Evaluation Manual for the Authorisation of plant protection products and biocides

NL part

Biocides

Chapter 2 Physical and chemical properties

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Board
for the authorisation
of plant protection products and biocides

Chapter 2 Physical and chemical properties

Category: biocides

GENERAL INTRODUCTION

This chapter describes the data requirements for the aspect physical-chemical properties and how these are evaluated in the NL framework.

1. NL FRAMEWORK

The NL framework describes the authorisation of biocidal products based on existing substances, included in Annex I, and new active substances. A new substance is a substance not authorised in any of the Member States of the EU on 14 May 2000.
The pesticide that contains such substances may be authorised if the criteria laid down in the Wgb (Plant Protection Products and Biocides Act) 2007 [1] are met.
The product is evaluated against the Common Principles on the basis of the Decision Common Principles Evaluation Biocides (Bgbbbio). The evaluation dossiers must meet Annex IIA, IIB, IIIA and IIIB of 98/8/EC.

The NL framework describes the data requirements, evaluation methodologies, decision making for which specific rules apply in the national approvals framework or where the national approvals framework has been elaborated in more detail than the EU framework.

The NL procedure described in of this chapter is used for evaluation of a substance for inclusion in Annex I in case no EU procedure has been described.

2.1 Introduction

For the aspect physical-chemical properties, the data requirements for active substance and product, and the evaluation methodology do not differ from the EU framework.
The NL procedure is only described if no EU procedure has been described.

2.2 Data requirements

2.1.1 Data requirements active substance

For the active substance the same data requirements apply as described in the EU part. Further details are given in the text below.

The European guidelines and guidance documents do not clearly state which requirements apply if instead of the active substance as such the salt or an ester of the substance is used in the product. Risk assessment does in principle require the (physical-chemical) properties of the substance that is used in the product. It is possible to provide a justified statement for each requirement. The evaluation then focuses on the objective of the question and the justification of the statement.

Common name proposed or ISO-accepted, and synonyms
[Ann IIA, II. 2.2.]
The nomenclature of the active substance follows the procedure as laid down by the Board of the Authorization of pesticides in the meeting of January 2006. This stipulates that there must be clarity about the active substance in the formulation and the substance as this has been tested in the various studies in view of the possibly different appearances of the active substance.

Method of manufacture (synthesis pathways) of the active substance
[Ann IIA, II. 2.6.]
The manufacturing process must be described to give insight into possible impurities, where the purity of the starting materials must also be given. Where the process is still

under development, the description must be submitted as soon as the process has been stabilised.
Any significant changes in the manufacturing process must be reported (if applicable with a new specification of the active substance), together with a complete description of the equivalence of the active substance produced according to the old and according to the new production process. The draft guidance document on equivalence [EU part, reference 7] is used for evaluation of the equivalence of the active substance.

Specification of purity of the active substance, in g/kg or g/l
[Ann IIA, II. 2.7.]
The technical material (TC) is the material in which the active substance has been isolated from all starting material, solvents and impurities. In a number of cases the active substance is not isolated but a technical concentrate (TK) is obtained.
This may, e.g., be because the active substance is not stable in pure form. Specifications are usually given for the TC. Because the highest (practically) possible purity is always aimed for, only a minimum concentration has been laid down instead of an upper limit. Specifications for a TK can be derived from the specifications of a TC; in that case an upper limit should still be specified (a concentration range).
Remark: When the TC is not isolated, the relevant physical-chemical properties of the TK should be determined and not those of the TC.

In case an FAO and/or WHO specification exists for the substance, the active substance should at least meet that specification. Where this is not the case, a full justification should be provided.
FAO specifications can be obtained via internet [2].
An acceptable specification can be obtained from a batch analysis if this is available.
An acceptable justification must be provided if the applicant proposes a specification that shows no relationship with the batch analysis.
This justification should deal with aspects such as the purity of the active substance that has been used in the various (eco)toxicological tests.

Identity of impurities and additives (e.g. stabilisers), together with the structural formula and its concentration interval, expressed as g/kg or g/l
[Ann IIA, II.2.8.]
All impurities with a concentration > 1 g/kg (0.1 %m/m) must be included in an unambiguous and dated specification of the active substance, with a maximum concentration. Relevant impurities, toxicologically and/or ecotoxicologically relevant impurities, with a maximum concentration, should always be included in this specification. This concentration may also be lower than 1 g/kg. Whether a substance is relevant and what the maximum concentration may then be is decided when evaluating the risk for man and environment. The applicant should always indicate whether or not relevant impurities are present in the active substance as manufactured.

For added components, other than active substance and other than impurities resulting from the manufacturing process, the function of the component (additive) must be given:

Dutch name	**English name**
Antischuimmiddel	Antifoaming agent
Antivriesmiddel	Antifreeze
Bindmiddel	Binder
Buffer	Buffer
Dispergeermiddel	Dispersing agent
Stabilisator	Stabilizer

Oplosmiddel	Solvent
Overig (specificeren)	Miscellaneous (specify)

Absorption spectra (UV/VIS, IR, NMR),and mass spectrum and molecular extinction at relevant wavelengths, where applicable
[Ann IIA, III. 3.4.]
The wavelengths at which molecular extinction of UV/VIS light takes place should be determined and reported. If a photolysis study is not considered necessary, because the active substance has no absorption in the spectrum of sunlight (>290 nm), this can be demonstrated with the molecular extinction at 290 nm. If this molecular extinction has a value below 10 ε a photolysis study may be refrained from (to be decided by environment).

Optical purity should be measured and reported if the active substances are separate optical isomers,

2.2.2 Data requirements product

For the product the same requirements apply as described under EU framework. Where the product has a clear formulation type (question Ann IIB, III. 3.8, with types as given in Appendix 2 to the EU part) the data requirements and criteria as included in the evaluation for plant protection products are used.
The prescribed use of the biocide has a strong effect on the data requirements; this means that the plant protection requirements do not always apply. Supplements are given in the text below and in Appendix 1 to this chapter.

Detailed quantitative and qualitative information on the composition of the biocide, e.g. active substance(s), contaminants, co- formulants, inert components
[Ann IIB, I. 2.2.]
The way in which in the EU framework the composition should be given is not unequivocal. For reasons of clarity the way in which this should be given for a national application in the Netherlands is given here.
The composition of solids and aerosols should be given in g/kg.

To avoid uncertainties the composition of liquids must be given in g/kg (and/or in %m/m) as well as in g/l.
Where the active substance is added to the product as ester or salt, the concentration of the active substance must also be given as free acid, e.g.:

X g/kg of the ester/the salt corresponds with Y g/kg of the free acid

Where the active substance is added to the product as hydrate, the concentration of the active substance must also be given as waterfree, e.g.:

X g/kg of the active substance as hydrate corresponds with Y g/kg of the active substance waterfree

The concentration of the active substance must be given as the *pure* active substance and also the active substance as manufactured.

Where co-formulants are used in a diluted form, the actual concentration of the co-formulant in question in the product should be given as well.

The function of the co-formulants should be expressed as follows:

Dutch name	**English name**
Kleefstof	Adhesive (sticker)
Antischuimmiddel	Antifoaming agent
Antivriesmiddel	Antifreeze
Bindmiddel	Binder
Buffer	Buffer
Afweermiddel	Repellant
Conserveermiddel	Preservative
Drijfgas	Propellant
Carrier	Carrier
Beschermstof	Safener
Reukstof	Odourant
Parfumeermiddel	Perfume
Deodorans	Deodorant
Kleurstof	Dye
Dispergeermiddel	Dispersing agent
Emulgeermiddel	Emulsifier
Meststof	Fertilizer
Stabilisator	Stabilizer
Braakmiddel	Emetic
Oplosmiddel	Solvent
Verdikkingsmiddel	Thickener
Bevochtiger	Wetting agent
Synergist	Synergist
Uitvloeier	surfactant
Overig (specificeren)	miscellaneous (specify)

The template in Appendix 2 must be used to give a full description of the composition of the product.

Storage stability and shelf life. Effects of light, temperature and humidity on the technical characteristics of the biocidal product; reactivity to the material of the recipients [Ann IIB, III. 3.7.]
MT 46.3 is a revised method for the accelerated storage test.
At European level no agreement has yet been reached about the method according to which the zero measurements must be carried out. For reasons of clarity, the NL requirements are given here.

The product must at least be tested as long as the claimed shelf life (if the applicant has given specific storage conditions for the biocide, shelf life must be tested under these conditions).
Depending on the extent of decline, and whether or not the specifications are met after the decline, additional questions about the effectiveness and possible breakdown products may be asked, to demonstrate that the decline in active substance has no effect on the effectiveness and that the risk after storage does not increase as result of the breakdown products. A fixed limit for the maximum decline of the active substance cannot be given. A maximum decline of 5% is used as guidance. In case the decline is higher a

complete and acceptable justification must be given why this would still be acceptable, taking into account the (eco)toxicological properties of the breakdown products that are formed.
The concentration of the active substance after (and also before) decline should still come within the tolerances laid down for the active substance in the product. See §1.4.1 for the tolerances used.

For aerosols it should be demonstrated that the nozzle is not blocked after storage. No corrosion of the nozzle may be visible after storage. The aerosol must sometimes be opened for determination of the properties of its content.
This can, e.g., be done according to the method described in the FAO manual under 8.11 (aerosol dispensers). More methods for determination of the physical properties of an aerosol can be obtained from the 'European Aerosol Federation' [3] in Belgium.

Besides the stability of the active substance, the physical stability of the product must also be studied in the storage tests.

The test method used, including test conditions where necessary, and if applicable the validated analytical method, should in any case be given for each result.

It should also be checked in the storage tests whether the trade pack is suitable for its content (e.g. by checking for: corrosion, leakage, malformation, closure). This means that the test must be carried out with the trade pack or a pack of comparable material. Where different packaging materials are used, these should all be investigated and described in the test, insofar as these show essential mutual differences (to be indicated by the applicant).

To enable determination of the possible decline in active substance concentration in the product, measurements must be carried out in the same production batch.
The concentration should also be measured prior to the test (initial measurement). Determination of a (possible) decline against a reference (stated) concentration is not permitted. Intermediate measurements are in principle not required in a storage test but can be useful in case there are problems with the results of the storage test after the claimed storage period.

Because the claimed storage life must be established, it is not possible to use an accelerated storage test instead of a storage test during the claimed shelf life (and storage conditions if claimed).
An accelerated storage test, at 54°C for 2 weeks, is not required for the Dutch application in case a storage test for the claimed shelf life has already been executed.

Physical and chemical compatibility with other products, including other biocidal products, if authorisation for combined use with the other products is envisaged
[Ann IIB, III. 3.9.]
The data requirements for mixing products has not been elaborated in EU framework because this does not, or hardly, occur in the evaluation of a substances for inclusion in Annex I. Some Member States do, however, have regulations for answering this question in the national evaluation. For reasons of clarity, the Dutch method of evaluation is included here.
If it is stated in the WGGA (Statutory Use Instructions/Directions for Use) or on the label that mixing with a different product is possible or recommended (or similar phrasing), this should be justified with a test for physical compatibility.
There is no test for chemical compatibility. This can be included in the test for physical

compatibility by observing reactions such as gas formation, heat development of colour changes.

Currently, two methods are described for testing physical compatibility of plant protection products. The procedure “EVALUATION OF THE PHYSICAL COMPATIBILITY OF TANK MIXTURE” of the BAA (British Agrochemical Association) and the ASTM method E1518-99 “standard practice for evaluation of physical compatibility of pesticides in aqueous tank mixtures by the dynamic shaker method” [4].

There is no specific test method for biocides. The method above can, if necessary be adjusted to the use of the biocidal product in question.
All adjustments must be described.

Material safety data sheet
In EU framework, no clear term has been agreed for a material safety data sheet being up-to-date. Because up-to-date information is important for the risk evaluation, a clear term has been laid down for the Dutch application. The material safety data sheets may not have been prepared or revised longer than 5 years ago.

Supplementary questions technical characteristics
The questions regarding technical characteristics of products have not been elaborated in EU framework. For reasons of clarity, the NL requirements for a number of specific products are given below.

Tablets
It should be demonstrated for tablets that must be dissolved in water that they do rapidly disintegrate in water. Good attrition and friability properties should be demonstrated for all tablets (see also Appendix 1 to this chapter).

Smoke generators
The *burning rate* of smoke generators must be determined to establish how long it takes before the preparation stops generating smoke (important in view of operator risk).
Burning completeness must be determined by weighing the preparation before and after use. It should be demonstrated that by far the largest part of active substance has gone up in smoke.
The residue after burning must be analysed for concentration active substance and the composition of the produced smoke must be analysed for concentration active substance and possible decomposition products (see also Appendix 1 to this chapter).

Aerosols
Where the capacity of the container is at least 50 ml and the content is pressurised, this packaging (also) comes under the Food and Drug Order Pressurised Packs [5]. Testing methods and requirements are given in Directive 75/324/EC [EU part, reference 15].

The spraying pattern should be studied for homogeneousness according to FEA method 644 [3]. In addition, the spray diameter should be determined at 30 cm distance.

Packaging
According to 98/8/EC, Article 20, biocidal products must be packed in accordance with Article 6 of Directive 88/379/EEC.
For reasons of clarity the way in which the packaging must be described is given here because this is not given in the Application Form or its explanatory notes.

Packaging must be described with at least the following data:
– material of the pack (inner and outer)
– material of an additional barrier, if any
– details of the closure
– childproof closure
– diameter of the opening
– minimum and maximum size of the pack
– minimal thickness of the pack
– whether the packaging is intended for re-use
– outer pack, if applicable
– other details, if applicable

Child-proof closure
A preparation for household use which must be labelled as very toxic, toxic, or corrosive (see Chapter 4 Human toxicology, toxicological dossier), or which contains more than 3% methanol or 1% dichloromethane, ór a product to which risk phrase R65 has been assigned, must be fitted with a child-proof closure in accordance with the Food and Drug Order Safe Packaging Household Chemicals [6], with exception of aerosols, unless the preparation is not dangerous according to Article 15f of the Further Regulations Packaging and Identification Environmentally Harmful Substances [7]. The child-proof closure should meet ISO standard 8317.

2.3 Risk assessment
Risk is assessed is in compliance with the European regulations, please refer to the EU part of the evaluation manual.

2.4 Approval
A pesticide will only be authorised if the pesticide and its metabolite(s), and if used in compliance with the provisions in or by virtue of the Pesticides Act (Bmw), in compliance with the Statutory Use Instructions and Directions for Use (Article 3, only relevant part taken):

Section 1, d. the physical-chemical properties of the pesticide are determined and are acceptable for the use of the pesticide in compliance with the provisions in or by virtue of this Act.
Section 2, b. the content of the active substance or substances and the further composition, colour, form, finishing, packaging and specifications and statements on or with the packaging comply with the regulations laid down by the Minister concerned.

The evaluation of products on the basis of existing active substances already included in Annex I, or new substances, has been laid down in the Decision Common Principles Evaluation Biocides (Bgbbbio) in which it is elaborated that these products are evaluated in compliance with the Common Principles.

2.4.1 Criteria and trigger values

The principles (approval framework with criteria and trigger values) as regards the assessment concerning the evaluation of the effects on man and environment in NL framework are the same as in EU framework. Where the criteria in the European framework have not been described adequately, more clarity for the NL framework is given below.

Tolerance concentration active substance in product

Directive 98/8/EC and the TNsGs contain no criteria for the tolerance of the concentration of the active substance in the product. NL uses the tolerance as laid down by FAO and WHO [EU part, reference 12] (see table) as guidance.
The difference between given and actual concentration of the active substance of the plant protection product may during the total claimed shelf life nor exceed these values:

Stated concentration*		Tolerance
%	g/l or g/kg	
up to 2.5	up to 25	± 15% of the stated concentration homogeneous formulations (EC,SC,SL, etc.) ± 25% non-homogeneous formulations (GR, WG, etc.)
from 2.5 to 10	from 25 to 100	± 10% of the stated concentration
from 10 to 25	from 100 to 250	± 6% of the stated concentration
from 25 to 50	from 250 to 500	± 5% of the stated concentration
above 50%	above 500	± 25 g/kg or ±25 g/l or ±2.5 %

*) content at 20°C

An acceptable justification should be provided if the concentration of the active substance does not meet this criterion.

2.4.2 Decision on approval

The principles (approvals framework with criteria and trigger values) as regards the decision making concerning the evaluation of the effects on man and environment in NL framework are the same as in EU framework.

2.5 Developments

The developments in EU framework will also affect the applied data requirements and evaluation methodologies in NL framework in view of the aim for the largest possible harmonisation of data requirements and evaluation methodologies.

3. APPENDICES

Appendix 1: Requirements concerning the product, NL elaboration

EU question 98/8	EU question TNsG	description	explanatory notes	Method/guideline
IIB III 3.1	3.1	Appearance	Physical form of the preparation, and colour and odour if present. Odour needs only to be described where this is observed during safe use. The taste in water only is required if this information is already present Requirements: Any colouring of a product should be distinct (Art 4, Regeling Samenstelling Bestrijdingsmiddelen (Regulation Composition Pesticides) [8]). For odours, Art. 3 of the Regeling Samenstelling Bestrijdingsmiddelen applies.	
	3.10	Surface tension and viscosity	If the product contains more than 10% organic solvent, viscosity must be determined at at least 40°C. The capillary viscometer is used for liquids with a Newtonian behaviour (viscosity independent measurement), the rotation viscometer must be used for non-Newtonian liquids.	ISO 3104/3105, Capillary viscometer ISO 31269, rotation viscometer
			Where the product contains more than 10% organic solvent surface tension of the undiluted product must be determined at 25°C or 40°C to disprove, where applicable, the risk phrase R65.	EEC method A 5 OECD 115
IIB III 3.8		Dipersibility of tablets	It should be demonstrated that the tablets disintegrate rapidly in water and that the formulation dissolves or disperses rapidly. Test is required for all tablets that are dissolved in water before use. Requirements: not yet specified	Not yet available
		Attrition and friability tablets	Tablets must remain intact to avoid risk for the operator (dust formation) or the dose becoming at risk. For separately packed tablets only friability needs to be determined. Requirements: tablets may not break. Requirements for possible attrition	CIPAC MT 193

EU question 98/8	EU question TNsG	description	explanatory notes	Method/guideline
			have not yet been specified.	
		Burning rate smoke generators	The burning rate should be determined to establish how long it takes before the preparation stops generating smoke Requirements: the burring rate should correspond with the proposed use	
		Burning completeness smoke generators	Burning completeness must be determined by weighing the preparation before and after use. It should be demonstrated that by far the largest part of the active substance went up in smoke. This also requires determination of the concentration active substance in the residue. Requirements: The preparation may after use present no risk for operator or environment, and disposal should –if applicable- be possible in accordance with the instructions for use	
		Composition smoke of smoke generators	Smoke composition must be analysed for concentration active substance and decomposition products, if any, to guarantee that the produced smoke does indeed contain the active substance and no decomposition products. Requirements: The preparation may after use present no risk to operator or environment.	
		Spraying pattern aerosols	Homogeneity must be determined according FEA method 644. Spray diameter must be determined at 30 cm distance. Requirements: none	FEA 644
IIB III 3.9	3.9	Physical and chemical compatibility with other products including other biocidal products with which its use is to be authorised	Chemical and physical compatibility must be demonstrated in case mixing with other (auxiliary) compounds is prescribed Requirements: no problems in case of mixing	ASTM E1518-99 or the BAA method

Appendix 2: Composition template product

	Components			function	CAS/Einecs/ Elincs no.	Concentration in formulation			minimal purity (%)
	(Trade) name (co)formulant	Chemical name	Chemical description			g/l or g/kg	different (indicate)	m/m (%)	
a.s.1				active substance					
				concentration as pure a.s.:					
				in case of salt: concentration free acid:					
a.s.2				active substance					
				concentration as pure a.s.:					
				in case of salt: concentration free acid:					
a.s.3				active substance					
				concentration as pure a.s.:					
				in case of salt: concentration free acid:					
a.s.4				active substance					
				concentration as pure a.s.:					
				in case of salt: concentration free acid:					
1									
2									
3									
4									
5									
6									
7									

8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
					Summation:	**0**	**0**	**0.0000**	

Composition applies as from	

	production location active substance(s)		
	producer	**country**	**address (several addresses and/or production locations possible)**
w.s.1			
w.s.2			
w.s.3			
w.s.4			

instruction for completing the table:

- give the concentration of the active substance as technical material as well as in the pure form (the last will be stated on the label)
- if the active substance is an ester, the concentration of this ester should be given
- if the active substance has been added to the product as a salt: also give the concentration of the acid

- all concentrations should at least be given in %m/m
- of a liquid, the concentration should be given in g/l as well as in %m/m
- dark grey fields do not need to be completed

4. REFERENCES

1 Wgb (Plant Protection Products and Biocides Act) 2007. See www.overheid.nl/wetten.
2 FAO specifications: http://www.fao.org/agriculture/crops/core-themes/theme/pests/pm/jmps/ps/en/
3 European Aerosol Federation (FEA), http://www.aerosol.org/
4 American National Standards Institute, ASTM method E1518-05, http://www.astm.org/Standards/E1518.htm
5 Warenwetbesluit drukverpakking (Food and Drugs Order Pressurised Packs) NL acts, decisions, orders, etc. can be obtained via http://wetten.overheid.nl/
6 Warenwetbesluit veilige verpakking Huishoudchemicaliën (Food and Drugs Order Safe Packaging Household Chemicals) NL acts, decisions, orders, etc. can be obtained via http://wetten.overheid.nl/
7 Nadere Regels verpakking en aanduiding milieugevaarlijke stoffen (Further Regulations Packaging and Indications Environmentally Harmful Substances). NL acts, decisions, orders, etc. can be obtained via http://wetten.overheid.nl/