FINAL REGISTRATION REPORT

Part B

Section 5

Analytical Methods

Detailed summary of the risk assessment

Product code: GK-4

Product name: GORZKA KORA

Chemical active substance:

Active substance: quartz sand, 251 g/kg

Central Zone

Zonal Rapporteur Member State: Poland

CORE ASSESSMENT

(authorization)

Applicant: Przedsiębiorstwo Produkcyjno-Handlowe ADW Sp. z o.o.

Submission date: October 2022

MS Finalisation date: February 2023; May 2023

Version history

When	What
February 2023	zRMS assessment of dRR
May 2023	Final Registration Report

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5 Analytical methods

This document reviews the analytical methods for the product GORZKA KORA, a paste formulation containing 251 g/kg quartz sand for use in forestry and several minor crops. Quartz sand was first included in Annex I to Directive 91/414/EEC by Commission Directive 2008/127/EC of 18 December 2008.

Where appropriate this document refers to the conclusion of the EU review for quartz sand. This will be where:

- The active substance data are relied upon in the risk assessment of the formulation; or when
- the EU review concluded that the additional data/information should be considered at national re-registration.

This product was not the representative formulation and has not been previously evaluated according to the Uniform Principles.

The EFSA Scientific report for quartz sand (EFSA Journal ~~2011;9(7):2300~~ 2022;20(9):7552) is considered to provide the relevant review information or a reference to where such information can be found.

The Commission Implementing Regulation for quartz sand (540/2011) provides specific provisions under Part B which need to be considered by the applicant in the preparation of their submission and by the MS prior to granting an authorisation.

For the implementation of the uniform principles as referred to in Article 29(6) of Regulation (EC) No 1107/2009, the conclusions of the review report on quartz sand (SANCO/2628/2008) and in particular Appendices I and II thereof, as finalised in the Standing Committee on the Food Chain and Animal Health shall be taken into account.
Conditions of use shall include, where appropriate, risk mitigation measures.

Information on the detailed composition of GORZKA KORA can be found in the confidential dossier of this submission (Registration Report - Part C).

5.1 Conclusion and summary of assessment

Sufficiently sensitive and selective analytical methods are available for the active substance(s) and relevant impurities in the plant protection product.

Methods are not required.

Noticed data gaps are:

- No data gap identified

Commodity/crop	Supported/ Not supported
Not relevant	

5.2 Methods used for the generation of pre-authorization data (KCP 5.1)

5.2.1 Analysis of the plant protection product (KCP 5.1.1)

5.2.1.1 Determination of active substance and/or variant in the plant protection product (KCP 5.1.1)

An overview on the acceptable methods and possible data gaps for analysis of quartz sand in plant protection product is provided as follows:

Comments of zRMS:	The proposed analytical method is suitable for the determination of active substance quartz sand in the preparation Gorzka Kora. The proposed analytical method has been fully validated in terms of specificity, linearity, repeatability, and accuracy. Proposed method fulfils the requirements of SANCO/3030/99 rev.5 guidance. The validation of the analytical method has been accepted.

Reference:	KCP 5.1.1/01
Report	Determination of the Active Ingredient Content in GK-4 (Batch: 01 10 09 2021) Product, Including Validation of an Analytical Method and Emission of an Analytical Certificate, Giorgi S., 2022, Study number: 21326-01C
Guideline(s):	Yes, SANCO 3030/99 rev. 5 (22/03/2019)
Deviations:	No
GLP:	Yes
Acceptability:	Yes

Materials and methods

Test item was a GK-4, a product formulated as a paste containing 251 g/kg of quartz sand. Silicon dioxide was determined spectrophotometrically. Molybdenum blue complex was obtained from a solution prepared by fusion of the quartz sample with sodium hydroxide, the yellow silico-molybdate complex was reduced to molybdenum blue complex. The absorption measurements were acquired by a single beam UV/visible spectroscopy system at wavelength 816±2 nm with a 1 cm cell path length.

Validation - Results and discussions

Table 5.2-1: Methods suitable for the determination of active substances quartz sand in plant protection product GORZKA KORA

	Quartz sand
Author(s), year	Giorgi S., 2022
Principle of method	UV/Vis spectrophotometer
Linearity (linear between mg/L / % range of the declared content) (correlation coefficient, expressed as r)	14.56-36.39 %w/w[1] r2=0.994 Required: r2>0.98
Precision – Repeatability Mean	RSD = 0.61%.

	Quartz sand
n = 5 **(%RSD)**	RSDr %=1.65 Hr=0.37 Acceptable repeatability Hr≤1
Accuracy **(% Recovery)**	Marginal recovery was calcuated. Mean recovery: 102.1% Acceptable recovery: 97- 103 %
Interference/ Specificity	The spectrum of the Molybdenum blue complex obtained from test item was compared with spectrum of the Molybdenum blue complex obtained from reference item.
Comment	-

[1] Referred to the test item solution concentration at 0.02 mg/mL

Conclusion

The method for Silicon dioxide determination was validated for specificity, linearity, repeatability and accuracy, in compliance with SANCO/3030/99 rev.5 (22/03/19). The reagent blank solution showed no interference. The spectrum of active ingredient(s) in the sample solution matched the spectrum in the reference item(s) solution. The identity of the active ingredient was also demonstrated by XRPD. The detector response was linear (r2>0.98) for the active ingredient in the concentration range considered. Active ingredient concentrations in sample solutions were within the linear range of the detector response. Horrat was within limits (≤ 1). Accuracy was within the limits determined by the active ingredient's concentration. The data presented in this report demonstrate that the analytical method provides a specific, reliable, accurate and precise procedure for the determination of active ingredient in the GK-4 product

5.2.1.2 Description of analytical methods for the determination of relevant impurities (KCP 5.1.1)

Comments of zRMS:	According to EFSA Conclusions (EFSA Journal 2022;20(9):7552), crystalline silica with a diameter <10 µm is considered the relevant impurity of active substance quartz sand. The requirement for methods of analysis for monitoring the respirable crystalline silica in the representative formulations has been waived due to negligible inhalation exposure predicted for the proposed uses. The 5-batch analysis assessed in the equivalence report (RMS Latvia, 2022) indicates that the source of active substance to be used for Gorzka Kora production does not contain crystalline silica of a diameter <50 µm so also <10 µm. In the report, validation of an analytical method for quantification of crystalline silica with particles <10 µm as an impurity in quartz sand technical (Giorgi S. 2022) was assessed and found acceptable in terms of specificity, linearity, recovery and precision criteria specified under SANCO/3030/99 (rev.5, 22 March 2019). Therefore, the lack of an analytical method for the determination of crystalline silica with a diameter <10 µm should not be considered as a data gap.

Not relevant. No relevant impurity is present in GORZKA KORA.

Quartz sand included in GORZKA KORA does not contain relevant impurity crystalline silica <50 um, even though in accordance with Reg. 540/2011 0.1% of crystalline silica with diameter < 50 um is allowed. Since crystalline silica <50 um is not present in quartz sand used for production of GORZKA KORA, it will not be present in the final formulation as well and analytical method for determination of crystalline silica <50 um in GORZKA KORA is not necessary. In case the applicant change or add another source of quartz sand which contains crystalline silica <50 um, the appropriate method will be provid-

ed.

GORZKA KORA is a ready to use formulation in a form of paste and release of any ~~participles~~ particles in practice is not possible hence inhalation exposure for crystalline silica with diameter < 50 um is negligible. Such approach was also confirmed in Peer review of the pesticide risk assessment of the active substance quartz sand (EFSA Journal 2022;20(9):7552) where it was clearly indicated that the requirement for methods of analysis for monitoring the respirable crystalline silica in the representative formulations has been waived due to negligible inhalation exposure predicted for the proposed uses.

5.2.1.3 Description of analytical methods for the determination of formulants (KCP 5.1.1)

Not relevant. No analytical methods for the determination of formulants is required.

5.2.1.4 Applicability of existing CIPAC methods (KCP 5.1.1)

CIPAC MT 185 (wet sieve test) is method that may be applicable for determination of the active ingredient quartz sand in product GORZKA KORA.

5.2.2 Methods for the determination of residues (KCP 5.1.2)

Not relevant. No residue studies has been performed in residue section thus no analytical method for the determination of the residues of quartz sand in treated plant material, foodstuff of plant and animal origin as well as feedingstuff is required.

5.3 Methods for post-authorization control and monitoring purposes (KCP 5.2)

5.3.1 Analysis of the plant protection product (KCP 5.2)

Not relevant. Analytical method for the determination of quartz sand in GORZKA KORA presented in point 5.2.1.1. can be applied for post-authorisation monitoring purposes. However, CIPAC MT 185 (wet sieve test) method can be also routinely used as it employs the simplest approach.

5.3.2 Description of analytical methods for the determination of residues quartz sand (KCP 5.2)

5.3.2.1 Overview of residue definitions and levels for which compliance is required

Active substance quartz sand is ubiquitous substance that naturally occurs in the environment. No MRLs were assigned and quartz sand is in Annex IV of Regulation 396/2005.

5.3.2.2 Description of analytical methods for the determination of residues in plant matrices (KCP 5.2)

Active substance quartz sand is ubiquitous substance that naturally occurs in the environment. No MRLs were assigned, and quartz sand is in Annex IV of Regulation 396/2005. Regarding above analytical method for determination of quartz sand in plant matrices is not required.

5.3.2.3 Description of analytical methods for the determination of residues in animal matrices (KCP 5.2)

Active substance quartz sand is ubiquitous substance that naturally occurs in the environment. No residues are expected to occur on/in feed or food. No MRLs were assigned and quartz sand is in Annex IV of Regulation 396/2005. Regarding above analytical method for determination of quartz sand in animal matrices is not required.

5.3.2.4 Description of methods for the analysis of soil (KCP 5.2)

Active substance quartz sand is ubiquitous substance. It is impossible to distinguish between quartz sand applied in a form of GORZKA KORA and quartz sand naturally occurring in the environment. Regarding above analytical method for determination of quartz sand in soil is not required.

5.3.2.5 Description of methods for the analysis of water (KCP 5.2)

Active substance quartz sand is ubiquitous substance. It is impossible to distinguish between quartz sand applied in a form of GORZKA KORA and quartz sand naturally occurring in the environment. Regarding above analytical method for determination of quartz sand in water is not required.

5.3.2.6 Description of methods for the analysis of air (KCP 5.2)

Active substance quartz sand is ubiquitous substance. It is impossible to distinguish between quartz sand applied in a form of GORZKA KORA and quartz sand naturally occurring in the environment. Quartz sand is also not volatile thus analytical method for determination of quartz sand in air is not required.

5.3.2.7 Description of methods for the analysis of body fluids and tissues (KCP 5.2)

Active substance quartz sand is stable and insoluble in water. It does not degrade in the environment nor pass into plants, foodstuffs of plant or animal origin. Quartz sand is not classified as toxic, thus analytical method for determination of quartz sand in body fluids and tissues is not required

5.3.2.8 Other studies/ information

No other studies submitted.

Appendix 1 Lists of data considered in support of the evaluation

Tables considered not relevant can be deleted as appropriate.

MS to blacken authors of vertebrate studies in the version made available to third parties/public.

List of data submitted by the applicant and relied on

Data point	Author(s)	Year	**Title** **Company Report No.** **Source (where different from company)** **GLP or GEP status** **Published or not**	**Vertebrate study Y/N**	Owner
KCP 5.1.1/01	Giorgi S.	2022	Determination of the Active Ingredient Content in GK-4 (Batch: 01 10 09 2021) Product, Including Validation of an Analytical Method and Emission of an Analytical Certificate Study code: 21326-01C Renolab S.r.l. GLP Unpublished	N	ADW*
KCP 5.2.1.2	Giorgi S.	2022	Determination of the Crystalline silica <10µm in 5 batches of Quartz sand Technical, Including Validation of the Analytical Method Renolab S.r.l., Italy Study No: 21321-02C GLP: Yes Published: No	N	ADW*

* Przedsiębiorstwo Produkcyjno-Handlowe ADW Sp. z o.o.

List of data submitted or referred to by the applicant and relied on, but already evaluated at EU peer review

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Owner
-	-	-	-	-	-

The following tables are to be completed by MS

List of data submitted by the applicant and not relied on

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Owner
-	-	-	-	-	-

List of data relied on not submitted by the applicant but necessary for evaluation

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Owner
-	-	-	-	-	-

Data point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Owner

Appendix 2 Detailed evaluation of submitted analytical methods

A 2.1 Analytical methods for quartz sand

A 2.1.1 Methods used for the generation of pre-authorization data (KCP 5.1)

Reference:	KCP 5.1.1/01
Report	Determination of the Active Ingredient Content in GK-4 (Batch: 01 10 09 2021) Product, Including Validation of an Analytical Method and Emission of an Analytical Certificate, Giorgi S., 2022, Study code: 21326-01C
Guideline(s):	SANCO 3030/99 rev. 5 (22/03/2019)
Deviations:	No, not applicable
GLP:	Yes
Acceptability:	Yes

Materials and methods

Test item was a GK-4, a product formulated as a paste containing 251 g/kg of quartz sand. Silicon dioxide was determined spectrophotometrically. Molybdenum blue complex was obtained from a solution prepared by fusion of the quartz sample with sodium hydroxide, the yellow silico-molybdate complex was reduced to molybdenum blue complex. The absorption measurements were acquired by a single beam UV/visible spectroscopy system at wavelength 816±2 nm with a 1 cm cell path length. The specificity of the active ingredient Silicon Dioxide was confirmed by XRPD. The analysis was performed, in GLP, at the Redox test facility.

Equipment list

Standard laboratory glassware and equipment
Analytical Balance accurate to 0.1 mg
Technical balance accurate to 0.01 g
UV/Vis spectrophotometer

Test item solutions preparation

Before starting the analysis, the following solutions were prepared:
- Sodium hydroxide solution 15 % w/V
- Sodium molybdate solution 7.5 % w/V (7.5 g of sodium molybdate were diluted with 75 mL of pure water, 10 mL of H2SO4:H2O 2:1 V/V were added, then diluted to 100 mL)
- DL-Tartaric acid solution 10 % w/V
- Solution A = 0.7 g of sodium sulphite were dissolved in 10 mL of pure water, then 0.15 g of 4-Amino-3-hydroxy-1-naphthalenesulfonic acid were added and stirred until complete dissolution was reached;
- Solution B = 9 g of sodium bisulphite was dissolved in 90 mL of pure water.
- Reducing solution, obtained mixing solutions A and B.

In order to eliminate the matrix, aliquots of about 10g of test item, accurately weighted, were put on a 75 µm, 20 cm diameter sieve, and gently washed with a steady flux (4-5L/min) of water for 5 minutes. The residue was transferred to a tared glass dish with a jet of distilled water from a wash bottle, dried overnight at 54°C in an oven and weighted again.

10 mL of NaOH solution at 15 % were transferred to a nickel crucible of 55 mL capacity. (The crucible was cleaned with dilute HCl before using).
The solution was evaporated to dryness over gas burners. After cooling, about 50 mg accurately weighed (to the nearest 0.1 mg) of test item residue were added to the crucible containing NaOH.
The crucible was covered and heated to dull redness for about 5 minutes. The gas burner was removed and the crucible was swirled in order to push the melt around the sides. The melt was allowed to cool.
Approximately 40 mL of pure water were added, and the crucible was covered and left to stand overnight. The content was then transferred to a volumetric 1 L flask, containing 400 mL of pure water and 20 mL of H2O:HCl (1:1), then finally diluted to volume.
10 mL of the above solution were transferred to a 100 mL volumetric flask, then 1 mL of sodium molybdate solution, 4 mL of DL-tartaric acid solution and 1 mL of reducing solution were added, in this order. The mixture was well mixed, diluted to volume with pure water and allowed to stand at least 30 minutes before analysis.

Reagent blank solution preparation

Reagent blank solution was obtained like the reference item solutions, but omitting the Silicon dioxide. It was used as blank during the spectrophotometric measurement.

Reference item solutions preparation

Taking into account the analytical standard purity, the reference item stock solutions were prepared.

Results and discussions

Determination of the content of silicon in the form of silicic acid anhydride after isolation of it with an acid solution prepared alloy samples from carbonates of alkali metals using the process of dehydration by evaporation with hydrochloric acid was performed using analytical procedure developed and validated in Analytical Department of IPO. It was confirmed that the method is specific. Does not detect the content of silica in the placebo.

Validation - Results and discussions

Table 5.3-1: Methods suitable for the determination of active substances quartz sand in plant protection product GORZKA KORA

	Quartz sand
Author(s), year	Giorgi S., 2022
Principle of method	UV/Vis spectrophotometer
Linearity (linear between mg/L / % range of the declared content) (correlation coefficient, expressed as r)	14.56-36.39 %w/w[1] r2=0.994 Required: r2>0.98
Precision – Repeatability Mean n = 5 (%RSD)	RSD = 0.61%. RSDr %=1.65 Hr=0.37 Acceptable repeatability Hr≤1
Accuracy (% Recovery)	Mean recovery: 102.1% Acceptable recovery: 97- 103 %
Interference/ Specificity	The spectrum of the Molybdenum blue complex ob-

	Quartz sand
	tained from test item was compared with spectrum of the Molybdenum blue complex obtained from reference item.
Comment	-

[1] Referred to the test item solution concentration at 0.02 mg/mL

Conclusion

The method for Silicon dioxide determination was validated for specificity, linearity, repeatability and accuracy, in compliance with SANCO/3030/99 rev.5 (22/03/19).
The reagent blank solution showed no interference. The spectrum of active ingredient(s) in the sample solution matched the spectrum in the reference item(s) solution. The identity of the active ingredient was also demonstrated by XRPD.
The detector response was linear (r2>0.98) for the active ingredient in the concentration range considered.
Active ingredient concentrations in sample solutions were within the linear range of the detector response.
Horrat was within limits (≤ 1).
Accuracy was within the limits determined by the active ingredient's concentration.
The data presented in this report demonstrate that the analytical method provides a specific, reliable, accurate and precise procedure for the determination of active ingredient in the GK-4 product

A 2.1.2 Methods for post-authorization control and monitoring purposes (KCP 5.2)

A 2.1.2.1 Description of analytical methods for the determination of residues in plant matrices (KCP 5.2)

No new or additional studies have been submitted

A 2.1.2.2 Description of analytical methods for the determination of residues in animal matrices (KCP 5.2)

No new or additional studies have been submitted.

A 2.1.2.3 Description of Methods for the Analysis of Soil (KCP 5.2)

No new or additional studies have been submitted.

A 2.1.2.4 Description of Methods for the Analysis of Water (KCP 5.2)

No new or additional studies have been submitted.

A 2.1.2.5 Description of Methods for the Analysis of Air (KCP 5.2)

No new or additional studies have been submitted.

A 2.1.2.6 Description of Methods for the Analysis of Body Fluids and Tissues (KCP 5.2)

No new or additional studies have been submitted.

A 2.1.2.7 A.2.A.9 Other Studies/ Information

No new or additional studies have been submitted.