FOREWORD

(*Formal clause would be added later)*

1 SCOPE

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

2 REFERENCES

The standards, given below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards.

IS No.	*Title*
8190 (Part 2) : 1988	Requirements for packing of pesticides Part 2 liquid pesticides (*second revision*)
1070 : 1992	Reagent grade water - Specification (*third Revision*)
6940 : 1982	Methods of test for pesticide and their formulations (*first Revision*)
10627 : 1983	Methods for sampling of pesticidal formulations

3 REQUIREMENTS

3.1 Physical

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

3.1.1 *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.

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

TABLE 1 REQUIREMENTS FOR METIRAM + PYRACLOSTROBIN WG

(*Clause* **3.1** and **7.1**)

Sl. No.	**Characteristic**	**Requirement**	**Method of test, Refer to**
(1)	(2)	(3)	(4)
i)	Metiram content, % by weight. (*Min)*	Nominal value as declared on the Container	Annex A
ii)	Pyraclostrobin content, % by weight. (*Min*)	Nominal value as declared on the Container	Annex A
iii)	Suspensibility, % by mass. (*Min*)	80.0	IS 6940
iv)	Wettability, (seconds) (*Max*)	120	IS 6940
v)	Wet Sieve Test (material passing through 75 µm sieve), % by mass. (*Min*)	90.0	IS 6940
vi)	Attrition resistance, % by mass. (*Min*)	90.0	IS 6940
vii)	Moisture content	2.0	IS 6940
viii)	pH (1% w/v aq. Dispersion)	6.0 to 8.0	Annex B
ix)	Persistent foam (mL) after one minute	10	Annex C
x)	Dust content (mg) (*Max*)	30	Annex D
xi)	Degree of dispersion (After 1 minute of stirring)	80.0	Annex E

3.2 Chemical

The material shall comply with the chemical requirement specified in3.2.1

3.2.1 *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, Percent*	
Up to 9	+10 -5	of the nominal value
10 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 **3.3.1**.

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

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 MARKING

5.1 The containers shall be securely closed and shall be bear legibly and indelibly the following information in addition to any other information as required under the *Insecticides Act,* 1968 and Rules framed thereunder:

a) Name of the material;

b) Name and address of the manufacturer;

c) Batch number;

d) Date of manufacture;

e) Date of expiry;

f) Net mass of content, percent (*m/m*);

g) Nominal Metiram and Pyraclostrobin content, percent (*m/m*);

h) Cautionary notice as worded in the *Insecticides Act*, 1968, and Rules framed thereunder; and

j) Any other information required under the *Legal Metrology* (*Packaged Commodities*) *Rules,* 2011.

5.2 BIS Certification Marking

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the *Bureau of Indian Standards Act*, 2016 and the Rules and Regulations framed thereunder, and the products may be marked with the Standard Mark.

6 SAMPLING

6.1 When freshly manufactured material in bulk quantity is offered for inspection, representative samples of the material shall be drawn and tested as prescribed in IS 10627 within 90 days of its manufacture. When the material is offered for inspection after 90 days of its manufacture, sampling shall be done as prescribed in IS 10627. However, the criteria for conformity of the material when tested, shall he the limits of tolerances, as applicable over the declared nominal value and given under clause **3.3.1** of the standard.

7 TESTS

7.1 Tests shall be carried out by the appropriate methods referred to Table **1**

7.2 Quality of Reagent

Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070) shall be employed in tests.

NOTE – 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

ANNEX A

[*Table* 1, *Sl. No.* (i)]

DETERMINATION OF MERITAM CONTENT

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-2 REAGENTS

Metiram reference standard known purity

Lead acetate solution – 10 percent (*m/v*)

Sulphuric acid – 1.1 n

Solution of potassium hydroxide in methanol – 2 N

Dilute acetic acid – 30 percent (*v/v*)

Standard iodine solution – 0.1 N

Starch indicator solution – freshly prepared

Phenolphthalein indicator solution – 1 percent (*m/v*) in 90 percent ethyl alcohol**.**

A - 2.2 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–3 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-4 CALCULATION

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.

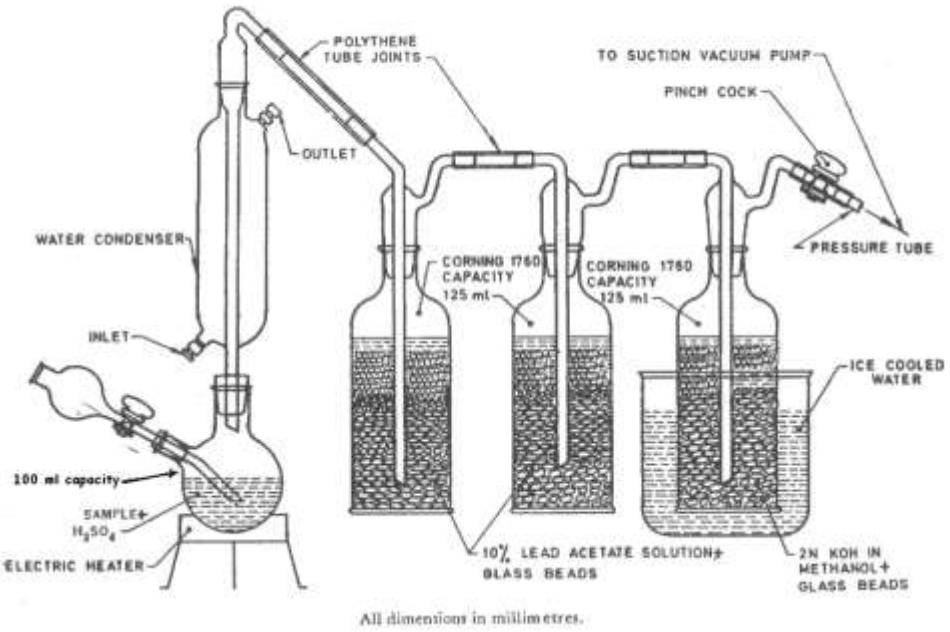

Figure – 1

Assembly of apparatus for the determination of Metiram Content

ANNEX A

[*Table* 1, *Sl. No.* (ii)]

DETERMINATION OF PYRACLOSTROBIN CONTENT

B-1 PRINCIPLE

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.

B-2 REAGENTS

Acetonitrile - HPLC grade

Millipore water

Pyraclostrobin Analytical Standard

Ammonium acetate – AR grade

B-3 APPARATUS

B-3.1 HPLC system, consisting of,

B-3.1.1 HPLC pump

B-3.1.2 Automatic HPLC sampler

B-3.1.3 Stainless steel HPLC separating column, 250 x 4.0 mm, packed with Nucleosil CN 5 µm

B-3.1.4 HPLC UV detector with variable wavelength adjustment

B-3.1.5 Electronic data evaluation system (TSP) with evaluation software

B-3.2 Injection bottles

B-3.3 Standard laboratory equipment

B-3.4 Ultrasonic bath

B-4 ANALYTICAL PROCEDURE

B-4.1 Chromotographic condition

Instrument	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	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
Injection Volume	5 µL
Flow rate	1.6 ml/min
Retention time (approximately) Pyraclostrobin	6.2 min

B-4.2 Sample Preparation

B-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.

B-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**.**

B-4.2.3 *Sample analysis*

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

B-5 Calculation

Pyraclostrobin content, percent by mass = $\frac{H_W \times M \times P}{H_S \times w}$

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 (%)

ANNEX C

[*Table* 1, *Sl. No.* (i)]

DETERMINATION OF PERSISTANT FOAM IN MERITAM AND PYRACLOSTROBIN CONTENT

The mass of sample to be taken is that mass required to make 200ml of a suspension with a concentration recommended in the directions for use supplied with the product. Where several concentrations are recommended, the maximum concentration shall be used. 180 ml of CIPAC standard water C was taken into a 250 ml measuring cylinder standing on a top pan balance. About 0.5 g of sample was weighed into a 50 ml beaker and was transferred quantitatively to the cylinder containing 180 ml of CIPAC standard water C and finally the volume was made up to 200 ml in the cylinder. The cylinder was stoppered and was invert 30 times. The stoppered cylinder was placed upright on the bench and stopwatch was immediately started the volume of foam produced and remaining after 1 minute was noted.

ANNEX D

[*Table* 1, *Sl. No.* (x)]

DETERMINATION OF DUST IN MERITAM AND PYRACLOSTROBIN CONTENT

Gravimetric method

Filter disc was weighed to the nearest 0.1 mg (W_1 g) and was put on the filter plate of the glass filter. The glass filter was connected with tubing to an air flow meter and a vacuum pump and then the glass filter was plugged into a measuring box. Vacuum pump was started and was adjusted the air flow of 15 lit. per min. 30 g of sample was weighed in a glass beaker to the nearest 0.1 g and was transferred with a single action into the pouring tube. At the same time stop watch was started. The liberated airborne dust was sucked off for 60 seconds and collected on the filter. Filter disc was removed with tweezers and was weighed to the nearest 0.1 mg (W_2 g). The difference in weights (W_2-W_1) was defined as the 'collected dust'.

ANNEX E

[*Table* 1, *Sl. No.* (xi)]

DETERMINATION OF DEGREE OF DISPERSIBILITY IN MERITAM AND PYRACLOSTROBIN CONTENT

E-1 PROCEDURE

A known amount of a water granule (WG) is added to a define volume of water and mixed by stirring to form a suspension. After standing for a short period, the top nine-tenth are drawn off and remaining tenth dried and determined gravimetrically. The method is virtually a shortened test of suspensibility and is appropriate for establishing the ease with which a WG dispersed uniformly in water.

Filled the tared beaker with 900 ml of CIPAC water D at 20 ± 1 °C. The stirrer was centrally located in the beaker and positioned in such a way that bottom of the stirrer blades were 15 mm above the base of the beaker. The pitch of the stirrer blades and the direction of rotation were such that the propeller pushes the water upward. Switched on the the stirrer with the speed set to 300 rpm.

Added a sample WG (approximately 9 gm weight to ± 0.1 gm) to the stirred water and continue the stirring 1 min. then switched off the stirrer and allowed the suspension to stand undisturbed for 1 min. withdrawn by means of a vaccum pump, nine- tenth (810 ml) of the suspension. Carried out the operation in 30 to 60 s by maintaining the tip of the glass tube just below the falling level of the suspension, taken care to minimize any disturbance of the suspension. Determined by gravimetric means the solid obtained in the remaining 90 ml in the beaker. This was done by evaporating the liquid in the rotary vacuum evaporator and dried to constant weight at temperature 60 to 70 °C in oven.

E-2 CALCULATION

Dispersibility, percent by mass = $\frac{10}{9} \times \frac{m-W}{m} \times 100$

Where

W = Mass of residue after drying (g)

m = mass of sample taken (g)