself and their potentially harmful metabolites. 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). Uncontrolled technical impurities accompanying any active substance or base material used for the formulation could worsen the toxicological properties of final products and thereby cause additional adverse health and environmental effects. By the same token, inappropriately defined concentrations can lead to overuse and misuse of pesticides by the user. Highly inefficient practices include using inappropriate products and incorrect dosage [3]. Pesticides can be generally classified into four main chemical groups: organophosphate (OP), organochlorines (OC), carbamates and synthetic pyrethroids. Synthetic pyrethroids

are known to have a high insecticidal activity, low toxicity in mammals and have no residue in biosphere [4]. Therefore, they have been used to control a wide variety of agricultural pests and accounted for more than 25% of the worldwide insecticide market [5]. Over the year many formulations have been developed, however their quality and performance is the major constraint faced by the users. Bureau of Indian Standard specifications (BIS), CIPAC, WHO specifications, FAO specification are developed with the basic objective to ensure the percentage purity of active ingredient in both technical grades and formulations as per the labeled claim by the manufacturers, the suitability of the pesticide formulation for its intended use, safe and judicious use of pesticides and the shelf life of active ingredient. Analytical quality control of pesticides analysis is crucial for ensuring their safe and effective use in agriculture.

Fenvalerate and Alphamethrin , are broad spectrum pyrethroid insecticide and available as EC, parts granules, ULV, LC, WP, and dust in market and are used for control of Aphids, Jassids, and bollworms in cotton and is highly used for control of wide range of pests include those are resistant to Organochlorine, Carbamates and Organophosphorous insecticides. Thus it has great significance in agriculture.With this background, commercially available and widely used formulations of Fenvalerate 20EC and Alphamethrin 10EC insecticides can be assessed for their physico-chemical properties as per BIS specification in order to know their standard. Similar studies on Samples of EC 2.8% formulations of Deltamethrin,a synthetic pyrethroid was tested [6] as per guidelines given in BIS specification, the samples were up to the mark.

## MATERIALS AND METHODS

According to BIS specification the physical tests and chemical tests like cold test, flashpoint, emulsion stability, acidity/alkalinity of Alphamethrin[7] and Fenvelarate [8] active ingredient Fenvelarate [9] and Alphamethrin[10]

**2.1 physical tests:** Following tests were performed for samples of Fenvalerate 20 EC and Alphamethrin 10 EC

**2.1.1Cold test**
Procedure: 50ml sample was taken in clean, transparent container and was closed with cork/stopper fitted with thermometer. The sample was cooled to $10^0$c by placing the container in ice cold water. The sample was stirred at short intervals for 1 hour maintaining the temperature of sample at $10^0$c. At the end of one hour, the material was examined for any turbidity or separated solid or oily matter or both. [11]

**2.1.2 Flash Point**
Procedure: Using Abel's apparatus, samples were tested for their flash point. In the 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 test flame causes the vapors above the sample to ignite with a distinct flash inside the cup. The flash point of the sample should be above $24.5^0$c. [12]

**2.1.3. Emulsion stability**
2ml sample was taken in clean, transparent container. Standard hard water (dissolve0.304g of calcium chloride anhydrous and 0.139g of magnesium chloride hexahydrate in distilled water and make up to 1 liter) was poured at $30^0$c in 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 hr. at $30^0$c. After 1 hour the volume of the creamed matter at the top and sediment at the bottom, if any was noted.

**2.2Chemical Tests:**
**2.2.1 Acidity/alkalinity test:**
Qualitative Test:
About 0.5ml of 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:**
10g of 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 above prescribed method, acidity should be 0.05percent by mass maximum

**2.2.2. Active ingredient test:**
For Fenvalerate pesticide, GLC with FID was used for active ingredient determination and for Alphamethrin, High Performance Liquid Chromatography (HPLC) was used.

**A. Active ingredient test: Fenvalerate (20 EC)**

**Table 1: Working condition for analysis by GLC**

| | |
|---|---|
| **1. Column:** | |
| Material | Stainless steel |
| Length × OD | 50 cm × 0.3 mm |
| Stationary phase | 5 percent OV-101 |
| Solid support | Chromosorb W, HP(80 to 100 mes4) |
| **2. Detector system:** | |
| Type | FID (Flame ionization detector) |
| *Temperature:* | |
| • Column oven | $240^0$ C |
| • Injection Port | $270^0$ C |
| • Detector | $300^0$ C |
| **3. Carrier Gas** :Nitrogen 30 ml/min | |
| **4. Volumetric Flask**: 50 ml and 100 ml capacity | |
| **5. Separating Funnel**: 100 ml capacity | |
| **6. Microsyringe**: 10µl syringe with a needle sufficient length to introduce the sample to the top of the column packing | |
| **7. Reagent:** | |
| A) Standard Fenvalrate | 92 percent (m/m) |
| B) Di(2-ethyhexyl) Phthalate | AR grade |
| C)Chloroform | Spectroscopic grade. |

***Procedure***
a) Preparation of Internal Standard Solution (Is):- Weigh accurately 0.5g DBP and dissolve in chloroform so as to make 1 liter of the solution.
b) Preparation of Standard Fenvalerate Solution: - Weigh accurately 0.075 g of standard Fenvalerate in a beaker and 2.5 ml of 'Is' solution. Shake well to dissolve the Fenvalerate. Transfer carefully into 50 ml volumetric flask and then make up to the mark.
c) Preparation of Sample Solution: - Weigh accurately about 0.075g of Fenvalerate solution and sample under test. Measure the areas of Fenvalerate and 'Is' peak in each case and compute the Fenvalerate content.

Using the formula given below, percentage by mass of Fenvalerate, is calculated
Fenvalerate, percentage by mass = $\frac{m_1 \times A_1 \times A_3 \times p}{m_2 \times A_2 \times A_4}$
Where, $m_1$ = mass in g of the standard Fenvalerate
$m_2$ = mass in g of the sample taken for the test
$A_1$= area of internal standard peak in standard solution
$A_2$ = area of internal standard peak in sample solution
$A_3$ = area of Fenvalerate peak in sample solution
$A_4$ = area of internal standard peak in standard solution,and

P= percentage purity of standard Fenvalerate

**B. Active ingredient test: Alphamethrin**

**Table 2: Working condition for analysis by HPLC**

| | |
|---|---|
| Column | Stainless steel, 250 mm × 4.6 mm inner diameter, packed with silica of 5 µm particle size |
| Detector | UV ,(λ=280 nm) |
| Mobile phase | 3.0 percent (v/v) Di- isopropyl ether in n-pentane. |
| Flow rate | 1.5 ml/min |
| Sample size | 20µl |
| Glassware | Standard volumetric flask. |
| Reagents | Di-isopropyl Ethers , n- Pentane,Toluene |

**Procedure:**

1. Preparation of sample solution: weigh 100mg of sample accurately in duplicate into two 100 ml standard volumetric flask. Dissolve the sample and make up the volume using mobile phase, and mix well.
2. Determination: Introduce 20µl of sample solution into HPLC unit. From computer printout, the peak area is noted down for percent of Alphamethrin isomers. The major peak in the chromatogram represents the cis-2 isomer. The peak immediately preceding this is of cis-1 isomer and the peaks after the major peak represents Trans - isomer

a) cis-1 isomer [(1 Rcis)R + (1 Scis)S] = 8.0 min
b) cis-2 isomer =9.0 min
c) trans-1 isomer =10.5 min
d) trans-2 isomer =12.0 min

**Calculations**

Alphamethrin isomer content,percentage of isomer = $\frac{Area\ of\ individual\ isomer\ peak}{Total\ area\ of\ isomer\ peak}$ **x 100**

## RESULTS

3.1 A] Result of the various physical and chemical tests performed on different samples of Alphamethrin is shown in Table 3

**Samples of Alphamethrin (10 EC)**

**Table 3: Showing results of Physico-chemical properties of Alphamethrin (10 EC).**

| No. | sample | Test performed | Result | Standard Result |
|---|---|---|---|---|
| 1 | $X_1$ | Cold test | No turbidity | No turbidity or separation of solid |
| | | Emulsion stability | Creamy layer was observed of 0.2mm | Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml |
| | | Flash point | $45^0$c | Shall be above $24.5^0$C |
| | | Acidity | 0.04121 | Shall be not more than0.25percent by mass |
| | | Active ingredient(a.i.) | 10.07 | Shall not differ from the declared value by more than the percent tolerance limits |
| 2 | $X_2$ | Cold test | No turbidity | No turbidity or separation of solid |
| | | Emulsion stability | Creamy layer was observed of 0.3mm | Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml |
| | | Flash point | $47^0$c | Shall be above $24.5^0$C |
| | | Acidity | 0.0309 | Shall be not more than0.25percent by mass |
| | | Active ingredient(a.i) | 9.94 | Shall not differ from the declared value by more than the percent tolerance limits |
| 3 | $X_3$ | Cold test | No turbidity | ▪No turbidity or separation of solid |
| | | Emulsion stability | Creamy layer was observed of 0.2mm | Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml |
| | | Flash point | $47^0$c | Shall be above $24.5^0$C |
| | | Acidity | 0.0462 | Shall be not more than0.25percent by mass |
| | | Active ingredient(a.i) | 9.94 | Shall not differ from the declared value by more than the percent tolerance limits |

Results of Active ingredient (a.i) for samples $X_1$,$X_2$ and $X_3$ of Alphamethrin EC formulation based on chromatogram obtained using High Performance Liquid Chromatography- Equipped with a printer plotter-cum-integrator and UV detector is presented in Fig 1

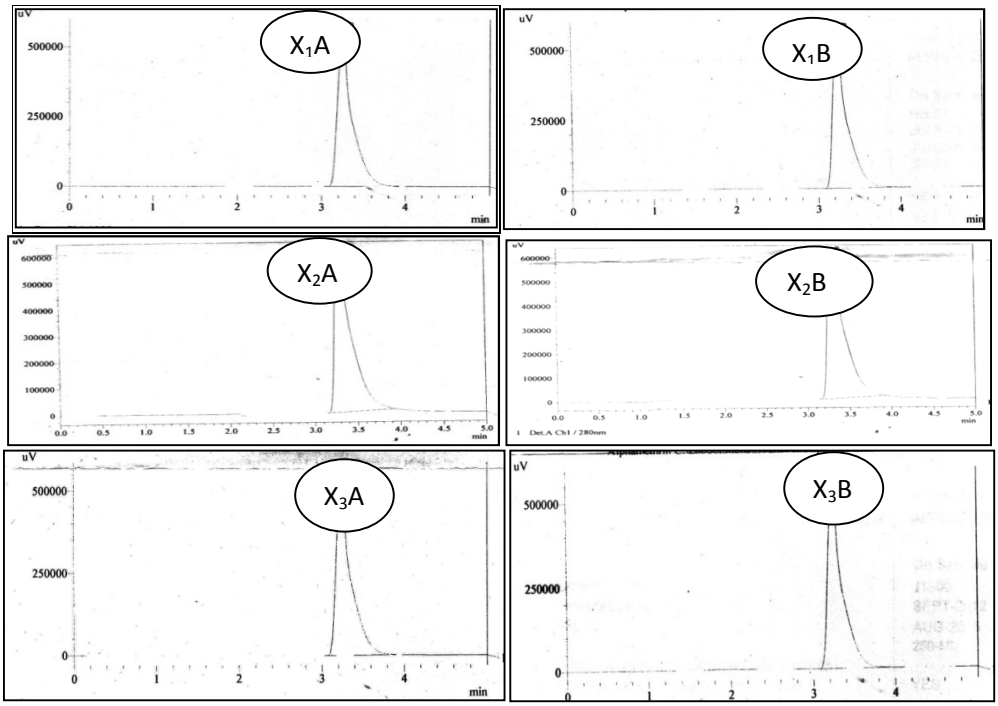


**Fig 1: Results of Active ingredient (a.i) for samples $X_1$,$X_2$ and $X_3$ of Alphamethrin (10 EC).**

3.2B] Result of the various physical and chemical tests performed on different samples of Fenvalerate EC formulations is shown in Table 4

**Samples of Fenvalerate (20 EC)**

**Table 4: Showing results of Physico-chemical properties of Fenvalerate (20 EC).**

| No. | sample | Test performed | Result | Standard Result |
|---|---|---|---|---|
| 1 | $Y_1$ | Cold test | No turbidity | No turbidity or separation of solid |
| | | Emulsion stability | Creamy layer was observed of 0.2mm | Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml |
| | | Flash point | $43^0$c | Shall be above $24.5^0$C |
| | | Acidity | 0.0204 | Shall be not more than0.25percent by mass |
| | | Active ingredient(a.i.) | 20.027≈20.03 | Shall not differ from the declared value by more than the percent tolerance limits |
| 2 | $Y_2$ | Cold test | No turbidity | No turbidity or separation of solid |
| | | Emulsion stability | Creamy layer was observed of 0.3mm | Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml |
| | | Flash point | $43^0$c | Shall be above $24.5^0$C |
| | | Acidity | 0.03090 | Shall be not more than0.25percent by mass |
| | | Active ingredient(a.i) | 20.4269≈20.43 | Shall not differ from the declared value by more than the percent tolerance limits |
| 3 | $Y_3$ | Cold test | No turbidity | No turbidity or separation of solid |
| | | Emulsion stability | Creamy layer was observed of 0.2mm | Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml |
| | | Flash point | $43^0$c | Shall be above $24.5^0$C |
| | | Acidity | 0.02575 | Shall be not more than0.25percent by mass |
| | | Active ingredient(a.i) | 20.8359≈20.84 | Shall not differ from the declared value by more than the percent tolerance limits |

Results of Active ingredient (a.i) for samples $Y_1$, $Y_2$ and $Y_3$ of Fenvalerate EC formulation based on chromatogram obtained using GC-FID detector is presented in Fig 2

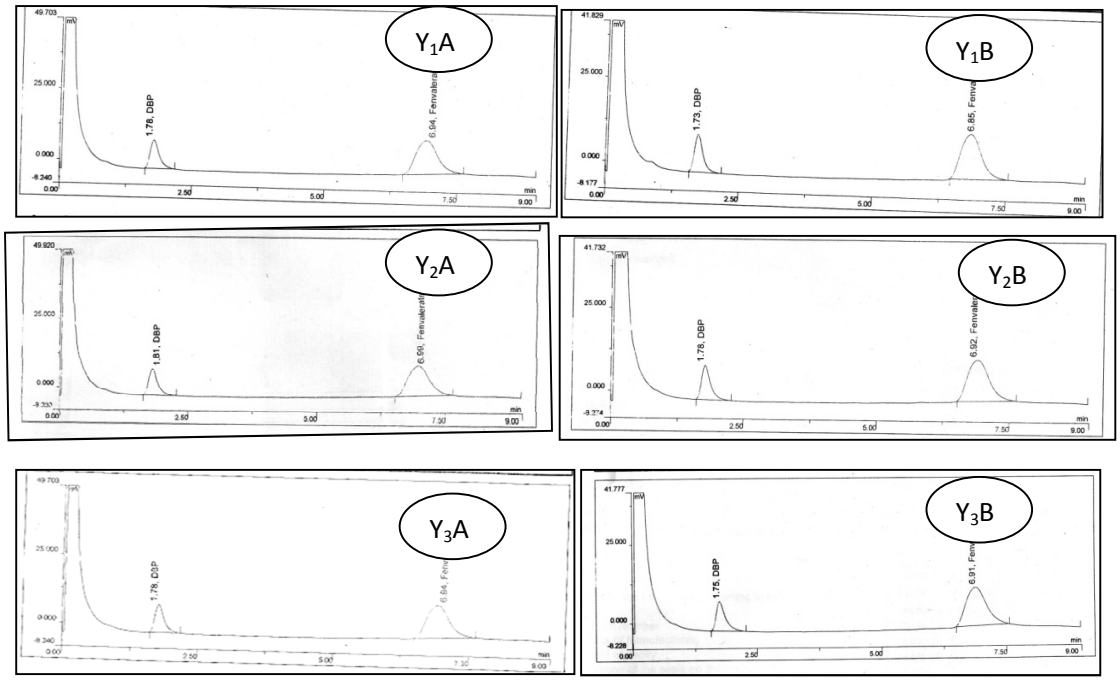


**Fig 2: Results of Active ingredient (a.i) for samples $Y_1$, $Y_2$ and $Y_3$ of Fenvalerate 20EC**

## RESULTS AND DISCUSSION

Samples of formulations of Alphamethrin 10% EC were tested as per guidelines given in BIS specification of EC formulations. There were three samples ($X_1$, $X_2$ and $X_3$ ) out of which one was from Indian manufacturing company and two were from International manufacturing company. All the samples were up to the mark in their results for cold test, emulsion stability test and acidity/alkalinity test. All the samples had flash point above $24.5^0$ c as per BIS specification. Even Active Ingredient in all the samples were around 10 [10].Samples of EC 20% formulations of Fenvalerate, were tested as per guidelines given in BIS specification of EC formulations. There were three samples ($Y_1$, $Y_2$ and $Y_3$) out of which one was from Indian manufacturing company and two were from 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 $24.5^0$c). Acidity/alkalinity test for all samples were up to the mark. In all samples active Ingredient was around 20.0 i.e. up to the mark. [9]. In India under the Insecticides Act 1968, every year the insecticide samples are analyzed to know the quality of insecticides .Last year 1100 samples out of 50,000 failed[13].Indian farmers spend about US $2.6 billion on unregistered or counterfeit chemicals. The untested and unregulated products in turn cause about $1.3 billion in crop damage, according to report by the Agrochemicals Policy Group (APG) [14] and these spurious and substandard pesticides accounted for nearly 40% of the pesticides sold in India in FY12 [15].Thus studying physico-chemical properties of the pesticides ensures that the product can be safely and efficiently applied.

## CONCLUSION

Studies on physico-chemical properties of EC formulations of Alphamethrin and Fenvalerate will ensure the percentage purity of active ingredient in both technical grades and formulations as per the labeled claim by the manufacturers, the suitability of the pesticide formulation for its intended use, safe and judicious use of pesticides and the shelf life of active ingredient. The results of the present studies will be further utilized for selection and also for it's application. Pesticides are produced by many manufacturers the composition of technical product may vary, particularly with respect to impurities and potentially also the toxicity of the product, depending on the manufacturing process and source of starting materials. Uncontrolled technical impurities accompanying any active

substance or base material used for the formulation could worsen the toxicological properties of final products and thereby cause additional adverse health and environmental effects. Thus present investigations have great importance as far as quality of pesticides is concerned as poor quality leads to poor efficacy so the users may increase doses or number of applications and unknowingly increase the risk to humans and environment.

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