Metiram 44 % + Dimethomorph 9 % WG

FOREWORD

Metiram 44% + Dimethomorph 9% Water Dispersible Granule (Acrobat Top 53% WG) is used as a Fungicide in Agriculture.

Metiram 44% + Dimethomorph 9% Water Dispersible Granule is generally manufactured to contain Metiram 44% and Dimethomorph 9% (Acrobat Top 53% WG).

In the preparation of this standard due consideration has been given to the provisions of the *Insecticides Act*, 1968 and the Rules framed thereunder. However, this standard is subject to the restrictions imposed under these, wherever applicable.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 2022 ‘Rules for rounding off numerical values (*second revision*)’. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

1 SCOPE

1.1 This standard prescribes the requirements and the methods of sampling and test for Metiram 44% + Dimethomorph 9% Water Dispersible 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 1) : 1988	Requirement for packing solid pesticide
1070 : 1992	Reagent grade water - Specification (*third Revision*)
6940 : 1982	Methods of test for pesticide and their formulations (*first Revision*)
10946 : 1984	Method of sampling for technical grade pesticides

3 REQUIREMENTS

3.1 Constituents

The material shall consist of Metiram technical and Dimethomorph technical, together with suitable ingredients.

3.2 Physical

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

Table 1 Requirements for Metiram 44 % + Dimethomorph 9 % WG

Sl. No	**Characteristics**	**Requirement**	**Method of Test**	
			Annex of this Standard	**Cl. No. of 6940 : 1982**
1	Appearance	The material is in the form of free flowing granules	-	-
2	Metiram content (% w/w)	44	Annexure A	-
3	Dimethomorph content (% w/w)	9	Annexure A	
4	pH of 1% aq. Solution	6-8	-	MT 75.2

	(25±0.5°C)			
5	Wettability (Seconds) max	60	-	11.4
6	Wet sieve through 75 micron testsieve retained (% by mass) Max	2	-	MT 167/ 11.1
7	Degree of dispersion (% w/w)	80	-	MT 174
8	Suspensibility (% by mass) Min	80	-	11.2
9	Persistent foam after 1 minute (ml)	60	-	MT 47.2
10	Dustiness	30	-	MT 171
11	Flowability (formulation passing through 5 mm sieve after 20 drops) %w/w Min	90	-	MT 172
12	Attrition resistance (% by mass) Min	90	-	MT 178.2

3.3 Chemical

The material shall comply with the chemical requirements specified in **3.1** and **3.2**.

3.3.1 Metiram and Dimethomorph content: When determined by the method prescribed (enclosed), the observed Metiram and Dimethomorph 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	of the nominal value
	-5	
10 and below 50	±5	
50 and above	+5	
	-3	

3.3.1.1 The actual value of Metiram and Dimethomorph 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 Dimethomorph content of all samples taken shall not be less than the declared nominal content.

4 PACKING

4.1 The product shall be packed in 100 g, 250 g, 500 g & 1.0 kg HDPE containers. 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 Fluxapyroxad and Epoxiconazole 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 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 (w/w), 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 **3.2**.

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.

ANNEXURE A

METHOD OF ANALYSIS FOR DETERMINATION OF METIRAM AND DIMETHOMORPH CONTENT

A-1 PRINCIPLE

Metiram content in Metiram 44% + Dimethomorph 9% WG samples is determined by UV at 208 nm. The identity of the active ingredient is determined by a comparison to a calibration curve prepared from pure carbon disulphide standard solutions. Dimethomorph content in Metiram 44% + Dimethomorph 9% WG samples was determined by a HPLC method. The identity of the active ingredient was established in comparison with the equivalent authentic standard.

Metiram

A-2 REAGENTS

Stannous chloride (AR grade)
n-Heptane (HPLC Grade)
Millipore water
Carbon disulfide (for standard calibration curve)
Hydrochloric acid (Excel-R grade)
EDTA-Di sodium salt (AR grade)

Apparatus:

UV Spectrophotometer (Calibrated)
Heating water bath
Weighing balance (Calibrated)

A-3 PREPARATION OF REAGENTS

A-3.1 Reagents - A (10% EDTA in water)

Weighed around 50 g of EDTA in 500 ml glass beaker, added about 250 ml pre heated (90 - 100°C) Millipore water and heat with stirring on hot plate at 100°C until clear solution is obtained. Transferred the content of the beaker to 500 ml standard volumetric flask and dilute up to the mark with Millipore water. Stoppard the volumetric flask, shaken well and kept aside to attain the room temperature.

A-3.2 Reagent-B (10% $SnCl_2$ in concentrated Hydrochloric acid)

Around 50 g of $SnCl_2$ was weighed in 500 ml glass beaker. Added about 250 ml of concentrated HCl to the beaker. Stirred the solution with glass rod until the $SnCl_2$ gets dissolved in HCl, and transferred the solution to 500 ml standard volumetric flask and dilute up to the mark with concentrated HCl. Stoppered the volumetric flask, shaken well and kept aside for further use.

A- 4 Standard Calibration Curve (CS2)

Accurately 103.6 mg of CS2 was weighed in 10 ml standard volumetric flask, the weighed CS2 was then diluted with n-heptane up to the mark and labelled as Stock solution-A (10000 ppm).From the stock solution-A 1 ml was taken into 250 ml standard volumetric flask, 10 ml of Millipore water was added to 25 ml Reagent-A (10% EDTA in water),25 ml n-Heptane and 25 ml of Reagent-B (10% SnCl2 in conc. HCl). The volumetric flask was stoppered with greased glass stopper and sealed with parafilm and kept on water bath (@95°C) for 1 hour. After 1 hour the volumetric flask was removed from water bath and cooled under running tap water for 5 min to attain room temperature. The glass stopper was removed and the grease present on the mouth of volumetric flask was cleared with tissue paper. The contents of the flask were transferred to 125 ml separating funnel and the volumetric flask was rinsed with 10 ml of n-heptane and transferred to separating funnel. The lower aqueous layer was discarded and the organic layer was collected quantitatively in 100 ml standard volumetric flask. The separating funnel was rinsed with 10 ml of n-heptane and transferred to 100 ml volumetric flask containing heptane layer. The organic layer was diluted upto the mark with n-heptane and labelled as (Stock solution-B) 100 ppm. From the stock solution-B one ml was taken in 10 ml standard volumetric flask and diluted upto the mark with n-heptane and labelled as stock solution-C (10 ppm).

Dilute solutions were prepared as given in Table-01 from stock solution-C using 1 ml calibrated pipette. The absorbances (UV-spectrophotometer) of diluted solutions at 208 nm (0.01 ppm to 2.0 ppm) were read with n-heptane as blank. Standard calibration curve of absorbance against concentration (ppm) was plotted. The correlation co-efficient is 0.9996.

A-4.1 Sample Preparation

Around 100 mg of sample was weighed into four different 250 ml dried standard volumetric flasks,10 ml of Millipore water was added to each flask and shaken gently.

The sample solutions become milky white after addition of 10 ml Millipore water to each flask.25 ml of Reagent-A (10% EDTA in Water),25 ml of n-heptane, and 25 ml of Reagent-B (10% SnCl2 in conc.HCl) were added to each flask and swirled gently. Each volumetric flask was stoppered immediately with greased glass stoppers and sealed with parafilm. The volumetric flasks were kept for digestion on water bath (@ 95°C for minimum 60 minutes). After 60 minutes the four volumetric flasks were removed and cooled under running tap water for 5 minutes to attain room temperature. The stoppers were removed and the grease which remained on the mouth of volumetric flasks was cleared with tissue paper. The contents of all four flasks were transferred into 125 ml four different separating funnels. All the four volumetric flasks were rinsed with 10 ml of n- heptane and transferred to separating funnels. The lower aqueous layer was discarded and the organic layer was collected quantitatively in 100 ml four volumetric flasks. The solutions were diluted up to the mark with n-heptane labelled as (Stock solution -A). The volumetric flasks were shaken. From the above solution (Stock-A) each one ml was taken in 10 ml of four different standard volumetric flasks and diluted up to the mark with n-heptane (Stock-B). From the above solution (Stock –B) each one ml taken in to 50 ml four different

standard volumetric flasks and diluted up to the mark with n-heptane. The four volumetric flasks were shaken and immediately the absorbance was measured.

Amount of CS2 released:

Value of X x DF = Z mg CS2.
Dilution factor (DF) = 50

1088 mg Metiram = 608 mg of CS2 (Metiram contains 8 CS2 groups.)

Therefore,

Conversion Factor for Metiram = F1 = 1.89

Amount of Metiram in sample = Z x F1 = A mg of Metiram.
% Content of Metiram = (A / Qty of Metiram weighed) *100

Dimethomorph

A-5 Reagents

Acetonitrile - Merck India Limited, Mumbai
Water – Millipore purified
Ortho phosphoric acid Merck India Limited., Mumbai
Dimethomorph - Analytical Standard

A-5.1 Preparation of Calibration Solution

Weighed accurately 70.46 mg, 70.52 mg of Dimethomorph analytical standard was weighed into two different 50 mL volumetric flasks and a small amount of acetonitrile was added to it. The flasks were sonicated for 5 minutes. The flasks were allowed to cool to room temperature. The flasks were filled up to the mark using acetonitrile and mixed well. From these flasks, 5.0 mL was pipetted out and transferred into two different 50 mL volumetric flasks, diluted and filled up to the mark using acetonitrile and coded as C1 and C2.

A-5.2 Preparation of sample solution

Weighed accurately 83.84 mg and 82.91 mg of the test item was weighed into two different 50.0 mL volumetric flasks. A 5.0 ml of water was added to suspend the sample. The flasks were sonicated for 5 minutes. The flasks were allowed to cool to room temperature. The flasks were filled up to the mark using acetonitrile and mixed well. From these flasks, 5.0 mL solution was pipetted out and transferred into two different

50.0 mL volumetric flasks, diluted and filled up to the mark using acetonitrile and coded as S1 and S2. The solutions were centrifuged and transferred in to a HPLC vials for analysis.

A-5.3 Sample analysis

The solutions were injected in the sequence C1, S1R1, S1R2, C1, C2, S2R1, S2R2, C2 and calculated for Dimethomorph content.

A-6 CHROMATOGRAPHIC SEPERATION PARAMETERS: DIMETHOMORPH

Instrument	Agilent HPLC 1200 series system equipped with Quaternary pump, degasser column oven
Detector	DAD detector interfaced with Chemstation software system.
Column used	Agilent zorbax SB C18 (75mm length x 4.6mm x 3.5µm)
Mobile phase	Acetonitrile : 0.1% H3PO4 in milli-Q-water (35:65)
Wave length	246 nm
Flow rate	1.00 ml/min
Injection volume	15 µL
Retention time(approximately) Dimethomorph	
Cis	9.3 minutes
Trans	10.5 minutes

A-6.1 FORMULA FOR CALCULATION:

DIMETHOMORPH

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

Where

Hs = Peak area of Dimethomorph in the Standard solution (mAU*sec)

Hw = Peak area of Dimethomorph in the sample solution (mAU*sec)

M = Mass of Dimethomorph in the Standard solution (mg)

w = Mass of sample taken (mg)

P = Purity of Dimethomorph reference standard (%)

METIRAM

CS_2 content = $\frac{(Absorbance - Intercept)}{Slope} \times Dilution\ factor\ (DF)$

Metiram Content (% w/w) = $\frac{(CS_2 content\ x\ conversion\ factor)}{Weight\ of\ Sample} \times 100$

Metiram Content (% w/w) = $\frac{(CS_2 \text{ content x conversion factor})}{\text{Weight of the sample}}$