

AGP:CP/314

FAO SPECIFICATIONS FOR PLANT PROTECTION PRODUCTS

METRIBUZIN

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

Rome, 1994

Group on Pesticide Specifications

FAO Panel of Experts on Pesticide Specifications,
Registration Requirements and Application Standards

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CONTENTS

DISCLAIMER	1
SUBMISSION OF DRAFT SPECIFICATIONS TO FAO.....	5
INFORMATION	7
METRIBUZIN TECHNICAL	8
METRIBUZIN TECHNICAL CONCENTRATES.....	9
METRIBUZIN WETTABLE POWDERS	10
METRIBUZIN AQUEOUS SUSPENSION CONCENTRATES.....	12
METRIBUZIN WATER DISPERSIBLE GRANULES.....	15

DISCLAIMER¹

FAO specifications are developed with the basic objective of promoting, as far as practicable, the manufacture, distribution and use of pesticides that meet basic quality requirements.

Compliance with the specifications does not constitute an endorsement or warranty of the fitness of a particular pesticide for a particular purpose, including its suitability for the control of any given pest, or its suitability for use in a particular area. Owing to the complexity of the problems involved, the suitability of pesticides for a particular purpose and the content of the labelling instructions must be decided at the national or provincial level.

Furthermore, pesticides which are manufactured to comply with these specifications are not exempted from any safety regulation or other legal or administrative provision applicable to their manufacture, sale, transportation, storage, handling, preparation and/or use.

FAO disclaims any and all liability for any injury, death, loss, damage or other prejudice of any kind that may arise as a result of, or in connection with, the manufacture, sale, transportation, storage, handling, preparation and/or use of pesticides which are found, or are claimed, to have been manufactured to comply with these specifications.

Additionally, FAO wishes to alert users to the fact that improper storage, handling, preparation and/or use of pesticides can result in either a lowering or complete loss of safety and/or efficacy.

FAO is not responsible, and does not accept any liability, for the testing of pesticides for compliance with the specifications, nor for any methods recommended and/or used for testing compliance. As a result, FAO does not in any way warrant or represent that any pesticide claimed to comply with a FAO specification actually does so.

¹ This disclaimer applies to all specifications published by FAO.

INTRODUCTION TO FAO SPECIFICATIONS DEVELOPED UNDER THE OLD PROCEDURE

Between 1975 and 2000, FAO published booklets of specifications for technical materials and related formulations of plant protection products. Revisions of, and additions to, already published specifications will be issued when necessary. However, all changes and revisions of FAO specifications are now subject to the new procedure described in the *Manual on the development and use of FAO and WHO Specifications for Plant Protection Products*, FAO Plant Production and Protection Paper No. 173, Rome 2002 (*Revised First Edition* available only on the FAO home page of the Internet at: <http://www.fao.org/ag/agp/agpp/pesticid/>)

FAO specifications developed under the old procedure are based on the requirements defined in the Fourth Edition of the *Manual on the development and use of FAO specifications for plant protection products*, Plant Production and Protection Paper No. 128, Rome 1995.

This manual contained detailed definitions and other essential background information on basic procedures and technical principles adopted by the group on Pesticide Specifications of the FAO Panel of Experts on Pesticide Specifications, Registration Requirements, Application Standards and Prior Informed Consent, such as:

1. Categories of Specifications (Section 3.1 of the Manual)

FAO Tentative Specifications (Code 'S/T', formerly 'TS') are those which have been recommended by FAO as preliminary specifications and which are based on minimum requirements. The methods of analysis cited are normally supplied by the manufacturer or may already have been published or be the subject of collaborative work.

FAO Provisional Specifications [Code 'S/P', formerly ('S')] are those for which more evidence of the necessary parameters is available and where some collaborative study of the methods of analysis has been carried out.

FAO (full) Specifications (Code 'S/F', formerly 'S').

Specifications that have all necessary requirements together with CIPAC (full) methods, or other collaboratively studied (proven) methods.^{2,3}

Wherever possible, standards for apparatus and common names for pesticides are those approved by the International Organization for Standardization (ISO).

2. Expression of active ingredient content (Section 4.2.5 of the Manual)

- for solids, liquid technical materials, volatile liquids (of maximum boiling point 50°C) and viscous liquids (with minimum kinematic viscosity of $1 \times 10^3 \text{ m}^2/\text{s}$ at 20°C) the FAO Specification shall be based on expression of the content as g/kg;

- for all other liquids the active ingredient content of the product shall be declared in terms of g/kg *or* g/l at 20°C. If the customer requires both g/kg *and* g/l at 20°C, then in case of dispute the analytical results shall be calculated as g/kg.

3. Tolerance on content (Section 4.2.7 of the Manual)

A declared content of active ingredient must be included in all specifications, and one of the problems immediately arising is the level of tolerance acceptable about the nominal figure. The tolerance is influenced by (a) the reproducibility of the method of analysis, (b) the sampling error and (c) the manufacturing variance.

Allowable variations in analytical results (i.e. tolerances in content of active ingredient) with respect to specific pesticide consignments are intended to cover reasonable variations in the contents of active ingredients. For examples of such tolerances, see the table in Section 4.2.7 of the Manual.

4. Containers/packaging

FAO guidelines are in preparation.

Containers shall comply with pertinent national and international transport and safety regulations.

Technical materials, dustable powders and granules

Containers shall be suitable, clean, dry and as specified, and shall not adversely affect, or be affected by, the contents, but shall adequately protect them against external conditions.

Wettable powders

The product shall be packed in suitable, clean, dry containers as specified in the order. The container shall provide all necessary protection against compaction, atmospheric moisture, loss by vaporization and/or contamination to ensure that the product suffers no deterioration under normal transit and storage conditions.

The product shall be protected by an adequate moisture barrier. This may be a suitable bag of polyethylene or alternative means of giving equal or better protection.

Solutions and emulsifiable concentrates

Containers shall be lined, where necessary, with a suitable material, or the interior surfaces shall be treated to prevent corrosion and/or deterioration of the contents.

Additional information should be given in all specifications where particular pesticides present problems in packaging.

5. Biological information

Phytotoxicity

No test can be specified to cover the possible phytotoxicity of a formulation to all crops. When a crop is not mentioned in the instructions for use, purchasers should check with the supplier that the material is suitable, always provided that such a use is not restricted or legally forbidden.

Wetting of crops

The dilute spray should satisfactorily wet the leaves of the specified crops when used in accordance with the instructions. Test method MT 53.2, CIPAC F, p.162, may be useful.

¹ *Should national pesticide specifications developed from these approved FAO specifications deviate from them, the National Authority responsible for making such changes is requested to inform the FAO Plant Protection Service of the nature of, and the reasons for, the modifications.*

² *Methods of analysis and miscellaneous techniques referred to in these specifications have been developed and adopted by CIPAC (Collaborative International Pesticides Analytical Council Ltd.). See CIPAC Handbooks 1 (1970), 1A (1980), 1B (1983), 1C (1985), D (1988), E (1993), F (1995), G (1995), CIPAC Proceedings 1980 and 1981, obtainable from Black Bear Press Limited, King's Hedges Road, Cambridge CB4 2PQ, England. The page numbers of specific methods are given in parentheses in the specifications. Copies of methods not yet published can be obtained from the FAO Plant Protection Service.*

³ *Information on standard waters for laboratory evaluation of pesticidal formulations will be found in CIPAC Monograph 1, Standard Waters and an FAO Survey on Naturally Occurring Waters (1972), Black Bear Press Limited, King's Hedges Road, Cambridge CB4 2PQ, England.*

SUBMISSION OF DRAFT SPECIFICATIONS TO FAO

Any organization, commercial firm or interested individual is encouraged to submit relevant specifications, or proposals for revision of existing specifications, for pesticide products for consideration and possible adoption by FAO. Correspondence should be addressed to the Pesticide Management Group, Plant Production and Protection Division, FAO, Viale delle Terme di Caracalla, 00153 Rome, Italy.

General guidelines on preparing draft specifications are given in the *Manual on the development and use of FAO and WHO Specifications for Plant Protection Products*, FAO Plant Production and Protection Paper No. 173, Rome 2002 (Revised First Edition available only on the FAO home page of the Internet at: <http://www.fao.org/ag/agp/agpp/pesticid/>).

Specifications which are considered suitable for further processing are assigned priorities and circulated to appropriate organizations and specialists to comment. Comments, together with other relevant information, are then reviewed in detail by the Group on Specifications of the FAO Panel of Experts on Pesticide Specifications, Registration Requirements, Application Standards and Prior Informed Consent. The drafts are converted into FAO Provisional Specifications, or full FAO Specifications.

METRIBUZIN

4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5(4*H*)-one

INFORMATION

COMMON NAME: metribuzin (ISO)

STRUCTURAL FORMULA:

EMPIRICAL FORMULA: $C_8H_{14}N_4OS$

RMM: 214.3

CAS REGISTRY NUMBER: 21087-64-9

CIPAC CODE NUMBER: 283

CHEMICAL NAMES:

4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5(4*H*)-one (IUPAC)

4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one (CA)

METRIBUZIN TECHNICAL

FAO Specification 283/TC/S/F (1991)

.1 DESCRIPTION

The material shall consist of metribuzin together with related manufacturing impurities and shall be a white to off-white powder free from visible extraneous matter and added modifying agents.

.2 ACTIVE INGREDIENT

.2.1 Identity tests (283/TC/(M)/2, CIPAC D, p.138)

An identity test is required if the identity of the active ingredient is in doubt.

.2.2 Metribuzin (283/TC/(M)/3, CIPAC D, p.138)

The metribuzin content shall be declared (not less than 930 g/kg) and, when determined, the content obtained shall not differ from that declared by more than ± 20 g/kg.

.3 IMPURITIES

.3.1 Water (MT 30.1, CIPAC 1, p.897)

Maximum: 10 g/kg.

.3.2 Material insoluble in acetone (MT 27, CIPAC 1, p.894)

Maximum: 10 g/kg.

.4 PHYSICAL PROPERTIES

.4.1 Acidity/alkalinity (MT 31.1, CIPAC 1, p.903)

Maximum acidity: 4 g/kg calculated as H₂SO₄.

Maximum alkalinity: 3 g/kg calculated as NaOH.

METRIBUZIN TECHNICAL CONCENTRATES

FAO Specification 283/TK/S/F (1991)

.1 DESCRIPTION

The material shall consist of metribuzin together with related manufacturing impurities and shall be a fine white powder, free from visible extraneous matter and added modifying agents except the stabilizer.

.2 ACTIVE INGREDIENT

.2.1 Identity tests (283/WP/(M)/2, CIPAC D, p.139)

An identity test is required if the identity of the active ingredient is in doubt.

.2.2 Metribuzin (283/WP/(M)/3, CIPAC D, p.139)

The metribuzin content shall be declared (not less than 800 g/kg) and, when determined, the content obtained shall not differ from that declared by more than ± 20 g/kg.

.3 IMPURITIES

.3.1 Water (MT 30.1, CIPAC 1, p.897)

Maximum: 15 g/kg.

.3.2 Material insoluble in acetone (MT 27, CIPAC 1, p.894)

Maximum: 150 g/kg.

.4 PHYSICAL PROPERTIES

.4.1 pH range (MT 75, CIPAC 1A, P.1589)

pH range: 6 to 8.

.4.2 Dry sieve test (MT 59.1, CIPAC 1, p.978)

Maximum: 5% retained on a 75 μ m test sieve.

Not more than $(0.005 \times X)\%$ of the mass of the sample used for the determination shall be present as metribuzin in the residue on the sieve, where X is the metribuzin content (g/kg) found under .2.2.

METRIBUZIN WETTABLE POWDERS

FAO Specification 283/WP/S/F (1991)

.1 DESCRIPTION

The material shall consist of a homogeneous mixture of technical metribuzin, complying with the requirements of FAO Specification 283/TC/S/F or TK/S/F (1991), together with filler(s) and any other necessary formulants. It shall be in the form of a fine powder, free from visible extraneous matter and hard lumps.

.2 ACTIVE INGREDIENT

.2.1 Identity tests (283/WP/(M)/2, CIPAC D, p.139)

An identity test is required if the identity of the active ingredient is in doubt.

.2.2 Metribuzin (283/WP/(M)/3, CIPAC D, p.139)

The metribuzin content shall be declared (g/kg) and, when determined, the content obtained shall not differ from that declared by more than the following amounts:

<u>Declared content</u>	<u>Permitted tolerance</u>
250 to 500 g/kg	± 5% of the declared content
above 500 g/kg	± 25 g/kg

.3 IMPURITIES

.3.1 Water (MT 30.1, CIPAC 1, p.897)

Maximum: 25 g/kg.

.4 PHYSICAL PROPERTIES

.4.1 pH range (MT 75, CIPAC 1A, p.1589)

pH range: 7 to 9.

.4.2 Wet sieve test (MT 59.3, CIPAC 1, p.981)

Maximum: 2% retained on a 75 µm test sieve.

.4.3 Suspensibility (MT 15.1, CIPAC 1, p.861) (Notes 1 and 2)

A minimum of 50% of the metribuzin content found under .2.2 shall be in suspension after 30 min in CIPAC Standard Water C at 25 °C (Notes 3 and 4).

Alternatively, if the buyer requires other CIPAC Standard Waters to be used, then this shall be specified when ordering.

.4.4 Persistent foam (MT 47, CIPAC 1, p.954) (Note 5)

Maximum: 15 ml after 1 min.

.4.5 Wetting of the product (MT 53.3.1, CIPAC 1, p.967)

The product shall be completely wetted in 3 min without swirling.

.5 STORAGE STABILITY

.5.1 Stability at 54 °C (MT 46.1.1, CIPAC 1, p.951)

After storage at 54 ± 2 °C for 14 days, the determined average active ingredient content must not be lower than 97% relative to the determined average content found before storage (Note 6) and the product shall continue to comply with .4.1, .4.2 and .4.3.

Note 1 This test will normally only be carried out after the heat stability test .5.1.

Note 2 Chemical assay is the only fully reliable method of measuring the mass of active ingredient still in suspension. However, simpler methods such as gravimetric and solvent extraction determination may be used on a routine basis provided that these methods have been shown to give equal results to those of the chemical assay method. In case of dispute, the chemical method shall be the "Referee method".

Note 3 Unless another temperature is specified.

Note 4 The product should be tested at the highest and lowest rates of use recommended by the supplier, provided this does not exceed the conditions given in method MT 15.1, CIPAC 1, p.891.

Note 5 The concentration of sample to be used in the test should be specified at the highest rate of use recommended by the supplier.

Note 6 Samples of the product taken before and after the storage stability test should be analysed together after the test in order to reduce the analytical error.

METRIBUZIN AQUEOUS SUSPENSION CONCENTRATES

FAO Specification 283/SC/S/F (1991)

.1 DESCRIPTION

The material shall consist of a suspension of fine particles of technical metribuzin, complying with the requirements of FAO specification 283/TC/S/F (1991), in an aqueous phase together with suitable formulants. After gentle agitation, the material shall be homogeneous (Note 1) and suitable for further dilution in water.

.2 ACTIVE INGREDIENT

.2.1 Identity tests (283/SC/(M)/2, CIPAC D, p.140)

An identity test is required if the identity of the active ingredient is in doubt.

.2.2 Metribuzin (283/SC/(M)/3, CIPAC D, p.140)

The metribuzin content shall be declared (g/kg or g/l at 20 °C Note 2) and, when determined, the content obtained shall not differ from that declared by more than the following amounts:

<u>Declared content</u>	<u>Permitted tolerance</u>
250 to 500 g/kg or g/l	± 5% of the declared content
above 500 g/kg or g/l	± 25 g/kg or g/l

.3 IMPURITIES

.3.1 Not relevant.

.4 PHYSICAL PROPERTIES

.4.1 Mass per millilitre at 20 °C (MT 3.3, CIPAC 1C, p.2247) (Note 2)

If required, the range of the mass per millilitre (g/ml) at 20 °C shall be declared.

.4.2 pH range (MT 75, CIPAC 1A, p.1589)

pH range: 6 to 7.

.4.3 Pourability (MT 148, CIPAC 1C, p.2282) (Note 3)

Maximum "rinsed residue": 0.5%.

.4.4 Spontaneity of dispersion (MT 160, CIPAC 1C, p.2291) (Note 4)

A minimum of 60% of the metribuzin content found under .2.2 shall be in suspension after 5 min in CIPAC Standard Water C at 25 °C (Note 5).

Alternatively, if the buyer requires other CIPAC Standard Waters to be used, then this shall be specified when ordering.

.4.5 Suspensibility (MT 161, CIPAC 1C, p.2294) (Notes 4 and 6)

A minimum of 90% of the metribuzin content found under .2.2 shall be in suspension after 30 min in CIPAC Standard Water C at 25 °C (Note 5).

Alternatively, if the buyer requires other CIPAC Standard Waters to be used, then this shall be specified when ordering.

.4.6 Wet sieve test (MT 59.3, CIPAC 1, p.981)

Maximum: 1% of the product shall be retained on a 75 µm test sieve.

.4.7 Persistent foam (MT 47.2, CIPAC 1C, p.2249)

Maximum: 20 ml after 1 min (Note 7).

.5 STORAGE STABILITY

.5.1 Stability at 0 °C (MT 39.1, CIPAC 1, p.930)

After storage at 0 ± 1 °C for 7 days, the product shall continue to comply with .4.4, .4.5 and .4.6.

.5.2 Stability at 54 °C (MT 46.1, CIPAC 1, p.951)

After storage at 54 ± 2 °C for 14 days, the determined average active ingredient content must not be lower than 97% relative to the determined average content found before storage (Note 8) and the product shall continue to comply with .4.2, .4.3, .4.4, .4.5 and .4.6.

Note 1 Before sampling to verify the product quality, inspect the commercial container carefully. On standing, suspension concentrates usually develop a concentration gradient from the top to the bottom of the container. This may even result in the appearance of a clear liquid on the top and/or of sediment on the bottom. Therefore, before sampling, homogenize the product according to the instructions given by the manufacturer or, in the absence of such instructions, by gentle shaking of the commercial container (for example by inverting the closed container several times). Large containers must be opened and stirred adequately. After this procedure, the container should not contain a sticky layer of non-dispersed product at the bottom. A suitable and simple method of checking for a non-dispersed sticky layer "cake" is by probing with a glass rod or similar device adapted to the size and shape of the container. All the physical and chemical tests must be carried out on a laboratory sample taken after the recommended homogenization procedure.

Note 2 Unless homogenization is carried out carefully, it is possible for the sample to become aerated. This can lead to errors in the determination of the density and in calculation of the active ingredient content in g/l if methods other than MT 3.3 are used.

If the buyer requires both g/kg and g/l at 20 °C  then in case of dispute the analytical results shall be calculated as g/kg.

Note 3 This test is to ensure that the user can make use of the maximum amount of the product in the container. Suspension concentrates are fairly viscous products. The test determines the ease with which the formulation can be poured out of the container and how easily it can be rinsed out. The rinsed residue figures are of primary importance.

Note 4 Chemical assay is the only fully reliable method of measuring the mass of active ingredient still in suspension. However, simpler methods such as gravimetric and solvent extraction determination may be used on a routine basis provided that these methods have been shown to give equal results to those of the chemical assay method. In case of dispute, the chemical method shall be the "Referee method".

The product should be tested at the highest and lowest rates of use recommended by the supplier, provided this does not exceed the conditions given in the method.

Note 5 Unless another temperature is specified.

Note 6 This test will normally only be carried out after the heat stability test 5.2.

Note 7 The concentration of sample to be used in the test should be specified at the highest rate of use recommended by the supplier.

Note 8 Samples of the product taken before and after the storage stability test should be analysed together after the test in order to reduce the analytical error.

METRIBUZIN WATER DISPERSIBLE GRANULES
FAO Specification 283/WG/S/F (1992)

.1 DESCRIPTION

The material shall consist of a homogeneous mixture of technical metribuzin, complying with the requirements of FAO Specification 283/TC/S/F or TK/S/F (1991), together with fillers and any other necessary formulants. It shall be in the form (Note 1) of granules that will be applied after disintegration and dispersion in water. The product shall be dry, free-flowing and free from visible extraneous matter and hard lumps.

.2 ACTIVE INGREDIENT

.2.1 Identity tests (283/WG/(M)/2, CIPAC D, p.140)

An identity test is required if the identity of the active ingredient is in doubt.

.2.2 Metribuzin (283/WG/(M)/3, CIPAC D, p.140)

The metribuzin content shall be declared (g/kg) and, when determined, the content obtained shall not differ from that declared by more than the following amounts:

<u>Declared content</u>	<u>Permitted tolerance</u>
250 to 500 g/kg	± 5% of the declared content
above 500 g/kg	± 25 g/kg

.3 IMPURITIES

.3.1 Water (MT 30.1, CIPAC 1, p.897)

Maximum: 20 g/kg.

.4 PHYSICAL PROPERTIES

.4.1 Wetting of the material (MT 53.3.1, CIPAC 1, p.967)

The product shall be completely wetted in 2 min without swirling.

.4.2 Wet sieve test (MT 167 CIPAC F, p. 416)

Maximum: 2% retained on a 75 µm test sieve.

.4.3 Suspensibility (MT 168)¹ (Notes 2 and 3)

A minimum of 50% of the metribuzin content found under .2.2 shall be in suspension after 30 min in CIPAC Standard Water C at 25 °C (Note 4).

Alternatively, if the buyer requires other CIPAC Standard Waters to be used, then this shall be specified when ordering.

.4.4 Persistent foam (MT 47, CIPAC 1, p.954) (Note 5)

Maximum: 20 ml after 1 min.

.4.5 Dustiness (MT 171, Gravimetric method, CIPAC F, p. 425)

Maximum: 30 mg collected dust (Note 6).

.4.6 Flowability (MT 172 CIPAC F, p. 430)

At least 95% of the product shall pass through a 5 mm test sieve after 20 drops of the sieve.

.5 STORAGE STABILITY

.5.1 Stability at 54 °C (MT 46.1.1, CIPAC 1, p.951)

After storage at 54 ± 2 °C for 14 days (Note 4), the determined average active ingredient content must not be lower than 97% relative to the determined average content found before storage (Note 7) and the product shall continue to comply with .4.2, .4.3, .4.5 and .4.6.

Note 1 To describe a specific product, it is recommended to add information about the form (e.g. irregular shape, nearly spherical, cylindrical, ...) and to mention the nominal size range.

Note 2 The product should be tested at the highest and lowest rates of use recommended by the supplier, provided this does not exceed the conditions given in method MT 168.

Note 3 Chemical assay is the only fully reliable method of measuring the mass of active ingredient still in suspension. However, simpler methods such as gravimetric and solvent extraction determination may be used on a routine basis provided that these methods have been shown to give equal results to those of the chemical assay method. In case of dispute, the chemical method shall be the "Referee method".

Note 4 Unless another temperature is specified.

Note 5 The concentration of sample to be used in the test should be specified at the highest rate of use recommended by the supplier.

- Note 6 The optical method MT 171 usually shows good correlation with the gravimetric method and can therefore be used as an alternative, where the equipment is available. Where the correlation is in doubt, it must be checked with the product to be tested. 30 mg collected dust with the gravimetric method corresponds to a dust value of no more than 25 with the optical method. In case of dispute, the gravimetric method shall be used.
- Note 7 Samples of the product taken before and after the storage stability test should be analysed together after the test in order to reduce the analytical error.