Analysis of Synthetic PyrethroidsTo Study Physico-Chemical Properties For Quality Control: An Overview

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Abstract:

The biological activity of a pesticide to the target pest species is greatly influenced by its physical and chemical properties. 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 formulation to use for a particular situation. It also helps to understand the quality of pesticides.The paper aims to study the Physico-chemical properties of the pesticides to ensure that the product can be safely and efficiently applied. In the present studies the physico-chemical properties of various commercially available EC formulations of synthetic pyrethroids like Alphamethrin and Fenvelerate insecticides, which are widely used for plant protection are described as per BIS specifications.

Key words: pesticides, physico-chemical properties , BIS specifications

Introduction

Synthetic pyrethroids represent the first example of molecules emanating directly from nature being modified to enhance their activity. Pyrethroids today are the most widely used class of insecticides and are widely used in agricultural and household activities to control pests [1], and accounted for more than 25% of the worldwide insecticide market [2]. Their good spectrum of activity is against economic crop damaging pests [3].Synthetic pyrethroids has led to a series of new compounds with a very favorable combination of properties. Their characteristics include outstanding potency to insects, low toxicity to mammals associated with rapid metabolic breakdown and, in appropriate cases, adequate stability on plant surfaces even in bright sunlight and even the more stable compounds are degraded rapidly in soil, so if the trials at present in progress reveal no toxicological or environmental hazards, within a few years synthetic pyrethroids will be available to control a wide range of domestic, veterinary, horticultural, agricultural, and forest pests at low rates of application.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 specifications are developed with the basic objective to ensure the percentage purity of active ingredient in both technical grades and formulations as per the labelled claim by the manufacturers ,to ensure the suitability of the pesticide formulation for its intended use,to ensure safe and judicious use of pesticides and to ensure the shelf life of active ingredient.

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 resistant to Organochlorine, Carbamates and Organophosphorous insecticides. Thus it has great significance in plant protection.With this background, commercially available and widely used formulations of Fenvelarate 20 EC and Alphamethrin 10 EC insecticides can be assessed for their physico-chemical properties as per BIS specification in order to know their standard.

Material and Methods:

According to BIS specification the physical tests and chemical tests like cold test, flashpoint, emulsion stability, acidity/alkalinity of Alphamethrin[4] and Fenvelarate [5] active ingredient Fenvelarate [6] and Alphamethrin[7]

Physical tests: Following tests can be performed for samples of Fenvelarate 20 EC and Alphamethrin 10 EC

1. Cold test:

Procedure: Take 50ml sample in clean, transparent container and close with a cork or stopper fitted with thermometer. Cool the sample to 10^0c by placing the container in ice cold water. Stir the sample at short intervals for 1 hour maintaining the temperature of the sample at 10^0c. At the end of one hour, examine the material for any turbidity or separated solid or oily matter or both. [8]

2. Flash Point:

Procedure: Using Abel's apparatus, samples are tested for their flash point. In this method sample under test is placed in the cup of the Abel's apparatus and heated at a prescribed rate. A small test flame is directed into the cup at regular intervals, and the flash point is 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^{0}C. [9]

3. Emulsion stability:

Procedure: Take 2ml sample 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) is poured at 30^0c to the sample at the rate of 15 to 20 ml/min. During addition, the contents of the beaker is stirred continuously with the glass rod and when the volume of diluted emulsion in the beaker reaches 100ml then addition of standard hard water is stopped. The diluted emulsion is immediately transferred to clean and dry graduated cylinder. The cylinder is 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 is noted. [8]

Chemical tests:

1. Acidity/Alkalinity test:

Qualitative Test:

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

Determination of Acidity **[8]**

Procedure: weigh accurately 10g of the sample into a dry conical flask and dilute with 100ml water. Titrate the contents of the flask immediately with the standard sodium hydroxide solution using methyl red or bromocresol purple as the indicator. A blank reading with 100ml. of water is also determined.

Calculations:

Acidity (as H2SO4) 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.]

Determination of Alkalinity[8]

Procedure - Weigh accurately about 10 g ofthematerial into a dry conical flask and dilute with 100 ml of water. Titrate the contents of the flask immediately with the standard hydrochloric acid, using methyl red or bromocresol as the indicator. Alternatively, the end-point may be determined potentiometrically. Carry out a blank determination with 100 ml of water.

Calculations:

Alkalinity (as NaOH) percent by mass = $\frac{4.0(V-v)N}{M}$

where

V = volume in ml of the standard hydrochloric acid required for the test,

v =volume in ml of the standard hydrochloric acid required for the blank determination,

N = normality of the standard hydrechlerlc acid, and

M =- mass in g of the material taken for the test.

2. Active ingredient test:

For Fenvalerate pesticide, use GLC with FID for active ingredient determination and for Alphamethrin use High Performance Liquid Chromatography (HPLC)

.A.Determination of Active ingredient of Fenvalerate(20 EC) [6]

Working condition for analysis:-

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 meshes)
2. Detector system:	
Type	FID (Flame ionization detector)
Temperature:	
Column oven	270^0 C
InjectionPort	240^0 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	Minimum 92 percent (m/m)
B) Di(2-ethyhexyl) Phthalate	AR grade Spectroscopic grade.
C)Chloroform	

Procedure:

a) Preparation of Internal Standard Solution (Is):- Weigh accurately 0.5g DBP and dissolve in chloroform so as to made 1 liter of the solution.

b) Preparation of Standard Fenvalerate Solution: - Weigh accurately 0.075 g of standard Fenvalrate in a beaker and 2.5 ml of 'Is' solution. Shake well to dissolved the Fenvalerate. Transferred carefully into 50 ml volumetric flask and then made 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 $= \frac{RF \times A1 \times M1}{A2 \times M2} \times 100$

Where, RF = response factor.

A_1 = area of the Fenvalerate peak in the sample.

M_1 = mass in gram of internal standard added.

A_2 = area of the internal standard peak.

M_2 = mass in gram of the sample taken for test.

B. Determination of Active ingredient test of Alphamethrin[7]

C. Working condition for analysis:

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: AR grade

Procedure:

1. Preparation of sample solution: weigh 100mg of sample accurately in duplicate into two 100 ml standard volumetric flask. Dissolve the sample and made 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.

Conclusion:

Study on Physico-chemical properties of EC formulations of Alphamethrin and Fenvelarate 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 ensure the shelf life of active ingredient. Thus study of Physico-chemical properties has great significance as far as quality of pesticide is concerned as poor quality leads to poor efficacy, users may increase doses rates or number of applications and unknowingly increase the risk to humans and environment.

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