



# **Draft Assessment Report (DAR)**

**- public version -**

**Initial risk assessment provided by the rapporteur Member State  
Germany for the existing active substance**

**CALCIUM PHOSPHIDE**

**of the third stage (part B) of the review programme  
referred to in Article 8(2) of Council Directive 91/414/EEC**

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# **Draft Assessment Report**

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**Calcium phosphide**

**Volume 3**

**Annex B**

**Summary, Scientific  
Evaluation and Assessment**

**Rapporteur Member State: Germany**

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

## Contents

### **B Rapporteur Member State summary, evaluation and assessment of the data and information**

<b>B.1</b>	<b>Identity .....</b>	<b>3</b>
B.1.1	Identity of the active substance (Annex IIA 1 and 3.1) .....	3
B.1.1.1	Name and address of applicant(s) for inclusion of the active substance in Annex I (Annex IIA 1.1) .....	3
B.1.1.2	Common name and synonyms (Annex IIA 1.3) .....	3
B.1.1.3	Chemical name (Annex IIA 1.4) .....	3
B.1.1.4	Manufacturer's development code number (Annex IIA 1.5) .....	3
B.1.1.5	CAS, EEC and CIPAC numbers (Annex IIA 1.6) .....	3
B.1.1.6	Molecular and structural formulae, molecular mass (Annex IIA 1.7) .....	3
B.1.1.7	Manufacturer or manufacturers of the active substance (Annex IIA 1.2) .....	4
B.1.1.8	Method or methods of manufacture (Annex IIA 1.8) .....	4
B.1.1.9	Specification of purity of the active substance (Annex IIA 1.9) .....	4
B.1.1.10	Identity of isomers, impurities and additives (Annex IIA 1.10) .....	4
B.1.1.11	Analytical profile of batches (Annex IIA 1.11) .....	4
B.1.2	Identity of the plant protection product (Annex IIIA 1) .....	4
B.1.2.1	Current, former and proposed trade names and development code numbers (Annex IIIA 1.3) .....	4
B.1.2.2	Applicant (Annex IIIA 1.1) .....	5
B.1.2.3	Manufacturer or manufacturers of the plant protection product (Annex IIIA 1.2) .....	5
B.1.2.4	Type of the preparation and code (Annex IIIA 1.5) .....	5
B.1.2.5	Function (Annex IIA 3.1; Annex IIIA 1.6) .....	5
B.1.2.6	Composition of the preparation (Annex IIIA 1.4) .....	5
B.1.3	References relied on .....	6
<b>B.2</b>	<b>Physical and chemical properties .....</b>	<b>11</b>
B.2.1	Physical and chemical properties of the active substance (Annex IIA 2) .....	11
B.2.1.1	Summary of data presented under points B.2.1.1 to B.2.1.15 .....	19
B.2.1.2	Methods which do not meet the requirements .....	19
B.2.2	Physical, chemical and technical properties of the plant protection products (Annex IIIA 2) .....	20
B.2.2.11	Summary and evaluation of data presented under points B.2.2.1 to B.2.2.10 (IIIA 2.11) .....	25
B.2.3	References relied on .....	25
<b>B.3</b>	<b>Data on application and further information .....</b>	<b>31</b>
B.3.1	Data on application relevant to the active substance (Annex IIA 3.1 to 3.6) .....	31
B.3.1.1	Function .....	31
B.3.1.2	Effects on harmful organisms .....	31
B.3.1.3	Field of use .....	31
B.3.1.4	Harmful organisms .....	31
B.3.1.5	Mode of action .....	31
B.3.1.6	Information on the occurrence or possible occurrence of the development of resistance and appropriate management strategies .....	31

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B.3.2	Data on application relevant to the plant protection product (Annex IIIA 3).....	32
B.3.2.1	Field of use envisaged .....	32
B.3.2.2	Effects on harmful organisms.....	32
B.3.2.3	Details of intended use .....	32
B.3.2.4	Application rate .....	33
B.3.2.5	Concentration of active substance in material used .....	33
B.3.2.6	Method of application .....	34
B.3.2.7	Number and timing of applications and duration of protection .....	34
B.3.2.8	Necessary waiting periods or other precautions to avoid phytotoxic effects on succeeding crops.....	34
B.3.2.9	Proposed instructions for use .....	34
B.3.3	Summary of data on application.....	35
B.3.3.1	List of uses evaluated for Annex-I-inclusion .....	35
B.3.4	Further information on the active substance (Annex IIA 3.7 to 3.9).....	37
B.3.4.1	Recommended methods and precautions concerning handling, storage, transport or fire (Annex IIA 3.7) .....	37
B.3.4.1.1	Handling .....	37
B.3.4.1.2	Storage.....	38
B.3.4.1.3	Transport .....	38
B.3.4.1.4	Fire fighting measures .....	39
B.3.4.2	Procedures for destruction or decontamination (Annex IIA 3.8) .....	39
B.3.4.2.1	Controlled incineration.....	39
B.3.4.2.2	Others .....	39
B.3.4.3	Emergency measures in the case of an accident (Annex IIA 3.9) .....	40
B.3.5	Further information on the plant protection product (Annex IIIA 4) .....	40
B.3.5.1	Packaging (type, materials, size, etc.), compatibility of the preparation with proposed packaging materials (Annex IIIA 4.1) .....	40
B.3.5.1.1	Description of packaging (Annex IIIA 4.1.1).....	40
B.3.5.1.2	Suitability of packaging (Annex IIIA 4.1.2).....	41
B.3.5.1.3	Resistance of packaging material to its contents (Annex IIIA 4.1.3).....	41
B.3.5.2	Procedures for cleaning application equipment and protective clothing (Annex IIIA 4.2) .....	41
B.3.5.3	Re-entry periods, necessary waiting periods or other precautions to protect man, livestock and the environment (Annex IIIA 4.3).....	42
B.3.5.4	Recommended methods and precautions concerning handling, storage transport or fire (Annex III 4.4).....	42
B.3.5.5	Emergency measures in case of an accident (Annex IIIA 4.5).....	44
B.3.5.6	Procedures for destruction or decontamination of the plant protection product and its packaging (Annex IIIA 4.6).....	45
B.3.5.6.1	Possibility of neutralisation .....	45
B.3.5.6.2	Controlled incineration.....	45
B.3.5.6.3	Methods other than controlled incineration: .....	45
B.3.6	References relied on .....	45
<b>B.4</b>	<b>Proposals for the classification and labelling.....</b>	<b>49</b>
B.4.1	Proposals for the classification and labelling of the active substance (Annex IIA 10) .....	49
B.4.2	Proposals for the classification and labelling of preparations (Annex IIIA 12.3 and 12.4).....	50

B.4.3	References relied on .....	50
<b>B.5</b>	<b>Methods of analysis .....</b>	<b>53</b>
B.5.1	Analytical methods for formulation analysis (Annex IIA 4.1; Annex IIIA 5.1).....	53
B.5.1.1	Methods for the determination of pure active substance in the active substance as manufactured (Annex IIA 4.1).....	53
B.5.1.2	Analytical methods for the determination of the active substance in plant protection products (Annex IIIA 5.1.1 and 5.1.3) .....	56
B.5.1.3	Analytical methods for the determination of relevant impurities and formulants in plant protection products (Annex IIIA 5.1.2 and 5.1.3).....	59
B.5.2	Analytical methods (residue) for plants, plant products, foodstuffs of plant and animal origin, feedingstuffs (Annex IIA 4.2.1; Annex IIIA 5.2).....	59
B.5.2.1	Plant materials .....	59
B.5.2.2	Analytical methods (residue) for foodstuff of animal origin.....	61
B.5.3	Analytical methods (residue) soil, water, air (Annex IIA 4.2. 2 to 4.2.4; Annex IIIA 5.2) .....	61
B.5.3.1	Analytical methods (residue) for soil .....	62
B.5.3.2	Analytical methods (residue) for water .....	63
B.5.3.3	Analytical methods for air .....	65
B.5.4	Analytical methods (residue) for body fluids and tissues (Annex IIA 4.2.5; Annex IIIA 5.2) .....	69
B.5.5	Evaluation and assessment .....	73
B.5.5.1	Formulation analysis .....	73
B.5.5.2	Analytical methods for technical active substance and formulation analysis .....	73
B.5.5.3	Residue analysis .....	75
B.5.6	References relied on .....	78
<b>B.6</b>	<b>Toxicology and metabolism .....</b>	<b>83</b>
B.6.1	Absorption, distribution, excretion and metabolism (toxicokinetics) (Annex IIA 5.1) .....	83
B.6.2	Acute toxicity including irritancy and skin sensitisation (Annex IIA 5.2).....	87
B.6.2.1	Acute oral toxicity .....	90
B.6.2.2	Acute percutaneous toxicity .....	99
B.6.2.3	Acute inhalation toxicity .....	105
B.6.2.4	Skin irritation.....	109
B.6.2.5	Eye irritation.....	112
B.6.2.6	Skin sensitisation.....	115
B.6.3	Short-term toxicity (Annex IIA 5.3).....	116
B.6.3.1	Oral subchronic toxicity .....	117
B.6.3.1.1	Oral subchronic toxicity, rat.....	117
B.6.3.1.2	Oral subchronic toxicity, dog .....	120
B.6.3.2	Inhalation toxicity.....	121
B.6.3.2.1	14 – 28 day inhalation toxicity, rat and mouse.....	121
B.6.3.2.2	Inhalation 90-day toxicity – rat.....	124
B.6.3.2.3	Further inhalation studies .....	125
B.6.4	Genotoxicity (Annex IIA 5.4) .....	127
B.6.4.1	In vitro genotoxicity testing – bacterial gene mutation assay.....	129
B.6.4.2	In vitro genotoxicity testing – clastogenicity test in mammalian cells.....	135

B.6.4.3	In vitro genotoxicity testing – gene mutation assay in mammalian cells .....	136
B.6.4.4	In vivo genotoxicity testing .....	137
B.6.5	Long-term toxicity and carcinogenicity (Annex IIA 5.5) .....	149
B.6.5.1	Long-term (2 years) inhalation toxicity – rat .....	150
B.6.5.2	Long-term (2 years) oral toxicity – rat .....	153
B.6.5.3	Carcinogenicity study – mouse .....	156
B.6.6	Reproductive toxicity (Annex IIA 5.6) .....	156
B.6.6.1	Reproduction study in the rat with phosphine fumigated diet .....	157
B.6.6.2	Teratogenicity by the inhalation route – rat .....	159
B.6.6.3	Teratogenicity study – rabbit .....	161
B.6.7	Delayed neurotoxicity (Annex IIA 5.7) .....	161
B.6.7.1	Acute neurotoxicity – rat .....	162
B.6.7.2	Delayed neurotoxicity following acute exposure – hen .....	164
B.6.7.3	28-day delayed neurotoxicity – hen .....	164
B.6.7.4	Subchronic 90-day neurotoxicity – rat .....	165
B.6.7.5	Postnatal developmental neurotoxicity – rat .....	167
B.6.8	Further toxicological studies (Annex IIA 5.8) .....	167
B.6.9	Medical data and information (Annex IIA 5.9) .....	171
B.6.9.1	Report on medical surveillance on manufacturing plant personnel .....	171
B.6.9.2	Report on clinical cases and poisoning incidents .....	181
B.6.9.3	Clinical signs and symptoms of poisoning .....	185
B.6.9.4	First aid measures .....	188
B.6.9.5	Therapeutic regimes .....	188
B.6.9.6	Expected effects and duration of poisoning as a function of the type, level and duration of exposure or ingestion .....	190
B.6.9.7	Expected effects and duration of poisoning as a function of varying time periods between exposure or ingestion and commencement of treatment .....	191
B.6.10	Summary of mammalian toxicology and proposed ADI, AOEL, ArfD and drinking water limit (Annex IIA 5.10) .....	192
B.6.10.1	Absorption, distribution, excretion and metabolism .....	192
B.6.10.2	Acute toxicity .....	193
B.6.10.3	Short term toxicity .....	196
B.6.10.4	Genotoxicity .....	198
B.6.10.5	Long term toxicity and carcinogenicity .....	200
B.6.10.6	Reproductive Toxicity .....	201
B.6.10.7	Neurotoxicity .....	201
B.6.10.8	Further toxicological studies .....	202
B.6.10.9	Medical data and information .....	203
B.6.10.10	Acceptable Daily Intake (ADI) .....	203
B.6.10.11	Acceptable Operator Exposure Level (AOEL) .....	203
B.6.10.12	Acute Reference Dose (ArfD) .....	203
B.6.11	Acute toxicity including irritancy and skin sensitisation of preparations (Annex IIIA 7.1) .....	204
B.6.11.1	Acute oral toxicity – Polytanol .....	205
B.6.11.2	Acute percutaneous toxicity – Polytanol .....	207
B.6.11.3	Acute inhalation toxicity – Polytanol .....	208
B.6.11.4	Skin irritation – Polytanol .....	210
B.6.11.5	Eye irritation .....	211
B.6.11.6	Skin sensitisation – Polytanol .....	211
B.6.11.7	Supplementary studies for combinations of plant protection products .....	212

B.6.12	Dermal absorption (Annex IIIA 7.3) .....	213
B.6.13	Toxicological data on non active substances (Annex IIIA 7.4 and point 4 of the introduction) .....	213
B.6.14	Exposure data (Annex IIIA 7.2) .....	214
B.6.14.1	Operator exposure .....	214
B.6.14.1.1	Estimation of operator exposure assuming personal protective equipment is not used/is used .....	215
B.6.14.1.2	Measurement of operator exposure .....	215
B.6.14.2	Estimation and measurement of bystander exposure .....	216
B.6.14.3	Worker exposure .....	216
B.6.14.3.1	Estimation of worker exposure assuming personal protective equipment is used .....	216
B.6.14.3.2	Measurement of worker exposure .....	217
B.6.15	References relied on .....	218
<b>B.7</b>	<b>Residue data .....</b>	<b>237</b>
B.7.1	Metabolism, distribution and expression of residues in plants (Annex IIA 6.1; Annex IIIA 8.1) .....	239
B.7.2	Metabolism, distribution and expression of residues in livestock (Annex IIA 6.2; Annex IIIA 8.1) .....	240
B.7.2.1	Lactating ruminants (goat or cow) .....	240
B.7.2.2	Laying hens (poultry) .....	240
B.7.2.3	Pigs .....	240
B.7.3	Definition of the residue (Annex IIA 6.7; Annex IIIA 8.6) .....	240
B.7.3.1	Residue definition in plant matrices .....	240
B.7.3.2	Residue definition in animal matrices .....	241
B.7.4	Use pattern .....	241
B.7.5	Identification of critical GAPS .....	242
B.7.6	Residues resulting from supervised trials (Annex IIA 6.3; Annex IIIA 8.2) .....	243
B.7.6.1	Residues in target crops .....	243
B.7.6.2	Storage stability .....	243
B.7.7	Effects of industrial processing and/or household preparation (Annex IIA 6.5; Annex IIIA 8.4) .....	244
B.7.7.1	Effects on nature and level of residue .....	244
B.7.7.2	Effects on the magnitude of residues .....	244
B.7.8	Livestock feeding studies (Annex IIA 6.4; Annex IIIA 8.3) .....	244
B.7.8.1	Ruminants .....	244
B.7.8.2	Poultry .....	244
B.7.8.3	Pigs .....	244
B.7.8.4	Calculation of dietary burden .....	244
B.7.9	Residues in succeeding or rotational crops (Annex IIA 6.6; Annex IIIA 8.5) ....	245
B.7.10	Proposed pre-harvest intervals for envisaged uses, or withholding periods, in the case of post-harvest uses (Annex IIA 6.8; Annex IIIA 8.7) .....	245
B.7.10.1	Proposed pre-harvest intervals (PHIs) .....	245
B.7.10.2	Withholding period for animal feeding-stuffs .....	245
B.7.10.3	Waiting period between last application and sowing or planting of the crops to be protected .....	245
B.7.10.4	Waiting period between application and handling treated product .....	245

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B.7.10.5	Waiting period between last application and sowing or planting of succeeding crops.....	245
B.7.11	Community MRLs and MRLs in EU Member States (Annex IIIA 12.2) .....	246
B.7.12	Proposed EU MRLs and justification for the acceptability of those residues (Annex IIA 6.7; Annex IIIA 8.6).....	246
B.7.12.1	Products of plant matrices .....	246
B.7.12.2	Products of animal origin .....	246
B.7.12.2.1	Cattle products.....	246
B.7.12.2.2	Chicken products.....	246
B.7.12.2.3	Pig products.....	246
B.7.12.3	Acceptability of MRLs in acute and chronic dietary risk assessment .....	247
B.7.13	Proposed EU Import tolerances and justification for the acceptability of those residues .....	247
B.7.14	Basis for differences, if any, in conclusion reached having regard to established or proposed Codex MRLs.....	247
B.7.15	Estimates of potential and actual dietary exposure through diet and other means (Annex IIA 6.9; Annex IIIA 8.8).....	247
B.7.15.1	Long-term dietary risk assessment .....	247
B.7.15.2	Short-term dietary risk assessment.....	247
B.7.15.3	Exposure via water .....	247
B.7.15.4	Exposure via air.....	248
B.7.16	Summary and evaluation of residue behaviour (Annex IIA 6.10; Annex IIIA 8.9).....	248
B.7.16.1	Metabolism in plants .....	248
B.7.16.2	Metabolism in livestock .....	248
B.7.16.3	Residues in plants.....	248
B.7.16.4	Storage stability .....	248
B.7.16.5	Processing studies.....	248
B.7.16.6	Rotational crop studies .....	249
B.7.16.7	Livestock feeding studies .....	249
B.7.16.8	MRL proposal.....	249
B.7.16.9	Dietary risk assessment .....	249
B.7.16.9.1	Long-term dietary risk assessment .....	249
B.7.16.9.2	Short-term dietary risk assessment.....	249
B.7.17	References relied on .....	249
<b>B.8</b>	<b>Environmental fate and behaviour .....</b>	<b>255</b>
B.8.1	Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1).....	255
B.8.1.1	Route of degradation (Annex IIA 7.1.1.1).....	255
B.8.1.1.1	Aerobic degradation .....	255
B.8.1.1.2	Anaerobic degradation.....	255
B.8.1.1.3	Soil photolysis .....	255
B.8.1.2	Rate of degradation (Annex IIA 7.1.1.2; Annex IIIA 9.1.1) .....	256
B.8.1.2.1	Laboratory studies .....	256
B.8.1.2.2	Field studies.....	257
B.8.1.2.3	Soil residue study .....	258
B.8.1.2.4	Soil accumulation study .....	258
B.8.2	Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and 7.1.3; Annex IIIA 9.1.2) .....	259

B.8.2.1	Adsorption and desorption (Annex IIA 7.1.2).....	259
B.8.2.2	Mobility in soil (Annex IIA 7.1.3; Annex IIIA 9.1.2) .....	259
B.8.2.2.1	Aged residue column leaching studies .....	260
B.8.2.2.2	Lysimeter studies or field leaching studies.....	260
B.8.3	Predicted environmental concentrations in soil ( $PEC_{soil}$ ) (Annex IIIA 9.1.3).....	260
B.8.4	Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2.1; 9.2.3) .....	264
B.8.4.1	Hydrolytic degradation (Annex IIA 7.2.1.1) .....	264
B.8.4.2	Photochemical degradation (Annex IIA 7.2.1.2).....	265
B.8.4.3	Biological degradation (Annex IIA 7.2.1.3).....	266
B.8.4.3.1	Ready biodegradability .....	266
B.8.4.3.2	Water/sediment study .....	266
B.8.4.3.3	Degradation in the saturated zone .....	266
B.8.5	Impact on water treatment procedures (Annex IIIA 9.2.2).....	266
B.8.6	Predicted environmental concentrations in surface water and in ground water ( $PEC_{sw}$ , $PEC_{gw}$ ) (Annex IIIA 9.2.1, 9.2.3).....	267
B.8.6.1	Predicted environmental concentrations in surface water ( $PEC_{sw}$ ).....	267
B.8.6.2	PEC in ground water .....	267
B.8.6.3	Monitoring data (Annex IIA 7.4) .....	267
B.8.7	Fate and behaviour in air (Annex IIA 7.2.2; Annex IIIA 9.3) .....	268
B.8.8	Predicted environmental concentrations in air ( $PEC_A$ ) (Annex IIIA 9.3) .....	271
B.8.9	Definition of the residue (Annex IIA 7.3).....	271
B.8.10	References relied on .....	272
<b>B.9</b>	<b>Ecotoxicology .....</b>	<b>275</b>
B.9.1	Effects on birds (Annex IIA 8.1; Annex IIIA 10.1).....	275
B.9.1.1	Acute oral toxicity (Annex IIA 8.1; Annex IIA 10.1) .....	275
B.9.1.2	Dietary toxicity (Annex IIA 8.1.2; Annex IIIA 10.1.1).....	277
B.9.1.3	Subchronic toxicity and reproduction (Annex IIA 8.1.3; Annex IIIA 10.1) .....	284
B.9.1.4	Toxicity of the formulation (Annex IIIA 10.1) .....	285
B.9.1.5	Other studies (Annex IIIA 10.1.2; 10.1.3; 10.1.4).....	285
B.9.1.5.1	Supervised cage or field trials .....	285
B.9.1.5.2	Acceptance of bait, granules, or treated seeds by birds .....	285
B.9.1.6	Summary of effects on birds.....	285
B.9.1.7	Risk assessment.....	286
B.9.1.7.1	Risk assessment of the active substance.....	287
B.9.1.7.2	Risk assessment for metabolites.....	287
B.9.1.7.3	Refined risk assessment.....	287
B.9.1.7.4	Bioaccumulation and food chain behaviour.....	287
B.9.2	Effects on aquatic organisms (Annex IIA 8.2; Annex IIIA 10.2).....	288
B.9.2.1	Toxicity data (Annex IIA 8.2; Annex IIIA 10.2.1).....	288
B.9.2.1.1	Fish - acute toxicity .....	288
B.9.2.1.2	Fish - prolonged toxicity .....	289
B.9.2.1.3	Fish life cycle test.....	289
B.9.2.1.4	Bioconcentration in fish .....	289
B.9.2.1.5	Invertebrates - acute toxicity .....	289
B.9.2.1.6	Invertebrates - long-term toxicity .....	289
B.9.2.1.7	Algae .....	290
B.9.2.1.8	Effects on sediment-dwelling organisms.....	290
B.9.2.1.9	Aquatic plants.....	290

B.9.2.1.10	Microcosm or mesocosm studies .....	290
B.9.2.2	Summary of aquatic toxicity data .....	290
B.9.2.3	Risk assessment .....	291
B.9.3	Effects on other terrestrial vertebrates (Annex IIIA 10.3) .....	292
B.9.3.1	Summary of terrestrial vertebrate acute and reproductive studies .....	295
B.9.3.1.1	Effects of calcium phosphide and the product .....	295
B.9.3.2	Other studies .....	296
B.9.3.2.1	Supervised cage or field trials .....	296
B.9.3.2.2	Acceptance of bait, granules or treated seeds by terrestrial vertebrates .....	296
B.9.3.3	Summary of results used in the risk assessment .....	296
B.9.3.4	Risk assessment .....	296
B.9.3.4.1	Bioaccumulation and food chain behaviour .....	297
B.9.4	Effects on bees .....	298
B.9.4.1	Acute toxicity (Annex IIA 8.3.1, Annex IIIA 10.4) .....	298
B.9.4.1.1	Acute oral and contact toxicity of technical aluminium-phosphide (Annex II A; 8.3.1) .....	298
B.9.4.1.2	Acute oral and contact toxicity of formulated aluminium-phosphide to honeybees (Annex III A; 10.4) .....	298
B.9.4.2	Bee brood feeding test (Annex IIA 8.3.1.2) .....	298
B.9.4.3	Residue test (Annex IIIA 10.4.2) .....	298
B.9.4.4	Cage test (Annex IIIA 10.4.3) .....	298
B.9.4.5	Field test (Annex IIIA 10.4.4) .....	298
B.9.4.6	Tunnel test (Annex IIIA 10.5.5) .....	298
B.9.4.7	Risk assessment for honeybees .....	299
B.9.5	Effects on other arthropods species (Annex IIA 8.3.2; Annex IIIA 10.5) .....	299
B.9.5.1	Acute toxicity (Annex IIA 8.3.2; Annex IIIA 10.5.1) .....	299
B.9.5.1.1	Laboratory tests .....	299
B.9.5.2	Extended studies (Annex IIA 8.3.2; Annex IIIA 10.5.1) .....	299
B.9.5.2.1	Extended laboratory studies .....	299
B.9.5.2.2	Field tests .....	299
B.9.5.3	Summary of toxicity data on arthropods other than bees .....	299
B.9.5.4	Risk assessment .....	299
B.9.6	Effects on earthworms (Annex IIA 8.4; Annex IIIA 10.6.1) .....	300
B.9.6.1	Acute toxicity (Annex IIA 8.4.1; Annex IIIA 10.6.1.1) .....	300
B.9.6.2	Sublethal effects (Annex IIA 8.4.2; Annex IIIA 10.6.1.2) .....	301
B.9.6.3	Field study (Annex IIIA 10.6.1.3) .....	301
B.9.6.4	Summary of toxicity data on earthworms .....	301
B.9.6.5	Risk assessment .....	301
B.9.7	Effects on other soil non-target macro-organisms (Annex IIIA 10.6.2) .....	302
B.9.8	Effects on soil non-target micro-organisms (Annex IIA 8.5; Annex IIIA 10.7) .....	302
B.9.8.1	Laboratory testing .....	302
B.9.8.2	Additional testing .....	305
B.9.8.3	Summary of results and risk assessment .....	305
B.9.9	Effects on other non-target organisms (flora and fauna) believed to be at risk (Annex IIA 8.6) .....	305
B.9.10	Effects on biological methods of sewage treatment (Annex IIA 8.7) .....	306
B.9.11	References relied on .....	309
<b>B.10</b>	<b>Appendices .....</b>	<b>315</b>

B.10.1	Appendix I: Standard terms and abbreviations .....	315
B.10.2	Appendix II: Specific terms and abbreviations .....	327

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## **Annex B**

### **Calcium phosphide**

#### **B-1: Identity**

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WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

## B.1 Identity

### B.1.1 Identity of the active substance (Annex IIA 1 and 3.1)

#### B.1.1.1 Name and address of applicant(s) for inclusion of the active substance in Annex I (Annex IIA 1.1)

**Applicant:**

Chemische Fabrik Wülfel  
Postfachh 890109  
30514 Hannover  
Germany

**Contact:**

Name: Uta Köhler  
Phone: +49 (0511) 98496 20  
Fax: +49 (0511) 98496 40  
Email: CFW@wuelfel.de

#### B.1.1.2 Common name and synonyms (Annex IIA 1.3)

Calcium phosphide  
Polytanol (synonym)

#### B.1.1.3 Chemical name (Annex IIA 1.4)

IUPAC Tricalcium diphosphide  
CAS Calcium phosphide

#### B.1.1.4 Manufacturer's development code number (Annex IIA 1.5)

**Applicant:**

Chemische Fabrik Wülfel  
Hildesheimer Strasse 305  
30519 Hannover  
Germany

**Contact:**

Name: Uta Köhler  
Phone: +49 (0511) 98496 20  
Fax: +49 (0511) 98496 40  
Email: CFW@wuelfel.de

#### B.1.1.5 CAS, EEC and CIPAC numbers (Annex IIA 1.6)

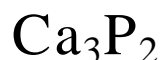
CAS 1305-99-3  
EC (EEC) 215-142-0  
CIPAC 505

#### B.1.1.6 Molecular and structural formulae, molecular mass (Annex IIA 1.7)

Molecular formular:  $\text{Ca}_3\text{P}_2$

Molecular mass: 182.19 g/mol

Structural formula:



**B.1.1.7 Manufacturer or manufacturers of the active substance (Annex IIA 1.2)**

**Manufacturer:**

Chemische Fabrik Wülfel GmbH & Co. KG  
Hildesheimer Str. 305  
30519 Hannover  
Germany

**Contact:**

Name: Dr. Gerald Just  
Phone: +49 (0511) 98496-0  
Email: CFW@wuelfel.de

**B.1.1.8 Method or methods of manufacture (Annex IIA 1.8)**

Confidential information, see Annex C.

**B.1.1.9 Specification of purity of the active substance (Annex IIA 1.9)**

Clarification on the specification of the technical material is still needed.

**B.1.1.10 Identity of isomers, impurities and additives (Annex IIA 1.10)**

Confidential information, see Annex C.  
Concerning relevant impurities.

**B.1.1.11 Analytical profile of batches (Annex IIA 1.11)**

Confidential information, see Annex C.

**B.1.2 Identity of the plant protection product (Annex IIIA 1)**

**B.1.2.1 Current, former and proposed trade names and development code numbers (Annex IIIA 1.3)**

Trade name: Polytanol



**B.1.2.2 Applicant (Annex IIIA 1.1)**

Name Chemische Fabrik Wülfel  
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City 30514 Hannover  
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Telefax No.: +49 (0511) 9 84 96 40  
E-mail address: [CFU@wuelfel.de](mailto:CFU@wuelfel.de)

**B.1.2.3 Manufacturer or manufacturers of the plant protection product (Annex IIIA 1.2)**

Name Chemische Fabrik Wülfel GmbH & Co. KG  
Street Hildesheimer Straße 305  
City 30519 Hannover  
Country Germany

Person to contact: Dr. Gerald Just  
Telephone No.: +49 (0511) 9 84 96-0  
E-mail address: [CFU@wuelfel.de](mailto:CFU@wuelfel.de)

**B.1.2.4 Type of the preparation and code (Annex IIIA 1.5)**

Gas generating product (GE)

**B.1.2.5 Function (Annex IIA 3.1; Annex IIIA 1.6)**

Rodenticide

**B.1.2.6 Composition of the preparation (Annex IIIA 1.4)**

Confidential information, see Annex C.

### B.1.3 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIA-1.8	Anonymous	1996	Synthesis of calcium phosphide. not GLP, unpublished CHE2005-1661	N	CFW
AIIA-1.8	Anonymous	1996	Synthese von Calciumphosphid. not GLP, unpublished CHE2002-443	N	CFW
AIIA-1.8	Anonymous	1911	Process for the production of phosphor. calcium from chalk and phosphorous, engl. transl of german doc.: Verfahren zur Darstel- lung von Phosphorcalcium aus Kalk und Phos- phor. Deutsche Patentschrift 240 189 not GLP, published CHE2006-1127	N	-
AIIA-1.8	Martens- Menzel, R.	2000	Darstellung von technischem Calciumphos- phid. not GLP, unpublished CHE2005-108	N	CFW
AIIA-1.11; AIIA-2.5.1	Berthold, H.J.	1981	Results of the x-ray spectroscopic tests per- formed by us on two Polytanol samples. not GLP, unpublished CHE2006-1059	Y	CFW
AIIA-1.11; AIIA-4.1.1; AIIA-4.1.2; AIIIA-5.1.1	Kiefer, R.	2006	Determination of calcium phosphide and six impurities in five batches of calcium phosphide technical. 20061152/01 GLP, unpublished CHE2006-1128	Y	CFW
AIIA-1.11; AIIA-4.1.1; AIIIA-5.1.1	Martens- Menzel, R.	2000	Validation of the Determination of Phosphine in Air by Means of IR Absorption Spectro- metry. GLP, unpublished CHE2005-115	Y	CFW
AIIA-1.11; AIIA-2.9.1	Martens- Menzel, R.	2000	Report about the Gas Development from Soil Fumigants Containing Phosphides. GLP, unpublished CHE2005-113	Y	CFW
AIIA-1.11	Martens- Menzel, R.	2000	Translation of important parts from 3th draft VSG GC 81. GLP, unpublished CHE2006-1171	Y	CFW

<sup>1</sup> Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIA-3.1; AIIIA-6.2	Anonymous	2000	Experimentalni podminky. not GLP, unpublished BIO2005-97	Y	CFW
AIIA-3.1; AIIA-3.3; AIIA-3.4.2; AIIIA-3.1; AIIIA-3.3; AIIIA-6.2	Deriu, P.	1996	Essai Polytanol Taupicide. not GLP, unpublished BIO2005-94	Y	CFW
AIIA-3.1; AIIIA-6.2	Jakowlew, A.A.	2001	Gutachten über die Prüfungsunterlagen für das Zoozid Polytanol 18 %. not GLP, unpublished BIO2005-99	Y	CFW
AIIA-3.1; AIIIA-3.3; AIIIA-6.2	Kirillowa, M.N.	2002	Report on a study of the biological efficacy of and the setting out of regulations for the use of a Chemische Fabrik Wülfel GmbH and Co. zoozide Polytanol (18%). not GLP, unpublished BIO2005-101	Y	CFW
AIIA-3.1; AIIIA-6.2	Kirillowa, M.N.	2001	Bericht über die Erforschung der biologischen Wirksamkeit und Festlegung von Reglement bei Anwendung von Polytanol. not GLP, unpublished BIO2005-98	Y	CFW
AIIA-3.1; AIIA-3.2.1; AIIA-3.3; AIIIA-3.2	Lauenstein, G.	1992	Gaskonzentrationsmessungen nach der An- wendung von Polytanol. P/2-282 not GLP, unpublished BIO2005-93	Y	CFW
AIIA-3.1; AIIIA-3.2	Ritter v. Herz, E.	1957	Verfahren zur Schädlingsbekämpfung durch Vergasung mittels Phosphorwasserstoff. 965 609 not GLP, published BIO2005-88	N	-
AIIA-3.1; AIIA-3.3; AIIA-3.4.2; AIIIA-3.1	Steiner	1957	Hauptprüfung 1957-Mittel gegen Wühlmäuse. II-2840 Z/PH not GLP, unpublished BIO2005-92	N	CFW
AIIA-3.1; AIIA-3.4.2; AIIIA-3.3; AIIIA-6.2	Truchetet, D.	2000	Compte-Rendue d'Essai officiel 2000 Toute culture-Campagnol terrestre. 99100021 not GLP, unpublished BIO2005-96	Y	CFW

**Codes of owner**

CFW: Chemische Fabrik Wülfel

# **Annex B**

## **Calcium phosphide**

B-2: Physical and chemical properties

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## B.2 Physical and chemical properties

### B.2.1 Physical and chemical properties of the active substance (Annex IIA 2)

**Table 2.1-1 Summary of the physical and chemical properties of the active substance Calcium phosphide**

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.1.1 (IIA 2.1.1)	Melting point, freezing point or solidification point of technical active substance	Statement	techn.		approx. 1600 °C	Only result is given. Method de- scription, raw data etc. are missing. Acceptable	-
B.2.1.1.2 (IIA 2.1.2)	Boiling point of technical active substance	Statement	techn.		Not measurable (no boiling point was observed up to 1600 °C)	Acceptable	-
B.2.1.1.3 (IIA 2.1.3)	Temperature of decomposition or sublimation	Statement			The melting point was de- termined to be above 1600 °C. No signs of de- composition or sublimation were observed.	Acceptable	-
B.2.1.2 (IIA 2.2)	Relative density of technical active substance	EEC A3 (air comparison pycnometer) OECD 109	20.7 %	N	$d_4^{22} = 1.2740 \text{ g/cm}^3$	Acceptable	Köhler, U. (2004) (CHE2005-117)

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.3.1 (IIA 2.3.1)	Vapour pressure of technical active substance	Statement		Y	below $1.0 \cdot 10^{-5}$ hPa at ambi- ent temperature (The measured vapour pres- sure for zinc phosphide is below $1.0 \cdot 10^{-5}$ hPa.)	Acceptable	Smeykal, H. (2001) (CHE2006-288)  Anonymous (CHE2006-1172)
B.2.1.3.2 (IIA 2.3.2)	Volatility, Henry's law constant of technical active substance	Statement			Not applicable because cal- cium phosphide decomposes rapidly into calcium hy- droxide and phosphine by contact with water.	Acceptable	-
B.2.1.4.1 (IIA 2.4.1)	Appearance: physical state	Statement	Techn.		solid granules	Acceptable	-
B.2.1.4.2 (IIA 2.4.1)	Appearance: col- our	Statement	Techn.		dark grey with redbrown areas	Acceptable	-
B.2.1.4.2 (IIA 2.4.2)	Appearance: odour	Statement	Techn.		garlic	Acceptable	-

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.5.1.5 (IIA 2.5.1)	Spectra of technical active substance	UV/VIS IR			Not applicable due to insolubility in organic solvents and instability in water.	Acceptable	-
		NMR MS			Not applicable due to the inorganic nature of the technical substance.	Acceptable	
		x-ray diffraction spectrum by Debye-Scherrer method	Techn.	N	Material consists of approx. 40-80 % CaP and a residue of hydroxyl apatite.	No spectra were submitted. Additional information.	Berthold, H. J. (1981) (CHE2006-1059)
B.2.1.5.2 (IIA 2.5.2)	Spectra of relevant impurities	Statement			No impurities of toxicological or environmental concern.	Acceptable	-
B.2.1.6 (IIA 2.6)	Solubility in water of technical active substance	Statement			Not applicable due to instability in water at pH 4 to 10 and decomposition in water.	Acceptable	-
B.2.1.7 (IIA 2.7)	Solubility in organic solvents of technical active substance	Statement			Not applicable. The active substance is an inorganic salt with an ionic structure and is therefore insoluble in organic solvents.	Acceptable	Gmelins Handbuch (1961) (CHE2006-1132)



Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.8 (IIA 2.8)	Partition coefficient of technical active substance (n-octanol/water)	Statement			Not applicable. The active substance decomposes rapidly in n-octanol/water into calcium hydroxide and phosphine.	Acceptable	-
	PH <sub>3</sub>	OECD 107 (1981)		N	$\log P_{O/W} = 0.6-1.2$ depending on mass of phosphine and ratio of octanol to water	The study contains minor discrepancies. Additional information.	Schlösser, W. (1989) (CHE2005-1895)
B.2.1.9.1 (IIA 2.9.1)	Hydrolysis rate of technical active substance	Determination of phosphine development in air		Y	The gas development behaviour under a relative atmospheric humidity of 55 and 75 % and a temperature of 20 °C of the active substance was examined by means of IR spectrometer. The maximum rates of gas (PH <sub>3</sub> ) development were determined to 38 (55 % humidity) and 80 $\mu\text{L} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$ (75 % humidity), respectively.	Acceptable	Martens-Menzel, R. (1998) (CHE2005-113)

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.9.2 (IIA 2.9.2)	Direct phototrans- formation of technical active substance	Statement		N	Not applicable due to fast hydrolysis in water. The active substance does not absorb light of any relevant wavelength.	Acceptable	-
	PH <sub>3</sub>	Statement			Phosphine absorbs UV light in the region 236-185 nm and decomposes in PH <sub>2</sub> , PH radical and hydrogen, re- spectively.	Acceptable	Calvert, J. and Pitts, J. (1966) (CHE2005-119) (literature)  Noyes, W.A. and Leighton, P.A. (1966) (CHE2005-120) (literature)
B.2.1.9.3 (IIA 2.9.3)	Quantum yield of direct photode- gradation	Statement			Not applicable due to fast hydrolysis in water. The active substance does not absorb light of any relevant wavelength.	Acceptable	-
B.2.1.9.4 (IIA 2.9.4)	Dissociation con- stant (pKa)	Statement			Not applicable due to fast hydrolysis in water. Instead of hydrolysis dissociation to phosphine and Calcium ca- tion occurs.	Acceptable	-

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.10 (IIA 2.10)	Estimated photochemical oxidative degradation	Statement			Data of the Estimated photochemical oxidative degradation is not submitted because the vapour pressure of the active substance is not measurable. Therefore, release to the atmosphere to any relevant degree is not to be expected.	Acceptable	-
B.2.1.11.1 (IIA 2.11.1)	Flammability		27.7 %  ~28 %	N  N	The active substance liberates extremely flammable gas in contact with water. The active substance has to be classified as highly flammable.  The active substance does not inflame under influence with a bunsen burner.	Acceptable  Acceptable  However, the ECB has classified calcium phosphide as F (highly flammable)	Karl, W. (1983) (CHE2006-1136)  Schlieper (1986) (CHE2006-1137)
B.2.1.12 (IIA 2.11.2)	Auto-flammability	EEC A16	27.6 %	Y	No self-ignition was observed under the test conditions up to 404 °C	Acceptable	Möller (2007) (CHE2007-406)

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.12 (IIA 2.12)	Flash point	Statement			Not applicable because melting point of active substance is above 40 °C.	Acceptable	-
B.2.1.13 (IIA 2.13)	Explosive properties	Statement to ECC A14	18 %		Not applicable. From the structural formulas of the parts of the product it can be concluded that the active substance is not explosive. The product does not contain any chemically instable or highly energetic groups that might lead to an explosion.	Acceptable	Lüth, P. (2004) (CHE2005-121)
B.2.1.14 (IIA 2.14)	Surface tension	Statement			Not applicable because calcium phosphide decomposes rapidly into calcium hydroxide and phosphine.	Acceptable	-

Section (Annex point)	Study	Method	Material/ Purity	GLP	Results	Conclusion/ Comment	Reference
B.2.1.15 (IIA 2.15)	Oxidising properties	Statement to ECC A17	18 %		Not applicable. From the structural formulas of the parts of the product it can be concluded that the active substance has no oxidising properties. The product does not contain any chemical group that might act as an oxidising agent.	Acceptable	Lüth, P. (2004) (CHE2005-121)

### **B.2.1.1 Summary of data presented under points B.2.1.1 to B.2.1.15**

Calcium phosphide (in POLYTANOL) is produced as dark grey solid granules with redbrown areas and garlic odour. It has a melting point of approx. 1600 °C and a density of 1.274 g/cm<sup>3</sup>. The active substance is an inorganic salt with an ionic structure and is therefore insoluble in organic solvents. Calcium phosphide is instable in water at pH 4 to 10 because of decomposition. By contact with water (air humidity) it rapidly evolves phosphine, a colourless gas which is toxic and extremely flammable. Calcium phosphide is not flammable and has no explosive or oxidising properties.

Polytanol is a grey to dark grey gas generating product (granules) with a garlicky odour. It has neither explosive nor oxidising properties and it is not highly flammable, but will evolve extremely flammable gas in contact with water. The results of the accelerated storage test and the shelf life test confirm its stability at least for two years under practical conditions. Its technical properties indicates no particular problems when used as recommended.

### **B.2.1.2 Methods which do not meet the requirements**

Following methods for calcium phosphide do not fulfil the requirements:

Anonymous (1961), Calcium und Phosphor-Calciumphosphid Ca<sub>3</sub>P<sub>2</sub>, 28, 1115 -1119 (1961), CFW, (CHE2005-116)

Schlösser, W. (1989), Octanol-Wasser-Verteilungskoeffizient von PH<sub>3</sub> Untersuchungsbericht, 05011, CFW, (CHE2002-448)

Anonymous (1996), Diacalciumphosphatschlamm, CFW, (CHE2005-118)

Karl, W. (1983), Calciumphosphid – Polytanol, CFW, (CHE2002-451)

Schlieper (1986), Beurteilung der Brennbarkeit von Polytanol, CFW, (CHE2002-450)

Justification:

The submitted studies are in German language.

## B.2.2 Physical, chemical and technical properties of the plant protection products (Annex IIIA 2)

Product name: **Polytanol** (containing 180 g/kg calcium phosphide, *GE*)

**Table B.2.2-1: Summary of the physical, chemical and technical properties of the plant protection product**

Section (Annex point)	Study	Method	Results	Comment/ Conclusion	Reference
B.2.2.1.1 (IIIA 2.1)	Appearance: colour	Visual assessment	Grey, dark grey with redbrown areas	acceptable	Document M-III
B.2.2.1.2 (IIIA 2.1)	Appearance: odour	Olfactory assess- ment	Garlicky (characteristic odour of phosphine)	acceptable	Document M-III
B.2.2.1.3 (IIIA 2.1)	Appearance: physical state	Visual assessment	Solid (granules)	acceptable	Document M-III
B.2.2.2.1 (IIIA 2.2)	Explosive properties	Statement	From the structural formulas of the parts of Polytanol it can be concluded that Polytanol is not explosive. The product does not contain any chemically instable or highly energetic groups that might lead to an explosion.	acceptable	Lüth, P. (2004) PHY2005-77
B.2.2.2.2 (IIIA 2.2)	Oxidising properties	Statement	From the structural formulas of the parts of Polytanol it can be concluded that Polytanol has no oxidising properties. The product does not contain a chemical group that might act as an oxidising agent.	acceptable	Lüth, P. (2004) PHY2005-77
B.2.2.3.1 (IIIA 2.3)	Flash point		No liquid preparation.		

Section (Annex point)	Study	Method	Results	Comment/ Conclusion	Reference
B.2.2.3.2 (IIIA 2.3)	Flammability	EEC A 12	<p>Polytanol glows but do not burst into flames Not highly flammable. (content of calciumphosphid: 28 %)</p> <p>Test material could not be ignited during 15 s with a Bunsen burner flame By contact with water a extremely flammable gas evolved (PH<sub>3</sub>). Polytanol is highly flammable (step 1 of EEC A 12) (content of calciumphosphide: 27.7 %)</p>	<p>acceptable</p> <p>acceptable</p>	<p>Schlieper (1986) PHY2006-701;</p> <p>Karl, W. (1983) PHY2006-700</p>
B.2.2.3.3 (IIIA 2.3)	Auto-flammability	EEC A 16	<p>Polytanol is not considered to be a self-heating substance. No self-ignition was observed under the test conditions up to 404 °C</p>	acceptable	<p>Karl, W. (1983) PHY2006-700 Möller (2007) (CHE2007-406)</p>
B.2.2.4.1 (IIIA 2.4)	Acidity/alkalinity		The determination of acidity/alkalinity of Polytanol in aqueous solution is technically not feasible due to the violent reaction of calcium phosphide in contact with water.		
B.2.2.4.2 (IIIA 2.4)	pH	CIPAC MT 75	12.4 +/- 0.2 (1 % in CIPAC water D).	acceptable	Köhler, U. (1996) PHY2006-702
B.2.2.5.1 (IIIA 2.5)	Kinematic viscosity		Not applicable.		
B.2.2.5.2 (IIIA 2.5)	Dynamic viscosity		Not applicable.		
B.2.2.5.3 (IIIA 2.5)	Surface tension		Not necessary.		



Section (Annex point)	Study	Method	Results	Comment/ Conclusion	Reference
B.2.2.6.1 (IIIA 2.6)	Relative density		Not applicable.		
B.2.2.6.2 (IIIA 2.6)	Bulk (tap) density	CIPAC MT 186  EEC A 3 gas comparison pycnometer	Pour: 1140 g/L Tap: 1170 g/L  Pour: 1030 – 1330 g/L  1.2258 ... 1.3464 g/cm <sup>3</sup>	acceptable  <b>Further information</b>	Walter, D. (2007) (PHY2007-210)  Köhler, U. (1996) PHY2006-702  Köhler, U. (2004) PHY2005-81
B.2.2.7.1 (IIIA 2.7)	Storage stability	CIPAC MT 46	Physically and chemically stable after storage for 14 days at 54 °C. Polytanol shows less than 2 % decrease in the active substance content. The alteration of the observed physical properties (appearance, dust content) are negligible. Dust content: 0.20 % (before storage); 0.46 % (after storage)	acceptable	Martens-Menzel, R. (1998) PHY2005-83
B.2.2.7.2 (IIIA 2.7)	Low temperature stability		No liquid preparation.		

Section (Annex point)	Study	Method	Results	Comment/ Conclusion	Reference
B.2.2.7.3 (IIIA 2.7)	Shelf-life	GIFAP Mono- graph 17	Physically and chemically stable after storage for 2 years at ambient temperature. Polytanol shows about 5 % decrease in the active substance content. The alteration of the observed physical properties (appearance, dust content) are negligible Dust content: 0.20 % (before storage); 0.51 % (after storage).	acceptable	Martens-Menzel, R. (2000) PHY2005-84
B.2.2.8.1 (IIIA 2.8.1)	Wettability		Not applicable.		
B.2.2.8.2 (IIIA 2.8.2)	Persistent foaming		Not applicable.		
B.2.2.8.3.1 (IIIA 2.8.3)	Suspensibility		Not applicable.		
B.2.2.8.3.2 (IIIA 2.8.3)	Spontaneity of dispersion		Not applicable.		
B.2.2.8.4 (IIIA 2.8.4)	Dilution stability		Not applicable.		
B.2.2.8.5 (IIIA 2.8.5)	Dry sieve test		max. 0.3 % on 50 µm sieve	acceptable	Köhler, U. (1996) PHY2006-702
B.2.2.8.6.1 (IIIA 2.8.6)	Particle size distribution	sieve analysis	≤ 90 % - 5600 µm 0.3 % - ≤ 50 µm  16.3 % > 10 mm 10.1 % < 1 mm	acceptable	Köhler, U. (1996) PHY2006-702  Anonymous (2002) PHY2005-86
B.2.2.8.6.2 (IIIA 2.8.6)	Dust content		Not applicable.		

Section (Annex point)	Study	Method	Results	Comment/ Conclusion	Reference
B.2.2.8.6.3 (IIIA 2.8.6)	Friability and attrition		Not applicable.		
B.2.2.8.7.1 (IIIA 2.8.7)	Emulsifiability, emulsion stability and re-emulsifiability		Not applicable.		
B.2.2.8.7.2 (IIIA 2.8.7)	Stability of dilute emulsion		Not applicable.		
B.2.2.8.8.1 (IIIA 2.8.8)	Flowability	Statement	Complete flowable; particle size 3 ... 12 mm	acceptable	Köhler, U. (1996) PHY2006-702
B.2.2.8.8.2 (IIIA 2.8.8)	Pourability (rinsability)		Not applicable.		
B.2.2.8.8.3 (IIIA 2.8.8)	Dustability		Not applicable.		
B.2.2.9.1 (IIIA 2.9)	Physical compatibility with other products		Not applicable (no tank mixtures recommended).		
B.2.2.9.2 (IIIA 2.9)	Chemical compatibility with other products		Not applicable (no tank mixtures recommended).		
B.2.2.10 (IIIA 2.10)	Adherence and distribution to seeds		No seed dressing formulation.		

Additional information see section B.2.1.

### B.2.2.11 Summary and evaluation of data presented under points B.2.2.1 to B.2.2.10 (IIIA 2.11)

Polytanol is a dark grey gas generating product (granules) with a garlicky odour. It has neither explosive nor oxidising properties and it is not highly flammable, but will evolve extremely flammable gas in contact with water. The results of the accelerated storage test and the shelf life test confirm its stability at least for two years under practical conditions. Its technical properties indicates no particular problems when used as recommended.

### B.2.3 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIA-2.2	Köhler, U.	2004	Relative Density of Polytanol (Calciumphosphide). not GLP, unpublished CHE2005-117	Y	CFW
AIIA-2.3.1	Anonymous	2006	IIA, 2.3.1, Vapour pressure (Statement). not GLP, unpublished CHE2006-1172	N	CFW
AIIA-2.3.1	Smeykal, H.	2001	Zinc phosphide: Vapour pressure. 20010674.03 GLP, unpublished CHE2006-288	Y	CFW
AIIA-1.11; AIIA-2.5.1	Berthold, H.J.	1981	Results of the x-ray spectroscopic tests performed by us on two Polytanol samples. not GLP, unpublished CHE2006-1059	Y	CFW
AIIA-2.7	Anonymous	1961	Calcium and phosphorous - calciumphosphide, engl. transl. of german doc.: Calcium und Phosphor - calciumphosphid Ca <sub>3</sub> P <sub>2</sub> . Gmelins Handbuch der anorganischen Chemie, Calcium, Teil B - Lieferung 3 System-nummer 28, 1115-1119 not GLP, published CHE2006-1132	N	-
AIIA-2.8	Schlösser, W.	1989	Octanol/water partition coefficient of PH <sub>3</sub> , Engl. transl. of German doc.: Octanol-Wasser-Verteilungskoeffizient von PH <sub>3</sub> . 05011 not GLP, unpublished CHE2005-1895	Y	CFW

<sup>1</sup> Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIA-1.11; AIIA-2.9.1	Martens- Menzel, R.	2000	Report about the Gas Development from Soil Fumigants Containing Phosphides. GLP, unpublished CHE2005-113	Y	CFW
AIIA-2.9.2; AIIA-2.10	Calvert, J., Pitts, J.	1966	Photochemistry - The Interaction of Light with Simple Molecules. not GLP, unpublished CHE2005-119	N	CFW
AIIA-2.9.2	Noyes, W.A., Leighton, P.A.	1966	The Photochemistry of Gases - Absorption by Polyatomic Molecules. not GLP, published CHE2005-120	N	-
AIIA-2.10; AIIA-7.2.2	Fritz, B. et al	1982	Laboratory kinetic investigations of the tro- pospheric oxidation of selected industrial emis- sions. Physico-Chemical Behaviour of Atmospheric Pollutants, 1982, 192-202 not GLP, published LUF2002-39	N	-
AIIA-2.11.1	Karl, W.	1983	Calcium phosphide - "Polytanol"; engl. transl. of the german doc: Calciumphosphide - "Poly- tanol". not GLP, unpublished CHE2006-1136	N	CFW
AIIA-2.11.1	Schlieper	1986	Determination of flammability of polytanol; engl. transl. of the german doc: Beurteilung der Brennbarkeit von Polytanol. not GLP, unpublished CHE2006-1137	Y	CFW
AIIA-2.11.2	Möller, M.	2007	Auto-flammability A.16 (Solids - determinati- on of relative self-ignition temperature) GLP, unpublished CHE2007-406	Y	CFW
AIIA-2.13; AIIA-2.15	Lüth, P.	2004	Classification of product "Polytanol" in accor- dance with method EC A.14 - Explosive Pro- perties and method EC A.17 - Oxidising Pro- perties (Solids). not GLP, unpublished CHE2005-121	Y	CFW
AIIA-2.3	Karl, W.	1983	Calciumphosphid - Polytanol. not GLP, unpublished PHY2006-700	Y	CFW
AIIA-2.3	Karl, W.	1983	Calciumphosphid - Polytanol. not GLP, unpublished PHY2005-78	Y	CFW

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIIA-2.3	Möller, M.	2007	Auto-flammability A.16 (Solids - determination of relative self-ignition temperature) GLP, unpublished CHE2007-406	Y	CFW
AIIIA-2.3	Schlieper	1986	Beurteilung der Brennbarkeit von Polytanol. not GLP, unpublished PHY2006-701	N	CFW
AIIIA-2.4.2; AIIIA-2.6.2; AIIIA-2.8.6.1; AIIIA-2.8.6.3; AIIIA-2.8.8.1	Köhler, U.	1996	1. Information on the physical characteristics of the substance, 2. Flowability. not GLP, unpublished PHY2006-702	N	CFW
AIIIA-2.6	Walter, D.	2007	Pour and tap density of Polytanol GLP, unpublished PHY2007-210	Y	CFW
AIIIA-2.7.1; AIIIA-2.7.3; AIIIA-2.8.6.2	Martens-Menzel, R.	2000	Report of Examination 98/2 (Storage Stability of Polytanol Pellets). 98/2 GLP, unpublished PHY2005-84	Y	CFW
AIIIA-2.7.1; AIIIA-2.8.6.2	Martens-Menzel, R.	1998	Report of Examination 98/1 (Storage Stability of Polytanol Pellets). 98/1 GLP, unpublished PHY2005-83	Y	CFW
AIIIA-2.8.6.1; AIIIA-2.8.6.2; AIIIA-2.8.6.3	Anonymous	2002	Particle size distribution. not GLP, unpublished PHY2005-86	N	CFW

#### Codes of owner

CFW: Chemische Fabrik Wülfel

## **Annex B**

### **Calcium phosphide**

**B-3: Data on application  
and further information**

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.



## **B.3 Data on application and further information**

### **B.3.1 Data on application relevant to the active substance (Annex IIA 3.1 to 3.6)**

#### **B.3.1.1 Function**

Calcium phosphide is a rodenticidal active substance to control rodents and moles (and other non-rodent vertebrates).

#### **B.3.1.2 Effects on harmful organisms**

The lethal concentration for animals appears to be related to both the time of exposure and the concentration of phosphine. At the intended application rate, death of burrowing animals usually occurs within 2 days, although a second application may be required to control any surviving animals.

#### **B.3.1.3 Field of use**

Rodenticide in the field (cropland and non-cropland situations).

#### **B.3.1.4 Harmful organisms**

The good biological efficacy of Polytanol pellets against the target animals such as common field mouse, European mole and water vole was demonstrated in large scale field trials.

#### **B.3.1.5 Mode of action**

Phosphine is highly toxic; it can easily kill in relatively low concentrations. Because of this, the gas is used for pest control by fumigation. For farm use, it is often sold in the form of aluminium phosphide, calcium phosphide or zinc phosphide pellets, which yield phosphine on contact with atmospheric water or rodents stomach acid. These pellets also contain other chemicals which evolve ammonia which helps to reduce the potential for spontaneous ignition or explosion of the phosphine gas. They may also contain other agents, such as methanethiol, to give the gas a detectable garlic smell to help warn against its presence in the atmosphere.

#### **B.3.1.6 Information on the occurrence or possible occurrence of the development of resistance and appropriate management strategies**

The lack of development of resistance in the target organisms to this plant protection product is assumed to be related to the inorganic nature of the active substance.

## B.3.2 Data on application relevant to the plant protection product (Annex IIIA 3)

### B.3.2.1 Field of use envisaged

Rodenticide in the field. Polytanol is an effective product for voles and moles control.

### B.3.2.2 Effects on harmful organisms

Polytanol is a rodenticide fumigant containing 18 % calcium phosphide as a granular formulation for the control of voles (*Arvicola terrestris*) and moles (*Talpa europea*). It is sold unformulated as the technical active ingredient, and thus the composition of the formulation and the technical active ingredient are the same (see reference: Document K, Section 1, Annex IIA, point 3).

The following rodenticide products which contain calcium phosphide and manufactured by the sponsor are registered or are under development for registration:

Product	Code*	Calcium phosphide conc. [g/kg]	other active substances
Polytanol	GE	180	none

\*: codes assigned by BBA, Braunschweig, Germany

The good biological efficacy of Polytanol pellets against the target animals common field mouse, the European mole and the water vole, respectively, was demonstrated in large scale field trials.

### B.3.2.3 Details of intended use

The existing and intended use of Polytanol is the protection of agricultural crops, vegetable, fruit and ornamental growing and grassland against damage by water voles (*Arvicola terrestris*) and common voles (*Microtus arvalis*). These voles are widely spread harmful organisms in all types of cultivations and damage plants by eating roots, bulbs and seeds. Little damages of bark attracted the voles and stimulated their gnawing activity. Due to their high fertility, the voles can easily accumulate and cause extensive damage in cultivations.

Polytanol is a high effectively product against voles.

**Table B.3.2-1: Field trial to the efficacy of Polytanol (calcium phosphide) against voles (*Arvicola terrestris*) in comparison with reference products**

Substance	Number of voles trapped	Efficacy [%] in
Temoin	57	-
Bromadiolone	9	84
Polytanol (PH <sub>3</sub> )	11	81

The biological efficacy of Polytanol pellets against *Arvicola terrestris* and *Microtus arvalis* in grassland, winter wheat and winter rape is good. For general use the dosage applied must be raised. The proposal dosages for target animals are:

*Arvicola terrestris*    0.5 kg/ha  
*Microtus arvalis*     0.2 kg/ha.

Polytanol is a high effectively product against moles.

**Table B.3.2-2: Field trial to the efficacy of Polytanol (Calcium phosphide) against moles (*Talpa europaea* L.) in comparison with reference products**

Location	Essay Boujaillers (25)		Essay L'Hopital du rosbois (25)	
	Reference product:	Number of moles trapped	Efficacy [%]	Number of moles trapped
Sovitaup	3	84	4	73
Polytanol	4	79	4	73
Temoin	19	-	15	-

#### B.3.2.4 Application rate

The useful recommended mode of application is at a rate of 8 g/tunnel (21 pieces granule/tunnel). Depending on the context of infestation, this is considered to correspond to a maximum field application rate of 8 - 10 kg/ha.

#### B.3.2.5 Concentration of active substance in material used

Concentration in Polytanol: 18 % calcium phosphide

### B.3.2.6 Method of application

Polytanol is a ready-to-use solid granule for outdoor application. Its practical use is in agricultural crops, on grassland, in vegetable and fruit growing, in ornamental growing, in domestic and amateur gardening against damage by common voles (*Arvicola terrestris*) and moles (*Talpa europaea*) by covered application. It will be marketed in a 125g can, 250g can, 500 g can, 1 kg can and 5 kg can.

### B.3.2.7 Number and timing of applications and duration of protection

Character	Annotation
Application rate (open application):	8 g per run corresponding to 8 kg/ha (18.0 % as, corresponding to 1.8 kg as/ha)
Application:	covered
Time of application:	if required
Maximum number of treatments and interval:	in general 1 application. Repetition of application only, if after 2-4 days moles and voles holes are still inhabited.

### B.3.2.8 Necessary waiting periods or other precautions to avoid phytotoxic effects on succeeding crops

No impact on succeeding crops is to be expected, and no studies were conducted, since there is no danger that significant residues (> 5 % of the applied active substance as a total of unchanged calcium phosphide and its relevant metabolites or degradation product) remain in soil or in plant materials up to sowing or planting time of succeeding crops and which could lead to any residues at harvest. Instead, based on soil degradation studies with calcium phosphide, it is expected that degradation will be complete within approx. 4 - 5 days after contact with soil (if any).

### B.3.2.9 Proposed instructions for use

See Document C (all national labels are listed in Doc C) and the attached GAP of representative and intend crops (Document D).

### B.3.3 Summary of data on application

#### B.3.3.1 List of uses evaluated for Annex-I-inclusion

Crop and/or situation	Member State or Country	Product name	F G or I  (b)	Pests or Group of pests controlled  (c)	Formulation		Application				Application rate per treatment			PHI (days)  (l)	Remarks  (m)
(a)					Type	Conc. of as	method kind	growth stage & season	number min max  (k)	interval between applications (min)	kg as/hL min max	water L/ha min max	kg as/ha min max		
					(d-f)	(i)	(f-h)	(j)							
Vegetables (NNNWW) Fruit (NNNOO) Ornamental Plants (NNNZZ) Agricultural Crops (NNNAC) Grassland (NNNFW)	Germany  (Northern europe)	Polytanol	F	Arvicola terrestris (ARVCTE),  Talpa europaea (TALPEU)	GE	180 g/kg	Covered application with ancillary tools (e.g. drop gun, drop tube)	All stages	If required	without waiting-time	8 g/run	Not applicable	1.44 kg as/ha (min. 8 kg product/ha)  1.8 kg as/ha (max 10 kg product/ha)	Not required	

**Remarks:**

(a) For crops, the EU and Codex classifications (both) should be used; where relevant, the use situation should be described (e.g. fumigation of a structure)

(b) Outdoor or field use (F), glasshouse application (G) or indoor application (I)

(c) e.g. biting and suckling insects, soil born insects, foliar fungi, weeds

(d) e.g. wettable powder (WP), emulsifiable concentrate (EC), granule (GR)

(i) g/kg or g/L

(j) Growth stage at last treatment (BBCH Monograph, Growth Stages of Plants, 1997, Blackwell, ISBN 3-8263-3152-4), including where relevant, information on season at time of application

(k) The minimum and maximum number of application possible under practical conditions of use must be provided

- (e) GCPF Codes - GIFAP Technical Monograph No 2, 1989
- (f) All abbreviations used must be explained
- (g) Method, *e.g.* high volume spraying, low volume spraying, spreading, dusting, drench
- (h) Kind, *e.g.* overall, broadcast, aerial spraying, row, individual plant, between the plants - type of equipment used must be indicated

PHI - minimum pre-harvest interval

- (l) Remarks may include: Extent of use/economic importance/restrictions
- (m)

\* Uses for which the risk assessment can not be concluded are marked grey.

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## B.3.4 Further information on the active substance (Annex IIA 3.7 to 3.9)

### B.3.4.1 Recommended methods and precautions concerning handling, storage, transport or fire (Annex IIA 3.7)

References: Köhler, U. (2004), Health and Safety Data Sheet –Polytanol-, (CHE2005-127)

#### B.3.4.1.1 Handling

##### Information on safe handling:

Ventilation:	General ventilation adequate. LEV may be required in confined environments. Prevent dust and gas proliferation.
Prohibited procedures and equipment:	Water sprays
Temperature range:	0-30 °C
Humidity range:	Avoid damp or humid conditions. Contact with water liberates toxic extremely flammable gas.
Precaution against static discharge:	Yes
Fire and explosion prevention:	Avoid damp or humid conditions, dust and gas formation. Clean up dust collections.

##### Personal Precautions:

Industrial hygiene:	Wash hands, face and exposed skin before breaks and immediately after handling the product. Do not breathe dust. Avoid contact with skin or eyes.
Handling:	Avoid dust formation in confined areas. When handling do not eat, drink or smoke.
Keep away from:	Food, drink and animal stuffs, water, acids, oxidising agents.
Irritating to:	Skin and eyes. (Wear suitable protective clothing and gloves.)
Personal protective equipment:	Respirator: respirator with P2-B3 gas filter Eyes: goggles, face-shield Hands: chemical resistant gauntlet gloves Other: protective suit or coveralls and apron, rubber boots
Accident:	In case of accident or if you fell unwell, seek medical advice immediately (show the label where possible).

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### B.3.4.1.2 Storage

Storage:	Keep containers tightly closed in a dry, cool and well-ventilated place, out of reach of children and away from food, drink and animal feedings stuffs. Keep locked up and out of reach of children. Avoid release to the environment.
Fire:	In case of fire, use dry powder or dry sand. NEVER USE WATER !
Storage class:	4.3

### B.3.4.1.3 Transport

<u>Land transport:</u>	ADR/RID and GGVSE
ADR/RID and GGVSE class:	4.3
Classification code:	WT2
Packaging group:	I
UN-No:	1360
Allowable limit:	20 Kg net
Lower limit:	0 Kg (LQ 0)
<u>Sea transport:</u>	IMDG and GGVSea
ADR/RID and GGVSea class:	4.3
IMO Packaging class:	I
UN-No:	1360
EmS-No:	4.3-02
MFAG:	205
Propper shipping name:	Phosphide pesticide, solid toxic (contains calcium phosphide 25 %)
IMO labels:	6 Toxic + MARINE POLLUTANT
UK Emergency Action Code:	N/A
<u>Air transport:</u>	ICAO/IATAA-DGR
ICAO/IATA class:	4.3
UN/ID No:	1360
<u>Other data:</u>	
Postal despatch:	Inadmissible (calcium phosphide 25 %)



#### B.3.4.1.4 Fire fighting measures

Important:	Substance is stable up to 1600 °C. Contact with water will release toxic and highly flammable gas which is heavier than air. Use sand or earth bonding for fire-fighting if necessary. If without risk, remove intact containers from exposure to fire. Keep unopened containers cool.
Specific hazards:	Do not contaminate watercourses.
Suitable extinguishers:	Dry chemical CO <sub>2</sub> or dry powder of dry sand as suitable for fire conditions.
Unsuitable extinguishers:	Water jet, water spray or foam.
Personal protective equipment:	Wear self-contained breathing apparatus.
	Respirator: respirator with P2-B3 gas filter
	Eyes: goggles, face-shield
	Hands: chemical resistant gauntlet gloves
	Other: protective suit or coveralls and apron, rubber boots
Hazardous combustion products:	Oxides of phosphorous, calcium phosphide dust.
Special equipment or procedures for fire fighting:	None

#### B.3.4.2 Procedures for destruction or decontamination (Annex IIA 3.8)

##### B.3.4.2.1 Controlled incineration

The submission of data on controlled incineration of Polytanol (Calcium phosphide) is not considered to be required, since the halogen content is not higher than 60 %. In fact, calcium phosphide is not a halogenated molecule.

##### B.3.4.2.2 Others

No other methods are proposed to dispose of the active substance calcium phosphide. Unused Calcium phosphide material or other such waste and contaminated materials should be disposed of as specified by existing local, state and federal regulations concerning hazardous waste disposal. In accordance with regulations for special waste, must be taken after pre-treatment, to an authorised special waste disposal site.

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### B.3.4.3 Emergency measures in the case of an accident (Annex IIA 3.9)

Personal protection measures:	Respirator: respirator with P2-B3 gas filter Eyes: goggles, face-shield Hands: chemical resistant gauntlet gloves Other: protective suit or coveralls and apron, rubber boots
Safety precautions:	Avoid dust formation in confined areas. Wear suitable personal protective equipment.
Environmental precautions:	Avoid contaminating watercourses. Inform local authority if the material enters drains, rivers or sewers.
Clean-up procedure:	After spilling or leakage: Use personal protective equipment. Contain opened packages in containers of a similar material and close securely. Protect from water. Clean up straightaway by gently sweeping, scoop or vacuum. Avoid creating dust clouds or contact with water. Do not flush with water. Shovel into suitable marked container for disposal and close surely.

### B.3.5 Further information on the plant protection product (Annex IIIA 4)

#### B.3.5.1 Packaging (type, materials, size, etc.), compatibility of the preparation with proposed packaging materials (Annex IIIA 4.1)

##### B.3.5.1.1 Description of packaging (Annex IIIA 4.1.1)

125 g sealed-joint pack, body and base of polished tinplate, steel tear-off top, gold painted both sides, exterior painted white, orange-black printed, HKS 6, RAL 9005. Packaging for use in domestic gardens (home and allotments sector).

250 g tear-off top pack, size 78/88 mm, steel full tear-off top, gold painted inside and outside, opened, base smooth and exterior painted gold, release supplied, pack polished inside, however seam covered, body painted white outside and dual colour printed, black, orange.

500 g sealed-joint pack, body of polished tinplate, steel tear-off top, gold painted both sides, exterior painted white, orange-black printed, HKS 6, RAL 9005.

1 kg sealed-joint pack, body of polished tinplate, interior polished, steel tear-off top, gold painted both sides, exterior painted white, orange-black printed.

**Reference number:** PHY2005-733  
**Report:** Anonymous (2004)  
 Gesetz über die Beförderung gefährlicher Güter-  
 Überwachung der Serienfertigung von Gefahr-  
 gutverpackungen - Zulassungsschein Nr. D/BAM 5330/1A2W  
 und D/BAM 5331/1A2W  
 Chemische Fabrik Wülfel GmbH & Co. KG, Germany  
 unpublished

**Guidelines:** None  
**GLP:** No  
**Results:** Acceptable

#### **B.3.5.1.2 Suitability of packaging (Annex IIIA 4.1.2)**

**Reference number:** PHY2005-92  
 III.12 /90282 III.12/90283  
**Report:** Wienecke, B.-U. and Taegner, W. (2003)  
 Gesetz über die Beförderung gefährlicher Güter-Überwachung der  
 Serienfertigung von Gefahrgutverpackungen - Zulassungsschein  
 Nr. D/BAM 5330/1A2W und D/BAM 5331/1A2W  
 Bundesanstalt für Materialforschung und -prüfung GmbH, Berlin,  
 Germany  
 unpublished  
**Guidelines:** None  
**GLP:** No  
**Materials and methods:** Test item: sealed-joint pack with tear-off top and inner packaging  
 (plastic bag), for packaging of Polytanol (18 % calcium  
 phosphide).  
**Results:** The sealed-joint pack with tear-off top and inner packaging  
 (plastic bag) is tight against calcium phosphid. Acceptable.

#### **B.3.5.1.3 Resistance of packaging material to its contents (Annex IIIA 4.1.3)**

In an accelerated storage test, no changes in packaging were observed. In accordance with the report PHY2005-92 it is concluded that the packaging material is suitable for packaging and transport of Polytanol.

**Reference number:** PHY2005-92  
 III.12 /90282 III.12/90283  
**Report:** Wienecke, B.-U. and Taegner, W. (2003)  
 Gesetz über die Beförderung gefährlicher Güter-Überwachung der  
 Serienfertigung von Gefahrgutverpackungen - Zulassungsschein  
 Nr. D/BAM 5330/1A2W und D/BAM 5331/1A2W  
 Bundesanstalt für Materialforschung und -prüfung GmbH, Berlin,  
 Germany  
 unpublished  
**Guidelines:** None  
**GLP:** No

#### **B.3.5.2 Procedures for cleaning application equipment and protective clothing (Annex IIIA 4.2)**

The submission of information on procedures for cleaning application equipment for the product Polytanol is not considered to be required, since Polytanol is placed directly into the holes of voles with the aid of an ancillary tool (e. g. drop tube, drop gun), without the use of any further equipment which may become contaminated.

### **B.3.5.3 Re-entry periods, necessary waiting periods or other precautions to protect man, livestock and the environment (Annex IIIA 4.3)**

The following safety intervals as defined in Annex IIIA point 4.3 are adequately covered by information described in chapters mentioned below.

- pre-harvest interval for each relevant crop  
see chapters B.7.4 and B.7.10
- re-entry period for livestock to areas to be grazed  
see chapters B.7.4 and B.7.10
- re-entry period for man to crops, building or spaces treated  
see chapter B.6.14
- withholding period from animal feeding stuffs  
see chapters B.7.4 and B.7.10
- waiting period between application and handling to treated products  
see chapters B.7.4 and B.7.10
- waiting period between last application and sowing or planting succeeding crops  
see chapter B.3.2.8.

### **B.3.5.4 Recommended methods and precautions concerning handling, storage transport or fire (Annex III 4.4)**

#### **Reference:**

Köhler, U. (2004), Health and Safety Data Sheet acc. 91/155 EEC – Polytanol, CFW, (CHE2005-127)

#### **Information on handling and storage:**

Handling.	<p>Avoid contact with skin, eyes and clothing. Work with local exhaust or with breathing protection (combination filter: type P2-P3), wear protective gloves and safety goggles. Do not eat, smoke or drink during work with the substance.</p> <p>Avoid all contact with eyes, mouth or skin.</p> <p>Avoid raising dust.</p> <p>Maintain strict personal hygiene measures.</p>
Storage:	<p>Store separated from water and moisture. Store the substance in a cool and dry place. Keep container dry. Keep only in the original container. Keep it in a well-ventilated room. Wear suitable protective clothing and gloves. In case of accident or feeling unwell seek medical advice immediately (show the label where possible).</p>

**Transport information:**Road-/rail transport acc. to ADR/RID:

Class:	4.3
UN No.:	1360
Packing Group:	I
Description of goods:	calcium phosphide
Number/letter:	18 a
Gross mass acc.	RN10011 and RN 10012
GGVS:	20 kg

Sea transport acc. to IMDG-Code:

Class:	4.3
UN No.:	1360
Packing Group:	I
Proper shipping name:	calcium phosphide
Page:	4338
EmS-Code:	Not stated
MFAG:	601

Air transport acc. to IATA-DGR/ICAO-TI:

Class:	4.3
UN No.:	1360
Packing Group:	I
Proper shipping name:	calcium phosphide
Sea transport and packaging instructions:	412

Further data:

Dispatch by post not permitted.

**Risk from fire:**

Fire hazards:	Not flammable, but forms flammable gas on contact with water or acidic aqueous media.
Extinguishing media:	Extinguish media are dry powder or dry sand. Aqueous agent must not be used for safety reasons.
Special fire fighting procedures:	Fire fighters should use self-contained breathing equipment and special protective equipment for fire fighting.
Fire and explosion hazards:	Special hazards from the substance itself, its combustion products or from its vapours. Risk of formation of toxic pyrolysis products.
Environmental protection:	Calcium phosphide is toxic for mammals and fish. The decomposition occurs via oxidation finally to phosphates. Due to its toxicity to aquatic organisms, do not let calcium phosphide enter the water environment or sewage systems.

## Protective clothing and equipment:

General:	Take into account the usual safety measures in chemical handling. Keep away from food and feed stuff. When using, do not eat and drink. Misuse can cause adverse effects on health. After work careful washing of skin.
Hand protection:	Protective gloves (plant protection).
Eye protection:	Avoid all contact by eyes.
Skin protection:	Avoid all contact by mouth or with skin.
Breathing protection:	Do not breath gas. Work with local exhaust or with breathing protection (combination filter: type P2-P3)
Evaluation of suitability and effectiveness of protective clothing and equipment under realistic conditions:	No study or specific information on the effectiveness of PPE is available. However, in view of the preparation and in consideration of the toxicological properties of the active substance, no particular requirements in excess of standard expectations are considered to be given.

## Procedures to minimise the generation of waste:

Unused calcium phosphide material or other such waste and contaminated materials should be disposed of as specified by existing local, state and federal regulations concerning hazardous waste disposal. In accordance with regulations for special waste, must be taken after pre-treatment, to an authorised special waste disposal site.

## Combustion products generated in the event of fire:

In the event of fire and/or explosion, phosphorous oxides and phosphine may be formed.

### B.3.5.5 Emergency measures in case of an accident (Annex IIIA 4.5)

Eye contact:	In case of contact with eyes, rinse immediately with water for several minutes, remove contact lenses if easily possible and obtain medical aid at once.
Skin contact:	In case of contact with skin, remove contaminated clothing and wash affected area with soap and water. If swallowed, allow water to be drunk and give 0.1 % solution of $\text{KMnO}_4$ or a $\text{CUSO}_4$ -solution to drink, induce vomiting only in conscious persons and obtain immediate medical aid (show product label or this data sheet, if possible).
Inhalation:	If inhaled, remove to fresh air, keep at rest in half-right position and obtain medical aid.
Containment of spillage:	In case of leaking packaging, fill contents in similar leak-proof containers. Dust must be swept and picked up carefully without raising dust, filled into suitable containers and closed up tightly.
Decontamination of areas, vehicles and buildings:	Refer to “containment of spillages”.
Disposal of damaged packaging, adsorbents and other materials:	Contaminated material should be treated as hazardous waste and given to designated disposal sites. Hazardous waste incineration should be conducted with flue gas cleaning.

### **B.3.5.6 Procedures for destruction or decontamination of the plant protection product and its packaging (Annex IIIA.4.6)**

#### **B.3.5.6.1 Possibility of neutralisation**

No information submitted.

#### **B.3.5.6.2 Controlled incineration**

##### Justification for non-submission:

The submission of data on controlled incineration of Polytanol (calcium phosphide) is not considered to be required, since the halogen content is not higher than 60 %. In fact, calcium phosphide is not a halogenated molecule.

**Detailed instructions for safe disposal of the plant protection product and its packaging:**  
See above.

#### **B.3.5.6.3 Methods other than controlled incineration:**

Unused calcium phosphide material or other such waste and contaminated materials should be disposed of as specified by existing local, state and federal regulations concerning hazardous waste disposal. In accordance with regulations for special waste, must be taken after pre-treatment, to an authorised special waste disposal site.

### **B.3.6 References relied on**

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIA-3.7; AIIIA-4.4; AIIIA-4.6.1	Köhler, U.	2004	Health and Safety Data Sheet acc. 91/155 EEC - Polytanol. not GLP, unpublished CHE2005-127	N	CFW
AIIIA-4.1.1	Anonymous	2004	Gesetz über die Beförderung gefährlicher Güter- Überwachung der Serienfertigung von Gefahrgutverpackungen - Zulassungsschein Nr. D/BAM 5330/1A2W und D/BAM 5331/1A2W. not GLP, unpublished PHY2005-733	N	CFW

<sup>1</sup> Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIIA-4.1.2; AIIIA-4.1.3	Wienecke, B.- U., Taegner, W.	1998	Gesetz über die Beförderung gefährlicher Gü- ter- Überwachung der Serienfertigung von Gefahr-gutverpackungen - Zulassungsschein Nr. D/BAM 5330/1A2W und D/BAM 5331/1A2W. III.12 /90282 III.12/90283 not GLP, unpublished PHY2005-92	N	CFW

#### Codes of owner

CFW: Chemische Fabrik Wülfel

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.



## **Annex B**

### **Calcium phosphide**

**B-4: Proposals for the  
classification and labelling**

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

## B.4 Proposals for the classification and labelling

### B.4.1 Proposals for the classification and labelling of the active substance (Annex IIA 10)

#### Active Substance: Calcium phosphide

The following is proposed in accordance with the latest classification and labelling guidance under Directive 67/548/EEC (i.e. in the 29<sup>th</sup> ATP published as Directive 2004/73/EC):

Hazard symbol:	T+	N	F
Indication of danger:	Very toxic	Dangerous for the environment	Highly flammable
Risk phrases:	R 15/29	Contact with water liberates toxic extremely flammable gas.	
	R 28	Very toxic if swallowed.	
	R 32	Contact with acids liberates very toxic gas.	
	R 50	Very toxic to aquatic organisms.	

#### **Additional proposal of the RMS:**

Hazard symbol:	Xn	
Indication of danger:	Harmful	
Risk phrase:	R 21	Harmful in contact with skin.

#### Phosphine

The following is proposed in accordance with the latest classification and labelling guidance under Directive 67/548/EEC (i.e. in the 29<sup>th</sup> ATP published as Directive 2004/73/EC):

Hazard symbol:	T+	N	F+
Indication of danger:	Very toxic	Dangerous for the environment	Extremely flammable
Risk phrases:	R12-17	Extremely flammable, Spontaneously flammable in air	
	R 26-34	Very toxic by inhalation	
		Causes burns.	
	R 50	Very toxic to aquatic organisms.	

#### Justification

The proposed classification as N and R50 is based on aquatic toxicity data for the active substance resulting in a LC<sub>50</sub> on fish of 0.065 µg/L.

## B.4.2 Proposals for the classification and labelling of preparations (Annex IIIA 12.3 and 12.4)

### Preparations

Notifier	Preparation	
Chemische Fabrik Wülfel	Polytanol	Gas generating product GE as pellets

The following is proposed in accordance with Directive 1999/45/EC:

Hazard symbol:	T	N	F
Indication of danger:	Toxic	Dangerous for the environment	Highly flammable
Risk phrases:	R 15/29	Contact with water liberates toxic, extremely flammable gas.	
	R 21	Harmful in contact with skin.	
	R 25	Toxic if swallowed.	
	R 32	Contact with acids liberates very toxic gas.	
	R 36	Irritating to eyes.	
	R 50	Very toxic to aquatic organisms.	

### Justification

Although some studies are only considered supplementary or insufficient to make a decision regarding the respective classification/labelling, the overall information to metal phosphide containing preparations (see also DAR of aluminium phosphide) is considered sufficient to assess the preparations and for the sake of animal welfare and protection no further studies should be required. Based on the amount of pure active ingredient in Polytanol the acute oral toxicity was tested to be “toxic if swallowed” (R 25). With respect to the similarity of all phosphine generating formulations in discussion, the RMS proposes the above listed additional classification/labelling also for Polytanol. The proposed classification with regard to the environment is based on aquatic toxicity data for the active substance and its content in the preparation.

## B.4.3 References relied on

No references submitted.

# **Annex B**

## **Calcium phosphide**

### **B-5: Methods of analysis**

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

## B.5 Methods of analysis

### B.5.1 Analytical methods for formulation analysis (Annex IIA 4.1; Annex IIIA 5.1)

#### B.5.1.1 Methods for the determination of pure active substance in the active substance as manufactured (Annex IIA 4.1)

##### References:

- Köhler, U. (2001), Modified WHO/SRT/Method -Volumetric determination of phosphine-CFW, (CHE2005-128)
- Köhler, U. (2001), Specificity, linearity, accuracy, repeatability; enclosure to IIA, point 4.1, CFW, (CHE2006-1138)
- Martens-Menzel, R. (2000), Validation of the Determination of Phosphine in Air by Means of IR Absorption Spectrometry, CFW, (CHE2005-115)
- Asworth, R. (1970), CIPAC-Methode, CFW, \*69/1/(M)/1, CIPAC Handbook, Vol. I, Cambridge, UK, pp. 703-705, 1970, (CHE2005-129)
- Kiefer, R. (2006), Determination of calcium phosphide and six impurities in five batches of calcium phosphide technical, CFW, (CHE2006-1128)
- Martens-Menzel, R. (2000), Translation of important parts from 3th draft VSG GC 81, CFW, (CHE2006-1171)
- Martens-Menzel, R. (2001), Report of Examination 00/1 –Quantitative Chemical Analysis of Polytanol Pellets, CFW, (CHE2005-170)

##### Principle of the methods (phosphine):

###### Gas volumetry:

For the volumetric determination of the content of calcium phosphide the pellets are finely ground in a mortar. An exact amount of calcium phosphide is weighed into a volumetric flask. The flask is attached to a gas absorber filled with 10 % sulphuric acid which was previously evacuated. Air is removed from the volumetric flask containing the sample and a magnetic stirrer. Finally 10 % sulphuric acid is added drop by drop and a strong gas formation begins. After 24 hours the gas volume is read. Temperature, air pressure and fluid pressure of the sulphuric acid are determined and the content of calcium phosphide is calculated.

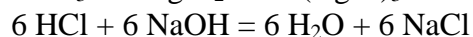
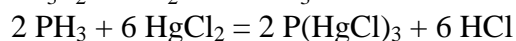
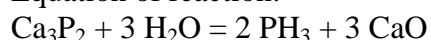
###### IR and GC-MS:

After the development of phosphine under the influence of constant atmospheric humidity from the technical calcium phosphide the phosphine content was determined by IR and GC-MS measurements. The IR measurements were performed at a wavelength of 9.5  $\mu\text{m}$ , a path length of 21.75 m and a geometric slit of 1 mm. The GC-MS analyses were conducted using a Chromapack Plot fused silica capillary (25 m x 0.32 mm; coating Poraplot Q) with helium as carrier gas and MS detection at 200 °C.

###### Titration:

The content of calcium phosphide in the technical batches was determined by hydrolysis of the test items in sulphuric acid. The releasing phosphine reacts with mercury chloride to generate hydrogen chloride. The amount of hydrogen chloride was determined by titration with sodium hydroxide.

Equation of reaction:



The calcium phosphide content in weight-% was calculated by the following equation:

$$R = \frac{V}{W} \cdot 304$$

with:

R Amount of  $\text{Ca}_3\text{P}_2$  in weight-%

V Volume of 0.1 N sodium hydroxide solution consumed [mL]

W Sample weight of calcium phosphide [mg]

### Findings:

**Table B.5.1-1 Validation data for the determination of phosphine in the technical material**

	<i>linearity (linear between), Coeff.</i>	<i>Precision – repeat- ability (%RSD)</i>	<i>interference</i>
phosphine (volumetric)	Not linear because outgassing of phosphine is depending on humidity and outgassing time.	3.8 (n = 10)	No interference* <sup>1</sup>
phosphine (IR)	0 – 1000 µL/L 0.999	2.9 for 250 µL/L (n = 5) 3.2 for 1000 µL/L (n = 5)	No interference* <sup>2</sup>
phosphine (GC-MS)	1000 µL/L* <sup>3</sup>	0.7-16.1 for 0.6-1.9 µg/g (n = 5)	No interference * <sup>2</sup>
phosphine (titration)	0.988* <sup>4</sup>	7.7* <sup>5</sup> for 17.7 % (n = 5)	No interference* <sup>1</sup>

\*<sup>1</sup> The described method is considered suitably specific because the development of other gases is impossible.

\*<sup>2</sup> The accuracy of the method was demonstrated by comparison between the IR and GC-MS results. The maximum relative difference of the IR results related to the GC-MS results was calculated to 15 %.

\*<sup>3</sup> The calibration is performed using a gas mixture with a well-known volume percentage of phosphine in helium, e.g. about 1000 µL/L. Because of the good linearity of the GC-MS determination itself it is sufficient to calibrate with one concentration near the content in the sample.

\*<sup>4</sup> The regression coefficient was calculated by RMS with the data of a recheck of the analytical method with zinc phosphide. Five different amounts of zinc phosphide were measured and compared the actually found amount of zinc phosphide (recovery 94.4 %; RSD 4.9 %). The regression coefficient was calculated from raw data by RMS.



\*5 A maximum RSD of 1.71 % is proposed by the Horwitz equation to be acceptable for an analyte content of 20 %. Regarding the difficulty in preparing a homogeneous analytical sample - the test item is flammable with traces of air humidity - the obtained RSD of 7.7 % at a mean analyte content of 17.7 % can be regarded as acceptable.

The specificity of the IR method was demonstrated by an increasing signal at increasing phosphine amounts.

#### Conclusion:

The methods are acceptably validated and allow to determine phosphine in the technical material.

#### CIPAC method:

The CIPAC Method for technical zinc phosphide (MT \*69/1/(M)/1) was modified for calcium phosphide.

#### Principle of the method (calcium):

Firstly, the phosphine is released by the reaction with water. Calcium is then determined by AAS (atomic absorption spectroscopy) with air acetylene flame at 339.9 nm.

#### Findings:

**Table B.5.1-2 Validation data for the determination of calcium in the technical material**

	<i>linearity (linear between), Corr. Coeff.</i>	<i>precision repeatability (%RSD)</i>	<b>Accuracy (n = 5)</b>		<i>interference</i>
			<b>fortification level (g/kg)</b>	<b>mean recovery (%)</b>	
Calcium (AAS)	(100- 700 mg/L) 1.000	1.5	0.15-0.25 g	99 %	* <sup>1</sup>

\*<sup>1</sup> The identity of the elements was verified by means of the element specific absorption wavelengths.

#### Conclusion:

The method is acceptably validated and allows to determine calcium in the technical material.

#### Principle of the method (calcium):

The inorganic impurities were determined after dissolving the homogenised test items in a mixture of hydrochloric acid and nitric acid (21:7, v/v), followed by ICP-AES. The quantification was carried out by external standard calibration (peak intensity).

#### Quantification wavelength

Calcium: 315.889 nm

**Findings:****Table B.5.1-3 Validation data for the determination of calcium in the technical material**

	<i>linearity (linear between), Coeff.</i>	<i>(linear Corr.</i>	<i>precision - repeatability (%RSD)</i>	<i>interference</i>
Calcium (AAS)	(1-200 µg/mL) 1.0000		3.7 (conc. 59 %)* <sup>2</sup> for 5 sub samples	* <sup>1</sup>

\*<sup>1</sup> The identity of the elements was verified by means of the element specific absorption wavelengths.

\*<sup>2</sup> The RSD value is too high according to Horwitz equation but is regarded as acceptable because of the difficulty in preparing a homogeneous analytical sample (the test item is flammable with traces of air humidity).

**Conclusion:**

The method is acceptably validated and allows to determine calcium in the technical material.

**B.5.1.2 Analytical methods for the determination of the active substance in plant protection products (Annex IIIA 5.1.1 and 5.1.3)****References:**

- Köhler, U. (2001), Modified WHO/SRT/Method -Volumetric determination of phosphine-CFW, (CHE2005-128)
- Köhler, U. (2001), Method of analysis for pure active substance in technical material, CFW, (CHE2006-1140)
- Martens-Menzel, R. (2000), Validation of the Determination of Phosphine in Air by Means of IR Absorption Spectrometry, CFW, (CHE2005-115)
- Kiefer, R. (2006), Determination of calcium phosphide and six impurities in five batches of calcium phosphide technical, CFW, (CHE2006-1128)
- Asworth, R. (1970), CIPAC-Methode, CFW, \*69/1/(M)/1, CIPAC Handbook, Vol. I, Cambridge, UK, pp. 703-705, 1970, (CHE2005-129)

**General remark:**

The formulation is identical with the technical active substance. Therefore the same analytical methods as used for the active substance as manufactured can be applied.

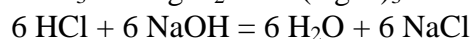
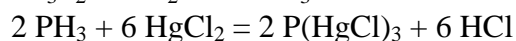
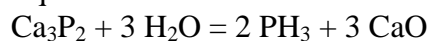
**Principle of the method**Gas volumetry:

For the volumetric determination of the content of calcium phosphide the pellets are finely ground in a mortar. An exact amount of calcium phosphide is weighed into a volumetric flask. The flask is attached to a gas absorber filled with 10 % sulphuric acid which was previously evacuated. Air is removed from the volumetric flask containing the sample and a magnetic stirrer. Finally 10 % sulphuric acid is added drop by drop and a strong gas formation begins. After 8 hours the gas volume is read. Temperature, air pressure and fluid pressure of the sulphuric acid are determined and the content of calcium phosphide is calculated.

**Titration:**

The content of calcium phosphide in the technical batches was determined by hydrolysis of the test items in sulphuric acid. The releasing phosphine reacts with mercury chloride to generate hydrogen chloride. The amount of hydrogen chloride was determined by titration with sodium hydroxide.

Equation of reaction:



The calcium phosphide content in weight-% was calculated by the following equation:

$$R = \frac{V}{W} \cdot 304$$

with:

R Amount of  $\text{Ca}_3\text{P}_2$  in weight-%

V Volume of 0.1 N sodium hydroxide solution consumed [mL]

W Sample weight of calcium phosphide [mg]

**Findings:**

**Table B.5.1-4 Validation data for the determination of calcium phosphide in the plant protection product Polytanol**

	Specificity/ interferences	Linearity (R <sup>2</sup> )	Accuracy		Repeatability (%)
			fortification level	mean recovery	
Gas volume-try	demonstrated; no interferences <sup>*1</sup>	Not linear because outgassing of phosphine is depending on humidity and outgassing time.	Not stated	Not stated	3.8 (n = 10)
titration	demonstrated; no interferences <sup>*1</sup>	0.988 <sup>*2</sup>	Not stated	Not stated	7.7 <sup>*3</sup> for 17.7 % (n = 5)

<sup>\*1</sup> The described method is not considered suitably specific because the development of other gases is impossible.

<sup>\*2</sup> The regression coefficient was calculated by RMS with the data of a recheck of the analytical method with zinc phosphide. Five different amounts of zinc phosphide were measured and compared the actually found amount of zinc phosphide (recovery 94.4 %; RSD 4.9 %). The regression coefficient was calculated from raw data by RMS.

<sup>\*3</sup> A maximum RSD of 1.71 % is proposed by the Horwitz equation to be acceptable for an analyte content of 20 %. Regarding the difficulty in preparing a homogeneous analytical sample - the test item is flammable with traces of air humidity - the obtained RSD of 7.7 % at a mean analyte content of 17.7 % can be regarded as acceptable.

**Conclusion:**

The methods are not acceptably validated. Validation data for the accuracy are missing.

**Principle of method (IR and GC-MS):**

After the development of phosphine under the influence of constant atmospheric humidity from the technical calcium phosphide the phosphine content was determined by IR and GC-MS measurements. The IR measurements were performed at a wavelength of 9.5 µm, a path length of 21.75 m and a geometric slit of 1 mm. The GC-MS analyses were conducted using a Chromapack Plot fused silica capillary (25 m x 0.32 mm) with helium as carrier gas and MS detection at 200 °C.

**Findings:**

**Table B.5.1-5 Validation data for the determination of calcium phosphide in the plant protection product Polytanol**

	Specificity/ interferences	Linearity (R <sup>2</sup> )	Accuracy (n = 5-10)		Repeatability (n = 5) (%)
			fortification level (pg)	mean recovery (%)	
IR	demonstrated; no interferences* <sup>1</sup>	0.999 (non-linear) (conc. 0 – 1000 µL/L)	Not stated	Not stated	2.9 (250 µL/L) 3.2 (1000 µL/L)
GC-MS	demonstrated; no interferences	1000 µL/L* <sup>2</sup>	10-113	103.5* <sup>3</sup>	0.7-16.1 (0.6-1.9 µg/g)

\*<sup>1</sup> The specificity of the IR method was demonstrated by an increasing signal at increasing phosphine amounts.

\*<sup>2</sup> The calibration is performed using a gas mixture with a well-known volume percentage of phosphine in helium, e.g. about 1000 µL/L. Because of the good linearity of the GC-MS determination itself it is sufficient to calibrate with one concentration near the content in the sample.

\*<sup>3</sup> The mean recovery was calculated by RMS.

**Conclusion:**

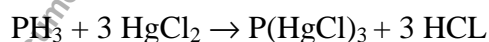
The GC-MS method is sufficiently validated. For the IR method validation data for the accuracy are missing.

**CIPAC method:**

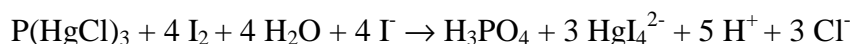
No existing CIPAC method was found. The CIPAC method for technical zinc phosphide (MT \*69/1/(M)/1) was modified for calcium phosphide.

**Principle of the CIPAC method:**

Phosphine, liberated from calcium phosphide by acid, is absorbed in mercuric chloride solution to yield mercuric phosphochloride according the following reaction scheme:



The mercuric phosphochloride is subsequently oxidised by a known amount of iodine according to the reaction:



Finally, the excess is back-titrated with sodium thiosulphate standard using starch as indicator.

#### **Conclusion:**

A statement for the applicability of the CIPAC method for calcium phosphide is missing.

#### **B.5.1.3 Analytical methods for the determination of relevant impurities and formu- lants in plant protection products (Annex IIIA 5.1.2 and 5.1.3)**

Whether or not relevant impurities must be determined is under discussion.

#### **B.5.2 Analytical methods (residue) for plants, plant products, foodstuffs of plant and animal origin, feedingstuffs (Annex IIA 4.2.1; Annex IIIA 5.2)**

##### **B.5.2.1 Plant materials**

The definition of a residue in plants is not considered to be required, since no residues of calcium phosphide in food or foodstuff of plant origin are to be expected.

**Reference:** Annex IIA, point 4.2.1

**Report:** Noack, S., Reichmuth, C., Wohlgemuth, R. (1983): Relationship of phosphine residues after fumigation to concentration, time of exposure and length of storage, Engl. Transl. of German doc.: PH3 – Rückstände bei Vorratsschutzbegasungen in Abhängigkeit von Konzentration, Einwirkungszeit und Lagerdauer nach der Begasung, published in: Z. Lebensm. Unters. Forsch. 177, pp. 87-93, 1983; MET2003-2 + MET2006-452

**Guidelines:** Not stated

**Deviations:** Not applicable

**GLP:** No

**Acceptability:** The study is considered to be not acceptable.

#### **Materials and Methods:**

Test material: commodities with high fat content, dry crops

Fortified analyte(s): Phosphine, generated from aluminium phosphide pellets.

Analyte(s) determined as: phosphine

**Principle of the method:** Hazelnuts, soy beans or wheat are fumigated with phosphine in a special apparatus under defined conditions, e.g. temperature, humidity. Three test series with 1.3 mg phosphine/L, 6.5 mg phosphine/L, and 20.5 mg phosphine/L, respectively, are performed. The fumigation time is varied from 1 to 14 days. For liberating of phosphine the target vegetables are purged with diluted sulphuric acid under vacuum. Determination of the phosphine residues after liberating and collecting in a gas holder by gas chromatography and phosphorus sensitive detector.

**Findings:**

No validated limit of quantification is determined. Blank values are not reported. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are not presented. No validated confirmatory method is presented.

**Conclusion:**

The dependence of phosphine residues after fumigation of dry crops and commodities with high fat content on dosage level, exposure time and storage conditions are investigated and discussed. A description of the analytical method is presented. No validation data are submitted. Therefore, the study is considered to be not acceptable.

**Reference:**

Annex IIA, point 4.2.1  
Annex IIA, point 4.2.4

**Report:**

Martens-Menzel, R. et al. (1995): Phosphine residues in Vegetables after Soil Fumigation for Rodent Control, Engl. Transl. of German doc.: Prüfung des Verbleibs von Phosphorwasserstoff-Rückständen in Gemüsekulturen nach Anwendung von Rodentiziden, published in: Nachrichtenbl. Deut. Pflanzenschutzd., 47, pp. 315-320, 1995; MET1999-917 + MET2006-453

**Guidelines:**

Not stated

**Deviations:**

Not applicable

**GLP:**

No

**Acceptability:**

The study is considered to be not acceptable.

**Materials and Methods:**

Test material: commodities with high water content

Fortified analyte(s): phosphine developed from following preparations: Calcium phosphide (Polytanol, Chemische Fabrik Wülfel, Hannover), 5 g preparation (0.5 g phosphine); Aluminium phosphide pellets (Wühlmauskiller, Detia Freyberg).

**Analyte(s) determined as:** phosphine

**Principle of the method:** The fumigations took place in three kinds of soil with relative high amounts of sand, clay, and humic substances, respectively. It was performed in the field using patches with radishes and carrots. Three types of measuring points are used: a 10 cm distance to preparation, a cavity in 250 and 500 cm distance to preparation, the underground of soil in depths of 10, 20, and 30 cm, respectively, about 30 cm distance to preparation. The fumigation period was 25 days. Following climatic conditions were measured in underground (10 cm): temperature:  $19 \pm 3$  °C, humidity = over 90 %. During fumigation samples of air were taken with a one-way-injector equipped with a steel needle about every hour at several locations in the soil. For liberating of phosphine the vegetables are purged with diluted sulphuric acid under vacuum. The phosphine was collected in a gas holder. The phosphine in the samples and the phosphine residues in the vegetables were determined by gas chromatography and phosphorus sensitive detector.

**Additional study:**

Martens-Menzel, R., Reichmuth, Ch. and Pieritz, W. (1994): Rückstandsverhalten von Phosphorwasserstoff in Rettichen und Möhren nach Begasungen zur Bekämpfung der Wühlmaus, published in: Mitt. a. d. Biol. Bundesanst. H 301, 1994; MET1999-919 (submitted as Document K, Section 2, Annex IIIA, point 5.2/02) is a summary of the study by Martens-Menzel, R. et al.(1995), MET1999-917 and MET2006-453 (English translation).

**Findings:**

No validated limit of quantification is determined. Blank values are not reported. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are not presented. No validated confirmatory method is presented. After a period of three days, the residues of phosphine are lower than 0.01 mg/kg. With regard to the agricultural methods, it is not necessary to propose a waiting period.

**Conclusion:**

Outdoor fumigations with phosphine were performed in patches with radish and carrots. After harvest of the vegetables phosphine residues were determined in these commodities with high water content. A description of the analytical method is presented. No validation data are submitted. Therefore, the study is considered to be not acceptable.

**B.5.2.2 Analytical methods (residue) for foodstuff of animal origin**

The definition of the residues in food of animal origin of calcium phosphide is considered not to be required, since no residues of calcium phosphide in plants or feed are to be expected, and therefore any uptake by domestic animals is not anticipated.

**B.5.3 Analytical methods (residue) soil, water, air (Annex IIA 4.2. 2 to 4.2.4; Annex IIIA 5.2)**

The proposed definition of residues of calcium phosphide in soil, water and air is phosphine. According to the Guidance Document SANCO/825/00 rev. 7 analytical methods for determination of residues in soil are not required because DT<sub>90</sub> is lower than three days.

### B.5.3.1 Analytical methods (residue) for soil

**Reference:** Annex IIA, point 4.2.2

**Report:** Koch, E. (1982): Measuring the diffusion of PH<sub>3</sub> in the soil, Engl. Transl. of German doc.: Messungen des Diffusionsstromes von PH<sub>3</sub> im Boden, April 26, 1982; MET2006-454+MET2005-87

**Reference:** Document K, Section 2, Annex IIA, point 4.2.2/01

**Report:** Koch, E. (1982): Messungen des Diffusionsstromes von PH<sub>3</sub> im Boden, April 26, 1982; MET2005-87

**Guidelines:** BBA- Leaflet No. 36

**Deviations:** Yes

**GLP:** No

**Acceptability:** The study is considered to be acceptable to demonstrate the rapid decomposition of phosphine in soil.

#### Materials and Methods:

Test material: soil with relative high amounts of sand and a mean humidity of 13.5 %.

Fortified analyte(s): calcium phosphide (Polytanol), as: 26 %.

Analyte(s) determined as: phosphine

Principle of the method: In field trials calcium phosphide (Polytanol) was applicated in underground 5 cm and 10 cm, respectively. A tin case was placed on the surface of the soil. After defined time the air containing in the tin case was analysed for its phosphine content. For the analysis of the gas a Dräger gas detector pump and Dräger tubes for phosphine were used.

#### Findings:

In the field trials the extension of phosphine in soil was estimated in the horizontal line to about 30 cm, in vertical line to about 25 cm. The half-life period of phosphine was estimated to 6 – 10 hours. After two days the degradation of phosphine was completely. The degradation products are non-hazardous phosphate, e.g. hydroxyl apatite. No validated limit of quantification is determined. Blank values are not reported. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are not presented.

No validated confirmatory method is presented.



**Conclusion:**

Phosphine is decomposed completely in soil within 48 h. According to the Guidance document on residue analytical methods SANCO/825/00 rev.7 analytical methods for residue in soil are not necessary, if the DT<sub>90</sub> values of the active substance and the relevant metabolites are lower than three days. Therefore, no analytical method is required for the determination of phosphine in soil.

**B.5.3.2 Analytical methods (residue) for water****Reference:**

Annex IIA, point 4.2.3

**Report:**

Werle, H. (1999): Method validation for the determination of residues of phosphine in surface water and potable water, report No.: 995040303, Biochem GmbH, Karlsruhe, Germany, unpublished report, December 7, 1999, MET2000-49

**Guidelines:**

Not stated

**Deviations:**

Not applicable

**GLP:**

Yes

**Acceptability:**

The study is considered to be acceptable.

**Materials and Methods:**

Test material: surface water

Fortified analyte(s): phosphine

Analyte(s) determined as: phosphine

Principle of the method: Aliquots of 10 mL surface water were fortified with phosphine at levels of 0.1 and 1.0 µg/L. All samples were analysed on phosphine using headspace gas chromatography (headspace volume = 12 mL) with phosphorus/nitrogen sensitive detection (NPD).

**Findings:**

The validated limit of quantification in water is 0.1 µg/L. Blank values are not reported but chromatograms demonstrate that the blanks are distinctly below 30 % of the LOQ. Acceptable chromatograms from sample at the LOQ and blank material, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented. No validated confirmatory method is presented.

**Conclusion:**

The analytical method for the determination of phosphine in surface water is successfully validated at the drinking water limit of 0.1 µg/L. Therefore, an additionally validated method for determination of phosphine in drinking water is considered to be not necessary.

**Table B.5.3-1 Validation data of analytical method 995040303 for the determination of phosphine in water**

Reference	Matrix	Detection method	Fortification level [µg/L]	Average recovery [%]	RSD [%]	No. of analyses
Werle, 1999 MET2000-49	Surface water	GC/PND	0.1	77	2	5
			1	82	2	5

**Reference:** Annex IIA, point 4.2.

**Report:** Shrimali A. (2001) Determination of phosphine concentration in water treated with aluminium phosphide bag; JAI Research Foundation (JRF), Gujarat, India, JRF study no. 3569, December 8, 2001, MET2002-40

**Guidelines:** **additional study, not submitted by the notifier**  
EPA OPPTS 830.1700

**Deviations:** Not applicable

**GLP:** No

**Acceptability:** The study is considered to be acceptable for confirmatory purposes.

#### **Materials and Methods:**

Test material: drinking and surface water

Fortified analyte(s): phosphine

Analyte(s) determined as: phosphine

Principle of the method: Phosphine is distilled from water samples by boiling for 30 minutes in a closed system. Water vapours are refluxed with a cooler and the expelled phosphine gas is collected in a receiver flask of known volume. After distillation, a suitable volume of air is injected into the distillation system, flushing any phosphine remaining in the gas phase into the receiver flask. Ambient pressure in the receiver flask is then established, the receiver flask is closed airtight and disconnected from the distillation system. An injection sample of known volume is taken from the receiver flask by means of a syringe and the phosphine content in water sample is determined by Gas Chromatography with Flame Photometric Detection (GC-FPD), using external standardisation.

#### **Findings:**

The validated limit of quantification in water is 0.1 µg/L. Appropriate calibration graphs, blank values, individual recovery data and information on the precision of the analytical method are presented. Chromatograms from samples and blank materials are missing. No confirmatory method is presented.

**Conclusion:**

The method is sufficiently validated for quantification of phosphine in drinking and surface water at the limit of quantification of 0.1 µg/L. Despite the missing chromatograms the study is considered to be acceptable for confirmatory purposes.

**Table B.5.3-2: Validation data of analytical method for the determination of phosphine in water**

Reference	Matrix	Detection method	Fortification level [µg/L]	Average recovery [%]	RSD [%]	No. of analyses
Shrimali, 2001 MET2002-40	Drinking water	GC-FPD	0.1	95.19	8.67	5
			1	89.85	9.54	5
	Pond water	GC-FPD	0.1	95.8	4.12	5
			1	89.71	6.04	5
	River water	GC-FPD	0.1	96.28	8.86	5
			1	92.19	7.51	5
	Sea water	GC-FPD	0.1	94.21	10	5
			1	86.52	3.62	5
	Ground water	GC-FPD	0.1	89.95	5.05	5
			1	92.04	4.13	5

**B.5.3.3 Analytical methods for air****Reference:**

Annex IIA, point 4.2.2

Annex IIA, point 4.2.3

Annex IIA, point 4.2.4

**Report:**

Mortensen, G. et al.(1989): ICP-AES and colorimetry as analytical tools the determination of phosphorus containing compounds, including phosphine, published in: Analytical Letters 22 (7), pp. 1791-1806 1989; MET2002-225

**Guidelines:**

NIOSH method No. S 332 (colorimetric method for determination of phosphine)

**Deviations:**

Yes

**GLP:**

No

**Acceptability:**

The study is considered to be not acceptable.

**Materials and Methods:**

Test material: air

Fortified analyte(s): KH<sub>2</sub>PO<sub>4</sub> standard solutions are used as “artificial” sample solutions for the comparison of the analytical detection methods.

Analyte(s) determined as: phosphomolybdate complex

Principle of the method: A method presents a direct quantitative determination of phosphine in gaseous mixtures or in air samples. Based on the oxidation of phosphine to phosphate the

method describes the analysing of phosphate either by inductively coupled plasma-atomic emission spectrometry (ICP-AES) or by a colorimetric method. For the colorimetric determinations a UV/VIS- spectrophotometer was used. All atomic emission measurements were performed on an ICP-AES Plasma II emission spectrometer. The colorimetric method is a modified version of the NIOSH method No. S 332. After addition of molybdate, phosphate forms a phosphomolybdate complex ( $\text{Mo}^{\text{VI}}$ ). This complex was extracted into a mixture of isobutanol and toluene. By adding stannous chloride the complex was reduced ( $\text{Mo}^{\text{VI}}$  to  $\text{Mo}^{\text{V}}$ ), and the absorbance of the reduced phosphomolybdate complex was measured at  $\lambda = 624 \text{ nm}$ . Possible interfering species can be all phosphorus containing compounds and organic phosphorus compounds. The following instrumental parameters of the ICP-AES have been found to give an optimal signal/noise ratio during all analyses: wavelength: 213.618 nm (automatic background correction used), source viewing height: 8 mm, RF-power: 1540 W and argon flows (plasma flow: 15 L/min; nebuliser flow: 0.91 L/min; auxiliary flow: 1 L/min). Interferences of iron may be avoided by using membrane filters. These filters collect Fe-containing particle during sampling of phosphine.

To demonstrate the usefulness of the ICP-AES method used for phosphorus analysis, the variance of the analytical results of both methods (ICP-AES versus colorimetric method) were compared. For this purpose,  $\text{KH}_2\text{PO}_4$  standard solutions ("artificial" sample solutions) were used as analytes. Up to 3 samples were prepared at each concentration level, each sample was analysed 3 times. All results are means of 3 determinations. The  $\text{PH}_3$ -concentrations are expressed in  $\mu\text{g/L}$  of solution.

### Findings:

The usefulness of the ICP-AES method as an analytical tool for the determination of phosphorus containing compounds, phosphine in the air of working environments has been demonstrated by comparison with a well established colorimetric method (NIOSH method No. S 332). No sampling procedure of phosphine is presented, "artificial" sample solutions ( $\text{KH}_2\text{PO}_4$  standard solutions) are used as analytes. No validated limit of quantification for determination of phosphine in air samples is presented. Blank values are not reported. Acceptable raw data from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are missing. No validated confirmatory method is presented.

### Conclusion:

A comparison of the different analytical detection methods is presented. But, the study does not fulfil the criteria of the Guidance Document SANCO/825/00 rev.7 for the acceptable validation of an analytical method. Therefore, the study is considered to be not acceptable.

### Reference:

Annex IIA, point 4.2.2  
Annex IIA, point 4.2.3  
Annex IIA, point 4.2.4

### Report:

Matsumura, Y. et al. (1993): Adsorption sampling of phosphine and some other semiconductor material gases, published in: Applied Occup. Environ. Hyg. 8 (4), pp.288-292, 1993; MET2002-226

### Guidelines:

NIOSH method No. S 332 (colorimetric method for determination of phosphine)

### Deviations:

No

**GLP:** No

**Acceptability:** The study is considered to be not acceptable.

### **Materials and Methods:**

Test material: air

Fortified analyte(s): Phosphine (further diborane, silane and arsine)

Analyte(s) determined as: phosphine was determined as phosphomolybdate complex

Principle of the method: The study presents adsorption sampling methods of airborne diborane, phosphine, arsine and silane for monitoring of workplaces. The study consists of three steps: 1) selection of adsorbents by screening examinations of surface areas and the amounts of extractable impurities; 2) evaluation of gas adsorption capacities and improvements by chemical impregnation; 3) effective desorption of adsorbed gases from the adsorbents into solutions. The amounts of extractable boron, phosphorus, silicon, and arsenic were measured at the extracts of different porous adsorbents (synthetic resin-active carbon, Coconut-shell active carbon, Barnebey-Cheney #580-20, silica gel and a membrane filter). Standard gases of diborane, phosphine, silane, and arsine at about 100 ppm in nitrogen were purchased in cylinders. Each standard gas was further diluted with nitrogen. A certain amount (100 - 300 mg) of each adsorbent was packed in a 4-mm diameter tube, and a test gas flow was introduced into the tube at a flow rate of 200 - 500 mL/min. The escaping gas from the adsorbent tube was detected with an electrochemical gas sensor, Type GDS-DB-1 to measure the adsorption breakthrough. To improve the adsorption capacities of the adsorbents, various types of chemicals were impregnated on the porous adsorbents using freeze-drying methods. The desorption efficiencies were measured at the samples prepared by passing a certain volume of a test gas through adsorbent tube without breakthrough. The determinations of extractable impurities in the adsorbents and desorption efficiencies of the objective gases into solutions were performed on six samples. The analytical instruments used were a graphite furnace AAS with a furnace temperature programmer and an autosampler sequencer), ICP-AES, and a spectrophotometer for the analyses of impurities and the desorbed species. Those adsorbents which showed the breakthrough times longer than 10 minutes for the test gases at concentrations equal to or higher than the personal exposure limits (PEL) were taken as useful adsorbents, and further submitted to the desorption tests. Phosphine was analysed as phosphate ion in the final solution with colorimetry (a molybdenum blue method). The procedures recommended by the National Institute of Occupational Safety and Health (NIOSH) in Method #S332 and K0102-46.1.2 were examined.

### **Findings:**

In the extracts of the adsorbents some impurities were detected. Purified silica gels were almost free of boron, phosphorus, and arsenic. The adsorbents free from interfering impurities with or without chemical impregnation were submitted to the adsorption breakthrough test. Acceptable breakthrough times for phosphine were reported for silica gel impregnated with  $\text{HgCl}_2 + \text{NaCl}$  at concentrations of 0.3 ppm and 3 ppm and for silica gel impregnated with  $\text{KMnO}_4$  at phosphine concentration of 0.3 ppm. Phosphine adsorbed on silica gel with  $\text{HgCl}_2 + \text{NaCl}$  impregnation was desorbed into a solution of  $\text{KMnO}_4$  (0.002 M) with  $\text{H}_2\text{SO}_4$  (0.1 M), but the desorption efficiency became lower when the phosphine concentration was lower than 0.3 ppm. Phosphine adsorbed on silica gel with  $\text{KMnO}_4$  was desorbed into hydroxylamine

hydrochloride (4 %) at high efficiency around 90 percent over the wide range of phosphine concentration. No validated limit of quantification for determination of phosphine in air samples is presented. Blank values are not reported. Acceptable raw data from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are missing. No validated confirmatory method is presented.

**Conclusion:**

A comparison of different adsorbents and different treatments of adsorbents (impregnation) for an efficient sampling of some airborne diborane, phosphine, arsine, and silane is presented. For phosphine sampling it is recommended to use a silica gel impregnated with  $\text{KMnO}_4$  (1 %). After desorption by hydroxylamine hydrochloride (4 %) a colorimetric detection was suggested. But, the study does not fulfil the criteria of the Guidance Document SANCO/825/00 rev. 7 for the acceptable validation of an analytical method. Therefore, the study is considered to be not acceptable.

**Reference:** Annex IIA, point 4.2.

**Report:** Breuer, D. (1994): Luftanalysen, Sonderdruck aus DFG – Deutsche Forschungsgemeinschaft. Band 1, Ed. Greim, H., MET2000-424 additional study, not submitted by the notifier

**Guidelines:** Modified method of NIOSH, Manual of analytical methods, No. S332 “Phosphine”, vol. 5, 1980

**Deviations:** Not applicable

**GLP:** No

**Acceptability:** The study is considered to be acceptable for the determination of phosphine in air at concentrations of the occupational exposure limit.

**Materials and Methods:**

Test material: air

Fortified analyte(s): phosphine

Analyte(s) determined as: molybdate phosphate complex

Principle of the method: Phosphine containing air samples were conducted (50 L/h, 2h) through silica gel adsorption tubes impregnated with mercury cyanide. Desorption was carried out with a potassium permanganate solution by oxidation of the formed mercury phosphine complex to phosphate. Following various steps of preparation involving incubation at 65 - 70 °C, addition of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ , water and molybdate, isobutyl alcohol/toluene (1/1) was added and the organic phase separated. Following further addition of sulphuric acid in methanol and  $\text{SnCl}_2$ , the resulting blue hetero-polymolybdate complex was quantified by photometric determination at 625 nm.

**Findings:**

The validated limit of quantification in air is  $25 \mu\text{g}/\text{m}^3$ . Blank values are not reported. An appropriate calibration graph and information on the precision of the method are presented. Recovery data are not reported for determination of phosphine at ambient temperature and a relative humidity of 40 - 50 %. Based on the results of the precision determination, the recovery was calculated to be in the range of  $100 \% \pm 5\text{-}7 \%$  (RSD). A single recovery value of 90 % was reported for determination of phosphine in air at relative humidity of 90 %. No validated confirmatory method is presented.

**Conclusion:**

The validated limit of quantification in air of the presented analytical method is  $25 \mu\text{g}/\text{m}^3$ . Despite some minor deficiencies the method is considered to be acceptable for the determination of phosphine in air at concentrations of the occupational exposure limit ( $150 \mu\text{g}/\text{m}^3$ ). But, the method is not appropriate for analysis of the limit of  $3.3 \mu\text{g}/\text{m}^3$  calculated on basis of the AOEL.

**Table B.5.3-3: Validation data of analytical method for the determination of phosphine in: air**

Reference	Matrix	Detection method	Fortification level [ $\mu\text{g}/\text{m}^3$ ]	Average recovery [%]	RSD [%]	No. of analyses
Breuer, 1994 MET2000-424	air (ambient temperature, humidity 40 - 50 %)	photometric determination at 625 nm	25	-	6.7	10
			150	-	5.1	10
			250	-	6.2	10

#### **B.5.4 Analytical methods (residue) for body fluids and tissues (Annex IIA 4.2.5; Annex IIIA 5.2)**

Calcium phosphide is classified as highly toxic. A sensitive analytical method for the determination of residues of phosphine in human blood could not be validated because phosphine reacted with components of the blood matrix. Phosphine is very quickly transformed in blood. Consequently, the transport into the tissues via blood is limited. Therefore, it seems to be not necessary to develop analytical methods for determination of phosphine in body fluids and tissues even if the active substance calcium phosphide is classified as highly toxic.

**Reference:** Annex IIA, point 4.2.5

**Report:** Witte, A.(2001): Residue analysis of Zinc phosphide in animal tissues –method validation, AG GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Niefern-Öschelbronn, Germany, unpublished report, no.: 20001426/01-RVAT, August 17, 2001; MET2002-60

**Guidelines:** SANCO/825/00 rev. 6

**Deviations:** No

**GLP:** Yes

**Acceptability:** The study is considered to be acceptable.

**Materials and Methods:**

Test material: milk (Hofgut Vollmilch, 3.5 % Fett, local supermarket), liver: pork (local butcher), muscle: lean pork neck (local butcher).

Fortified analyte(s): zinc phosphide

Analyte(s) determined as: phosphine

Principle of the method: Milk samples and homogenised liver and meat samples were fortified with a mixture of zinc phosphide and sodium sulphate at levels of 0.0025 and 0.025 mg Zn<sub>3</sub>P<sub>2</sub>/kg followed by addition of sulphuric acid. The released phosphine gas was analysed using headspace gas chromatography with phosphorus/nitrogen sensitive detection (PND).

**Findings:**

The validated limit of quantification in all matrices is 0.0025 mg/kg. Blank values are not reported but chromatograms demonstrate that the blanks are distinctly below 30 % of the LOQ. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

No validated confirmatory method is presented.

**Conclusion:**

The analytical method for the determination of phosphine in milk, liver and muscle was successfully validated. Because phosphine is very quickly transformed in blood it seems to be not necessary to develop analytical methods for determination of phosphine in body fluids and tissues even if the active substance calcium phosphide is classified as highly toxic. This study is classified as additional for matrices of animal origin.

**Table B.5.4-1: Validation data of analytical method for the determination of zinc phosphide determined as phosphine in body fluids and tissues**

Reference	Matrix	Detection method	Fortification level [mg/kg]	Average recovery [%]	RSD [%]	No. of analyses
Witte, 2001 MET2002-60	milk	GC/PND	0.0025	105	19	5
			0.025	82	16	5
	liver	GC/PND	0.0025	101	14	5
			0.025	87	18	5
	muscle	GC/PND	0.0025	83	16	5
			0.025	85	13	5

**Reference:** Annex IIA, point 4.2.5

**Report:** Mauldin, R.E. et al.(1996): Determination of zinc phosphide residues in the California ground squirrel (*Spermophilus beecheyi*) by gas chromatography-flame photometric detection, published in: J. Agric. Food Chem. 44, 189-194, 1996; MET2002-63

**Guidelines:** Not stated



**Deviations:** Not applicable

**GLP:** No

**Acceptability:** The study is considered to be not acceptable.

### **Materials and Methods:**

Test material: animal tissues (stomach, intestines)

Fortified analyte(s): zinc phosphide

Analyte(s) determined as: phosphine

Principle of the method: One hundred and nine ground squirrels were collected in Alameda County, California, in March 1991 and March 1994 from an area where no previous zinc phosphide baiting programs had been conducted. Additional 41 ground squirrels were also collected from Alameda County, California, in July 1994 to complete validation. Carcasses were immediately placed in sealed plastic bags, frozen, shipped to the Denver Wildlife Research Centre (DWRC), and kept frozen (- 30 °C) until processed. Ground squirrels were of both sexes, ranged in size from 350 to 950 g. The gastrointestinal (GI) tracts were removed, and the stomachs and intestines were separated. The content of emptied stomachs were fortified with varying combinations of zinc phosphide and partially digested range grass; intestines were fortified with zinc phosphide only. To assess the interaction of varying amounts of zinc phosphide and stomach/intestine contents on zinc phosphide recovery, carcasses from the March collection were randomly assigned to a design matrix in which stomachs were fortified with one of four levels of grass (0, 15, 35 and 50 g) and four levels of zinc phosphide (0.5, 2.5, 10 and 50 mg). Intestines were fortified with the same amount of zinc phosphide used in the corresponding stomach, but analysed with original contents intact. Liberating of phosphine with sulphuric acid in the flasks containing stomach and intestinal tissues the headspace gas of the flasks was analysed with the GC-FDP technique.

Five ground squirrels (three, March; two, July) were prepared and analysed by the procedures described above. Stomach tissues were fortified with 55 g of grass from the appropriate grass pool, and intestines were analysed with original contents intact. Zinc phosphide was not added to either tissue.

### **Findings:**

The validated limit of quantification in intestine tissue is 32 mg/kg. (The calculation based on the successfully validated fortification level of 2.5 mg zinc phosphide and the mean intestinal weight of 78 g). Blank values and chromatograms from samples and blank materials are not reported. Appropriate calibration data, individual recovery data and information on the precision of the method are presented. No validated confirmatory method is presented.

### **Conclusion:**

The analytical method for the determination of phosphine in intestine tissue was successfully validated at a LOQ of 32 mg/kg. This LOQ exceeds the expected LOQ for tissues by a factor of 300. According to the requirements of the Guidance Document SANCO/825/00 rev. 7 the LOQ in tissues (meat or liver) should be 0.1 mg/kg. Therefore, the study is considered to be not acceptable. Because phosphine is very quickly transformed in blood it seems to be not

necessary to develop analytical methods for determination of phosphine in body fluids and tissues even if the active substance calcium phosphide is classified as highly toxic.

**Table B.5.4-2: Validation data of analytical method for the determination of zinc phosphide determined as phosphine in body tissues**

Reference	Matrix	Detection method	Fortification level [mg/kg]	Average recovery [%]	RSD [%]	No. of analyses
Mauldin et al., 1996 MET2002-63	intestine	GC-FDP	32	71.6	7.1	12
			122	79.9	5.7	12
			675	87.2	3.7	12
			621	86.8	3.3	12

**Reference:** Annex IIA, point 4.2.5

**Report:** Heintze, A.(2001): Residue Analysis of Zinc Phosphide in Human Blood - Method Validation, AG GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Niefern-Öschelbronn, Germany, unpublished report, no.: 20001426/01-PVAT, October 09, 2001; MET2002-62

**Guidelines:** SANCO/825/00 rev. 6

**Deviations:** No

**GLP:** Yes

**Acceptability:** The study is considered to be not acceptable.

#### **Materials and Methods:**

Test material: human blood

Fortified analyte(s): zinc phosphide

Analyte(s) determined as: phosphine

Principle of the method: For fortification of human blood two solutions were prepared – a dispersion in water and a dispersion in Hydroxy-propyl-methyl cellulose (HPMC). Zinc phosphide was determined as phosphine (PH<sub>3</sub>) after acid hydrolysis. Phosphine was released from the sample by boiling with diluted hydrochloric acid and analysis in the head space by GC-NPD. Head space vials were filled with 1 mL of human blood and 0.5 mL of 6 M hydrochloric acid. Afterwards the vials were heated for a period of 60 min at 60 °C. After cooling off to room temperature the head space was fortified with the phosphine standard at three different fortification levels. Analytic determination was performed by GC-NPD in head space.

#### **Findings:**

The variances in “recovery” values obtained from the fortification solutions of zinc phosphide in water and HPMC proved to be too high for a reproducible fortification of blood. Whereas the HPMC medium obviously enhanced the homogeneity of fortified preparations (RSD = 25-

64 %) in comparison to the water solution (RSD = 34-153 %), the variance from vessel to vessel was still found unacceptable for the performance of valid fortifications of blood samples.

Alternatively, an effort was made to spike human blood samples with phosphide directly. Phosphine could be recovered only to a low extent. The results indicate a reaction of phosphine with the matrix blood within less than 4 hours after fortification at room temperature. No successfully validated limit of quantification could be established. The recovery data and information on the precision of the method do not fulfil the requirements of the Guidance Document SANCO/825/00 rev. 7. Blank values and an appropriate calibration graph for the determination of phosphine by head space GC-NPD are reported. No validated confirmatory method is presented.

### Conclusion:

The study is considered to be not acceptable. The validation of a sensitive method for the residue analysis of zinc phosphide in human blood was restricted since the fortification of the matrix human blood with defined amounts of test substance was impossible due to a lack of suitable solvents or other media to allow for a homogeneous fortification medium. Phosphine itself appears to react at low concentrations with the blood matrix within the period needed for a complete hydrolysis of zinc phosphide in blood, thus inhibiting a sensitive determination of zinc phosphide via phosphine release in this matrix. Because phosphine is very quickly transformed in blood it seems to be not necessary to develop analytical methods for determination of phosphine in body fluids and tissues even if the active substance calcium phosphide is classified as highly toxic.

**Table B.5.4-3: Validation data of analytical method for the determination of phosphine in body fluids**

Reference	Matrix	Detection method	Fortification level [mg/kg]	Average recovery [%]	RSD [%]	No. of analyses
Heintze, 2001 MET2002-62	human blood	GC-NPD	0	-	-	2
			0.198	-	-	5
			1.98	12	142	5
			9.9	23	22	5

## B.5.5 Evaluation and assessment

### B.5.5.1 Formulation analysis

### B.5.5.2 Analytical methods for technical active substance and formulation analysis

The submitted methods allow to determine the purity and the significant impurities of the technical active substance and the content of active substance in the formulation. The methods are fully validated in terms of the requirements of the technical active substance. Validation data for the fulfilment of the requirements for the analysis method of impurity 1 and 2 are missing.

**Table B.5.5-1 Summary of analytical methods for technical active substance and formulation analysis**

Matrix	Analyte	Type of method	Validation	References
Technical active substance	phosphine	gas volumetry	Fully validated	Köhler, U. (2001), (CHE2005-128) Köhler, U. (2001), (CHE2006-1138)
Technical active substance	phosphine	IR	Fully validated	Martens-Menzel, R. (2000), (CHE2005-115)
Technical active substance	phosphine	GC-MS	Sufficiently validated	Martens-Menzel, R. (2000), (CHE2005-115)
Technical active substance	phosphine	titration	Fully validated	Kiefer, R. (2006), (CHE2006-1128)
	calcium (impurity 3)	AAS	Fully validated	Martens-Menzel, R. (2001), (CHE2005-170)
	calcium (impurity 3)	ICP-AES	Fully validated	Kiefer, R. (2006), (CHE2006-1128)
	Impurity 1	ICP-AES	Not fully validated	Kiefer, R. (2006), (CHE2006-1128)
	Impurity 2	photometry	Fully validated	Martens-Menzel, R. (2001), (CHE2005-170)
	Impurity 2	ICP-AES	Not fully validated	Kiefer, R. (2006), (CHE2006-1128)
	Impurity 4	calcucaltion	Not applicable	Kiefer, R. (2006), (CHE2006-1128)
	Impurity 5, 7, 9	ICP-AES	Fully validated	Kiefer, R. (2006), (CHE2006-1128)

Formulation (identical with technical material)	phosphine	gas volumetry	Not fully validated	Köhler, U. (2001), (CHE2005-128) Köhler, U. (2001), (CHE2006-1138)
Formulation (identical with technical material)	phosphine	titration	Not fully validated	Kiefer, R. (2006), (CHE2006-1128)
Formulation (identical with technical material)	phosphine	IR	Not fully validated	Martens-Menzel, R. (2000), (CHE2005-115)
Formulation (identical with technical material)	phosphine	GC-MS	Sufficiently validated	Martens-Menzel, R. (2000), (CHE2005-115)

The CIPAC Method for technical zinc phosphide (MT \*69/1/(M)/1) was modified for calcium phosphide.

### B.5.5.3 Residue analysis

For the assessment of the analytical methods proposed for the enforcement of residues of calcium phosphide the following criteria were used:

- The submitted methods enable the enforcement of the following relevant residue limits (at the time of evaluation):

Matrix	Limit	Comment
plants and plant products (outdoor use)	-	no MRL proposed by the RMS no residue definition for monitoring
animal products	-	no MRL proposed by the RMS no residue definition for monitoring
soil	-	no method required, DT <sub>90</sub> < 3 days
drinking water (outdoor use)	0.1 µg/L	EU drinking water limit; residue definition: phosphine
surface water (outdoor use)	4.7 µg/L	based on NOEC of <i>Oncorhynchus mykiss</i> residue definition: phosphine
air	3.3 µg/m <sup>3</sup>	based on a proposed AOEL <sub>systemic</sub> of 0.011 mg/kg bw/d; residue definition: phosphine

tissues	-	No method required, since phosphine will be quickly exhaled or metabolised to phosphates should it be incorporated.
blood	-	No method required, since phosphine will be quickly exhaled or metabolised to phosphates should it be incorporated.

- Mean recovery rates at each fortification level in the range of 70 to 110 % with a relative standard deviation of  $\leq 20$  %
- No interfering blanks ( $< 30$  % of the LOQ)
- Methods must employ the simplest approach, involve the minimum cost, and require commonly available equipment.
- The enforcement method for food must be suitable for the determination of all compounds included in the residue definition (see B 7.3) and must be checked in an independent laboratory.
- The enforcement methods for environmental matrices must be able to analyse all compounds of toxicological and/or ecotoxicological significance in soil, water and air (see B 8.9).
- An additional confirmatory method for all matrices is supplied.

According to these criteria adequate analytical methods are listed in the Table B. 5.5-1.

**Table B.5.5-2 Studies, which describe appropriate analytical procedures:  
(Completeness check of analytical methods for monitoring purposes  
and post-registration control in accordance to guidance document  
SANCO/825/00 rev . 7)**

Matrix type/ crop group	Primary Method	Confirmatory method	Independent Lab Validation
Cereals and other dry crops	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Commodities with high water content	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Commodities with high fat content	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Fruits with high acid content	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Commodities which are difficult to analyse	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Milk	Witte, 2001 MET2002-60	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Egg	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Meat	Witte, 2001 MET2002-60	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Fat	Not necessary, no MRL proposed	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Kidney/liver	Witte, 2001 MET2002-60	Not necessary, no MRL proposed	Not necessary, no MRL proposed
Soil	Not necessary, DT <sub>90</sub> < 3 d	Not necessary, DT <sub>90</sub> < 3 d	Generally not required
Drinking water	<sup>1)</sup> Werle, 1999 MET2000-49	Shrimali, 2001 MET2002-40	Generally not required
Surface water	Werle, 1999 MET2000-49	Shrimali, 2001 MET2002-40	Generally not required
Air	<sup>2)</sup> Breuer, 1994 MET2000-424	Not necessary	Generally not required
Body tissues	Not necessary, quickly exhaled or metabolised	Not necessary, quickly exhaled or metabolised	Generally not required
Body fluids	Not necessary, quickly exhaled or metabolised	Not necessary, quickly exhaled or metabolised	Generally not required

1) The analytical method for determination of phosphine in surface water was sufficiently validated at the drinking water limit of 0.1 µg/L (Werle, 1999; MET2000-49). Therefore, a separate validation in drinking water is considered to be not necessary.

2) The analytical method for determination of phosphine in air is considered to be acceptable for enforcement of the occupational exposure level. But, the method is not appropriate for low concentrations as 3.3 µg/m<sup>3</sup> (LOQ calculated on basis of the AOEL).

This overview shows, that analytical methods are available for determination of phosphine in all relevant matrices. However, the proposed method for the determination of phosphine in air is insufficient for monitoring a concentration of 3.3 µg/m<sup>3</sup> (LOQ calculated on basis of the AOEL). But, the analytical method is considered to be appropriate for enforcement of the occupational exposure level.

### B.5.6 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner
AIIA-4.1.1; AIIIA-5.1.1	Asworth, R.	1970	CIPAC-Methode - Zinc phosphide. CIPAC Handbook, Vol. I, 703-705 not GLP, published CHE2005-129	N	-
AIIA-1.11; AIIA-4.1.1; AIIA-4.1.2; AIIIA-5.1.1	Kiefer, R.	2006	Determination of calcium phosphide and six impurities in five batches of calcium phosphide technical. 20061152/01 GLP, unpublished CHE2006-1128	Y	CFW
AIIA-4.1.1; AIIA-4.1.3	Köhler, U.	2001	Specificity, linearity, accuracy, repeatability; enclosure to IIA, point 4.1. not GLP, unpublished CHE2006-1138	N	CFW
AIIA-4.1.1; AIIIA-5.1.1	Köhler, U.	2001	Modified WHO/SRT/Method Volumetric determination of phosphine. not GLP, unpublished CHE2005-128	N	CFW
AIIA-1.11; AIIA-4.1.1; AIIIA-5.1.1	Martens- Menzel, R.	2000	Validation of the Determination of Phosphine in Air by Means of IR Absorption Spectro- metry. GLP, unpublished CHE2005-115	Y	CFW
AIIA-4.2.1; AIIA-4.2.5	Witte, A.	2001	Residue analysis of Zinc phosphide in animal tissues method validation - Method validation. 20001426/01-RVAT GLP, unpublished MET2002-60	Y	CFW
AIIA-4.2.2	Koch, E.	1982	Measuring the diffusion of PH <sub>3</sub> in soil; engl. transl. of the german doc.: Messung des Diffu- sionsstromes von PH <sub>3</sub> in Boden. not GLP, unpublished MET2006-454	Y	CFW
AIIA-4.2.2	Koch, E.	1982	Messungen des Diffusionsstromes von PH <sub>3</sub> im Boden. not GLP, unpublished MET2005-87	Y	CFW
AIIA-4.2.3; AIIIA-5.2	Shrimali, A	2001	Determination of phosphine concentration in water treated with Aluminium Phosphide bag, Jai research Nr. 3569 JRF study number 3569 not GLP, unpublished MET2002-40	N	UPL

<sup>1</sup> Only notifier listed



Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed  Y/N	Owner <sup>1</sup>
AIIA-4.2.3; AIIIA-5.2	Werle, H.	1999	Method Validation for the Determination of Residues of Phosphine in Surface Water and Potable Water. 995040303 GLP, unpublished MET2000-49	Y	CFW
AIIA-4.2.4; AIIIA-5.2	Breuer, D.	1994	Luftanalysen -Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe - Phosphorwasserstoff. VCH, 1, 1994, 1-10 2107 not GLP,published MET2000-424	N	-
AIIIA-5.1.1	Köhler, U.	2001	Method of analysis for pure active substance in technical material. not GLP, unpublished CHE2006-1140	N	CFW
AIIIA-5.1.2; AIIIA-5.1.3	Martens- Menzel, R.	2001	Report of Examination 00/1 - Quantitative. GLP, unpublished CHE2005-170	Y	CFW
AIIIA-5.2	Noack,S.,et al.	1983	Relationship of phosphine residues after fumigation to concentration, time of exposure and length of storage. not GLP, published MET2006-455	N	-

#### Codes of owner

CFW: Chemische Fabrik Wülfel

UPL: United Phosphorus Ltd.