PESTICIDE – METIRAM + PYRACLOSTROBIN WG - SPECIFICATION

1.0 SCOPE:

This standard prescribes the requirements and the methods of sampling and test for Metiram + Pyraclostrobin Wettable Granules.

2.0 REFERENCE:

The following Indian Standards are necessary adjuncts to this standard:

IS.No.	**Title**
1070:1992	Reagent grade water (third revision)
6940:1982	Methods of test for pesticide and their formulations (first revision)
10946: 1984	Methods of sampling
8190 (Part II): 1988	Requirement for packing liquid pesticides

3.0 REQUIREMENTS

3.1 Physical The material shall comply with the physical requirements specified in Table 1.

3.1 Description

The material shall be in the form of fine homogenous dry granular particles, grayish brown in colour containing Metiram and Pyraclostrobin as active ingredients together with suitable carriers and necessary formulants. It shall be free flowing, free from extraneous materials and hard aggregates.

3.2 The material shall also comply with the requirements given in Table 1.

Table 1. Requirements for Metiram + Pyraclostrobin WG

Sr. No.	***Characteristic***	***Requirement***	***Method of test, Ref to***	
			Annex of this Standard	Cl. No. of IS : 6940 – 1982*
(1)	(2)	(3)	(4)	(5)
i)	Appearance	Grayish brown granules	------	------
ii)	Metiram content, % by weight. (Min.)	Nominal value as declared on the Container	Annex A	------
iii)	Pyraclostrobin content, %	Nominal value	Annex A	

	by weight. (Min.)	as declared on the Container		
iv)	Suspensibility, % by mass. (Min.)	80.0	------	11.2
v)	Wettability, (seconds) (Max.)	120	------	11.4
vi)	Wet Sieve Test (material passing through 75 μm sieve), % by mass. (Min.)	90.0	------	12.1
vii)	Attrition resistance, % by mass. (Min.)	90.0	------	14.1
viii)	Moisture content	2.0	------	4.1
ix)	pH (1% w/v aq. Dispersion)	6.0 to 8.0	------	CIPAC MT 75.3
x)	Persistent foam (mL) after one minute	10	------	CIPAC MT 47.1
xi)	Dust content (mg) (Max.)	30	------	CIPAC MT 171.1
xii)	Degree of dispersion (After 1 minute of stirring)	80.0	------	CIPAC MT 174

* Methods of tests for Pesticides and their formulations.

3.3 Chemical :

The material shall comply with the chemical requirement specified in3.3.1

3.3.1 Metiram and Pyraclostrobin content :

When determined by the method prescribed (enclosed), the observed Metiram and Pyraclostrobin content (w/w), of any of the sample shall not differ from the declared nominal value by more than the percent tolerance limits indicated below :

Nominal value, Percent	Tolerance limit, Percent
Up to 9	+10 -5
Above 9 and below 50	±5
50 and above	+5 - 3

3.3.1.1 The actual value of Metiram and Pyraclostrobin content in the formulations shall be calculated to the second decimal place and then rounded off to the first decimal place before applying the tolerance given in 2.3.1.

3.3.1.2 The average Metiram and Pyraclostrobin content of all samples taken shall not be less than the declared nominal content.

* Rules for rounding off numerical values (revised).

** Methods of test for pesticides and their formulations (First revisions).

4 PACKING

4.1 The product shall be packed in HDPE containers with minimum 1 mm thickness, which shall be further packed in 5 ply corrugated fiber board boxes as transport packing. The specifications for the containers shall be as agreed between the supplier and the manufacturer.

5.0 MARKING

5.1 The container shall bear legibly and indelibly the following information and any other information as is necessary under the Insecticides Act, 1968 and Rules.

a. Name of the material
b. Name of the manufacturer
c. Batch number
d. Date of manufacturer
e. Metiram content, percent (w/w)
f. Pyraclostrobin content, percent (w/w)
f. Net mass of content, percent (w/w)
g. Minimum cautionary notice worded as in the Insecticides Act 1968, and Rules.

6 SAMPLING

6.1 When bulk manufactured material is offered for inspection, representative sample of the material shall be drawn as prescribed in IS 10627: 1983 and if tested within 90 days of its manufacture , the criteria for conformity shall be the contents in percent (m/m), shall not be less than the declared nominal value. The upper limit for conformity shall be the same as those given in clause No. 3.2.1 of this standard. When the material is offered for inspection after 90 days of its manufacture, sampling shall be done as prescribed in IS 10627:1983, however the criteria for conformity of the material shall be the limit of tolerance given under 3.3.1 of this standard.

7 TESTS

7.1 Tests shall be carried out by the appropriate methods referred to in Col 4 and 5 of Table 1.

7.2 Quality of reagents

Unless specified otherwise, pure chemicals and reagent grade water (see IS: 1070:1992, third revision) shall be employed in tests.

Note - “Pure chemicals” shall mean chemicals that do not contain impurities which affect the results of analysis.

ANNEX-A
Method of Analysis for Metiram

A – 1 Principle

Metiram is digested with sulphuric acid and liberated carbon disulfide is allowed to react with alcoholic potassium hydroxide. Potassium methyl xanthogenate so produced is titrated with iodine.

A - 1.1 Reagents

1. Metiram reference standard known purity
2. Lead acetate solution – 10 percent (m/v)
3. Sulphuric acid – 1.1 n
4. Solution of potassium hydroxide in methanol – 2 N
5. Dilute acetic acid – 30 percent (v/v)
6. Standard iodine solution – 0.1 N
7. Starch indicator solution – freshly prepared
8. Phenolphthalein indicator solution – 1 percent (m/v) in 90 percent ethyl alcohol.

A - 1.2 Apparatus

The apparatus (fig. 1) shall be consists of a 200 ml flask fitted with a condenser with an outlet tube connected to two absorbers and a 500 ml filter flask serving as a bubbler. The latter is connected to a water suction pump.

A - 2 Procedure

Pipette 25 ml of the 2N methanolic potassium hydroxide solution into a 500 ml wide mouth Erlenmeyer flask which contains 250 ml distilled water. Add 3 drops of phenolphthalein indicator solution and titrate with 30 percent acetic acid solution till just neutral. Add 5 ml starch indicator solution and titrate against 0.1 N iodine. If more than 0.1 ml of Iodine solution is consumed, the methanolic potassium hydroxide solution cannot be used for the determination of metiram content.

Transfer by pipette 25 ml of 10 percent lead acetate solution to the lead acetate trap and 25 ml of 2 N potassium hydroxide to the potash trap.

Transfer 0.4 g of sample to an accurately weighed clean dry glass vial. Wipe the outside of the vial with a tissue and reweigh the vial plus the sample accurately to determine the exact mass of the sample. Place the vial in the 200 ml flask and connect it back to the assembly. The needle valve is closed and the assembly is connected to the vacuum line (suction pump). Slowly, open the valve and adjust the rate of bubbling in the absorbers to **12-15 bubbles per minute**. Turn on the cooling water and maintain the temperature of the water jacket at 25 ± 2°C throughout the experiment. By graduated cylinder add carefully 50 ml of boiling 1.1 N sulfuric acid through the inlet tube of the distillation head. Make sure that

the inlet tube dips in the liquid. Turn on the gas burner and heat the contents of the flask to the boiling point as rapidly as possible, being careful not to allow the solution to go into the condenser. Continue the heating and bubbling for **exactly 1 hour and 45 minutes**. After the digestion is complete, quickly disconnect the potash trap and rinse the contents into a 500 ml Erlenmeyer flask, with about 250 ml distilled water. Add 3 drops of phenolphthalein indicator solution and titrate the solution immediately with 30 percent acetic acid until the solution is just neutral. Cool and then titrate the neutralised solution immediately with 0.1 N iodine solution till the colour changes.

A - 3. Calculation

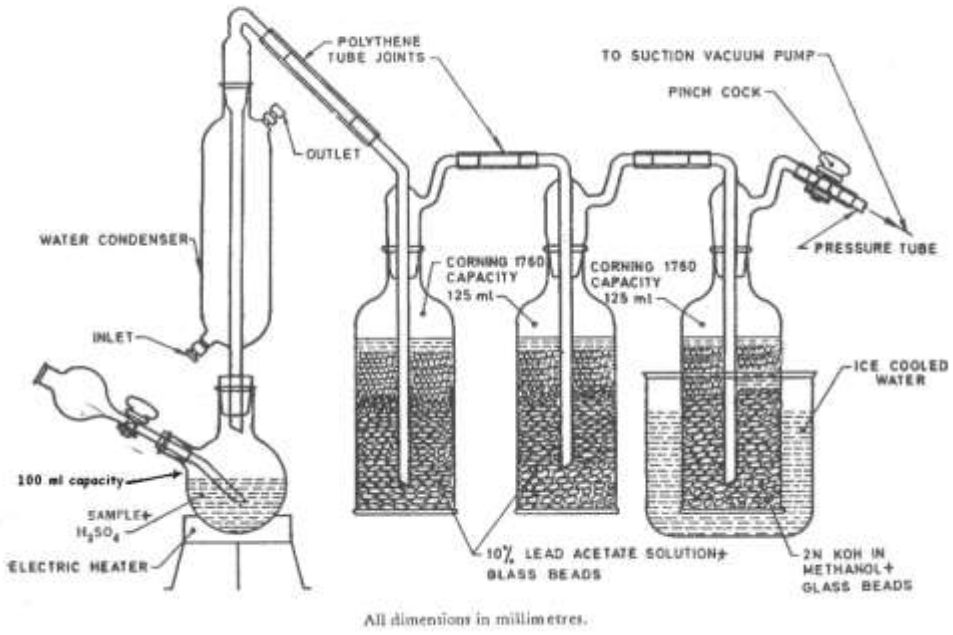
$$\text{Metiram content, percent by mass} = \frac{(V_1 - V_2) \times N \times 27.2}{M}$$

Where

V_1	=	volume, in ml, of iodine solution required for the sample;
V_2	=	volume, in ml, of iodine solution required for the blank;
N	=	normality of the iodine solution used; and
M	=	mass of the sample, in g, taken for the test

Figure – 1

Assembly of apparatus for the determination of Metiram Content



All dimensions in millimetres.

ANNEX-B
METHOD OF ANALYSIS FOR PYRACLOSTROBIN

1.0 Outline of the method

Pyraclostrobin content in Pyraclostrobin 20% w/w WG samples is determined by a HPLC method. The identity of the active ingredient is established by comparison with the equivalent authentic standard.

2.0 Reagents :

Acetonitrile - HPLC grade
Millipore water
Pyraclostrobin Analytical Standard
Ammonium acetate – AR grade

3.0 Apparatus :

3.1 HPLC system, consisting of,
3.1.1 HPLC pump
3.1.2 Automatic HPLC sampler
3.1.3 Stainless steel HPLC separating column, 250 x 4.0 mm, packed with Nucleosil CN 5 µm
3.1.4 HPLC UV detector with variable wavelength adjustment
3.1.5 Electronic data evaluation system (TSP) with evaluation software

3.2 Injection bottles

3.3 Standard laboratory equipment

3.4 Ultrasonic bath

4.0 Analytical procedure :

4.1 Chromatographic conditions :

Instrument	-	Shimadzu High Performance Liquid Chromatograph system equipped with LC-10 ATvp pump and SPD-10AV vp UV-VIS detector interfaced with CLASS LC-10 software system.
Column used	-	Phenomenex C_{18} (25cm length x 4.6mm i.d)
Mobile phase	-	Acetonitrile : Water + 771 mg ammonium Acetate (750:250+ 771 mg)
Wave length	-	275 nm

Flow rate - 1.6 ml/min

Retention time (approximate)

Pyraclostrobin - 6.2 minutes

4.2 Sample Preparation :

4.2.1 Standard Solution

Weigh about 15 mg of Pyraclostrobin reference standard (C1) into a 25 ml volumetric flask. Dissolve in 15 ml acetonitrile and make up to the mark with water. Then 2.5 ml of the solution should be pipette out into a 25 ml standard flask and add 15 ml of acetonitrile and make up to the mark with water. The diluted standard should be used as working standard solution.

4.2.2 Preparation of sample solution:

Weigh in duplicate (S1 and S2) about 75 mg of Pyraclostrobin 20% WG into a 25 ml standard flask and add 5 ml water. When the granules disintegrated, 15 ml of acetonitrile should be added and made up to the mark with water. Then 2.5 ml of this solution should be pipette out into a 25 ml standard flask and 15 ml of acetonitrile should be added and made up to the mark with water. This diluted standard is used as working sample solution.

4.3 Sample analysis:

Inject in the sequence C1, S1R1, S1R2 and analyse for Pyraclostrobin content.

5.0 Calculation :

$$\text{Pyraclostrobin content (\% w/w)} = \frac{H_w \times M \times P}{H_s \times w}$$

where,

H_s - Peak area of Pyraclostrobin calibration solution (µv-sec)
H_w - Peak area of Pyraclostrobin sample solution (µv-sec)
M - Mass of Pyraclostrobin in calibration solution (mg)
w - Mass of formulation sample taken (mg)
P - Purity of Pyraclostrobin reference standard (%)